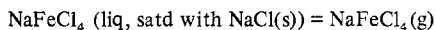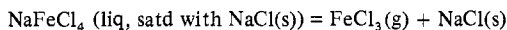phase. Measurement of the equilibrium constant for (5) does not, of course, require the presence of the liquid phase.

Our results shown in Figure 1 converge with those of ref 7 and 15 at higher temperatures but diverge at lower temperatures and lead to the following apparent enthalpies and entropies of vaporization.

$NaFeCl_4$ (liq, satd with NaCl(s)) = $NaFeCl_4$(g)

$\Delta H° = 19.9$ kcal mol^{-1}; $\Delta S° = 12.1$ cal deg^{-1} mol^{-1}

$NaFeCl_4$ (liq, satd with NaCl(s)) = $FeCl_3$(g) + NaCl(s)

$\Delta H° = 16.6$ kcal mol^{-1}; $\Delta S° = 6.2$ cal deg^{-1} mol^{-1}

The values for $NaFeCl_4$ are appreciably less than those based on the data of Cook and Dunn (27.5 kcal and 21.6 cal mol^{-1} deg^{-1}). The effect of the different compositions of the liquid phase must be considered, and in our case, the amount of material in the liquid phase is very small; i.e., the liquid droplets at the point of initial condensation must be extremely small, and surface effects may have a substantial influence.

In a fourth study[21] vapor pressures derived from amounts of condensates produced in a temperature-gradient, static sealed-tube system appear much higher than the results shown in Figure 1.

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The Acid–Base Chemistry of Oxide and Chalcogenide Ions in Sodium Tetrachloroaluminate Melts at 175 °C

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The acid–base chemistry of oxide, sulfide, selenide, and telluride ions in sodium tetrachloroaluminate melts at 175 °C has been investigated. These ions were found to be trichloro bases in acidic melts, the equilibrium with the solvent being $3Al_2Cl_7^-$ + X^{2-} ⇌ AlXCl + $5AlCl_4^-$, where X^{2-} is the oxide or chalcogenide ion. In basic melts these ions become dibases, the equilibrium being $2Al_2Cl_7^-$ + X^{2-} ⇌ $AlXCl_2^-$ + $3AlCl_4^-$. Within the precision of the present results the relative strengths of the tribases appear to be in the order Te^{2-}, Se^{2-} < S^{2-} < O^{2-}.

Molten tetrachloroaluminates (AlCl$_3$–alkali chloride mixtures) have in recent years been the subject of considerable experimental investigations, both as potential electrolytes in molten salt battery systems and also because of their interesting acid–base properties. A number of possible cathode systems for batteries have been investigated, including sulfur[1] and selenium,[1,2] while the use of oxygen has also been suggested. The electrochemistry of the above systems has been briefly studied, but very little is known about the chemistry involved, particularly concerning the interactions between basic oxide or chalcogenide ions and the acid moieties in the melt. These interactions might have considerable influence on the operation of any battery system based on these materials. The behavior of the oxide ion is also of considerable interest as it is liable to be present in all tetrachloroaluminate melts as an impurity (from traces of water).

In a previous paper from this laboratory, a study of the acidity dependence of the S_2/S^{2-} redox potential in NaAlCl$_4$ melts was reported.[3] From this it was suggested that an acid–base equilibrium existed between S^{2-} ions and the melt (eq 1). By consideri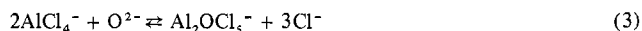ng the various equilibria that exist between the species in the melt,[4] equilibrium 1 can be rewritten as eq 2. The sulfide ion appears to be behaving as a trichloro

$AlCl_4^-$ + S^{2-} ⇌ AlSCl + $3Cl^-$ (1)

$3Al_2Cl_7^-$ + S^{2-} ⇌ AlSCl + $5AlCl_4^-$ (2)
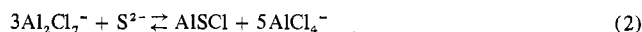
base under these conditions. The presence of these equilibria was also used to explain the very high solubility of metal sulfides observed in acidic melts.

Letisse and Tremillon have briefly investigated the chemistry of O^{2-} ions in NaAlCl$_4$ melts.[5] They titrated O^{2-} ions (introduced as barium hydroxide, which yields H$^+$ and O^{2-} ions on contact with the melt) with the melt and showed the oxide ion to be a strong trichloro base. They proposed equilibrium 3, where $Al_2OCl_5^-$ is the solvated form of AlOCl. This observation was, they stated, further supported by the fact that addition of water to the melt reduced its acidity; the oxide ion must therefore be more than a dibase (the water yields 2H$^+$ + O^{2-} on contact with the melt, and H$^+$ is a monochloro acid). In a more recent paper,[6] however, Tremillon et al. have proposed instead that equilibrium 4 exists, except in very acidic
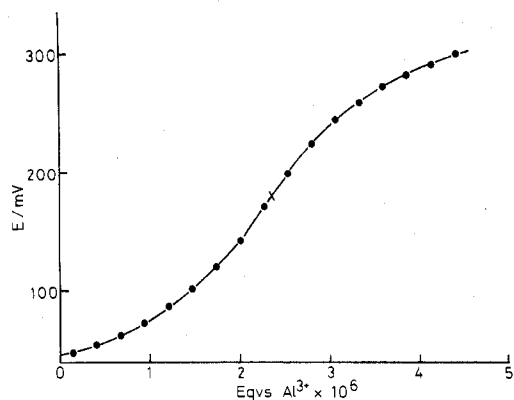
$2AlCl_4^-$ + O^{2-} ⇌ $Al_2OCl_5^-$ + $3Cl^-$ (3)

$2AlCl_4^-$ + O^{2-} ⇌ $Al_2OCl_6^{2-}$ + $2Cl^-$ (4)
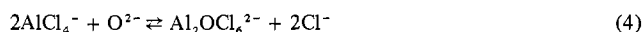
Figure 1. Titration of Na_2Se with Al^{3+}: 97.5 mg of Na_2Se was added to 56.3 g of melt at 175 °C. Initial potential of melt 180.5 mV.

melts where $Al_2OCl_5^-$ is formed. This behavior would suggest that the oxide ion is a strong dibase but only a very weak tribase.

There appears to be some controversy as to the basicity of oxide and chalcogenide ions in these melts; their reactions with $AlCl_3$ do, however, appear to be rather better understood. Metal oxides and chalcogenides will react with $AlCl_3$ in a sealed tube at temperatures around 300 °C to yield the species $AlOCl$,[7] $AlSCl$,[7] $AlSeCl$,[8] and $AlTeCl$[9] as the products of reactions such as equilibrium 5. In the work described here,

$$AlCl_3 + ZnS \rightleftarrows AlSCl + ZnCl_2 \qquad (5)$$

the acid–base chemistry of oxide and chalcogenide ions in $NaAlCl_4$ melts at 175 °C has been investigated, both by titration of these ions with the melt and by studying the acidity dependence of the X_2/X^{2-} redox potential, where X^{2-} is the chalcogenide ion.

Experimental Section

The preparation of NaCl-saturated $NaAlCl_4$ melts by the preelectrolysis of a molten mixture of $AlCl_3$ (AG iron free, Fluka) and NaCl (ACS, Fisher) has been described elsewhere.[10] After purification, a sample of the melt was filtered through a medium porosity frit and transferred to a small glass cell maintained at 175 °C. The reference electrode, with respect to which all electrode potentials are given, consisted of a coiled Al wire (99.999% pure Alfa Inorganics) immersed in NaCl-saturated $NaAlCl_4$ and separated from the bulk of the melt by a very thin soft-glass membrane. All potential measurements were made with a high-impedance digital voltmeter. The melt purification and subsequent experiments were performed under an argon atmosphere in a drybox (Vacuum Atmosphere Co.). Sodium sulfide, selenide, and telluride (Cerac Pure Inc.) were used without further purification. The most satisfactory way to introduce oxide into the melt quantitatively was found to be as barium carbonate, which reacts immediately with the melt to liberate carbon dioxide and leave oxide, which was completely soluble. Sodium carbonate, as was used by Tremillon et al.,[6] was found to be unsatisfactory as it was only partially soluble, even after many hours of stirring.

Potentiometric titrations of the oxide and chalcogenide species with the melt were performed using an Al indicator electrode which is sensitive to the melt composition.[4] An addition of oxide or chalcogenide was made to a melt of known composition, and after all the added material had dissolved and the electrode potential was stable, the melt was coulometrically titrated back to its starting composition with Al^{3+}, formed by the anodization of an Al wire using a constant current source (Sargent Coulometric Source Model IV). Great care had to be taken to ensure that the melt temperature remained very stable since fluctuations of only 2 °C could produce potential changes of several millivolts.

The acidity dependences of the Se_2/Se^{2-} and S_2/S^{2-} redox potentials at either vitreous carbon or tungsten electrodes were determined by preparing a solution of known Se and Se^{2-} or S and S^{2-} concentrations in an NaCl-saturated melt. The melt composition was then adjusted by adding weighted portions of a 60:40 $AlCl_3$–NaCl melt, and the electrode potential was measured.
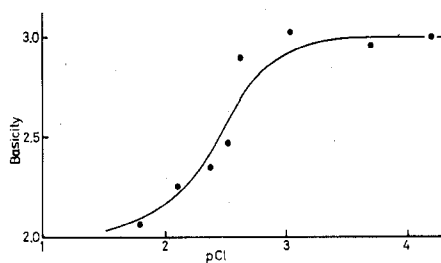

Figure 2. Plot of the acidity dependence of the basicity of Na_2S in $NaAlCl_4$ melts. Melt acidity is given as the pCl on the molal scale.
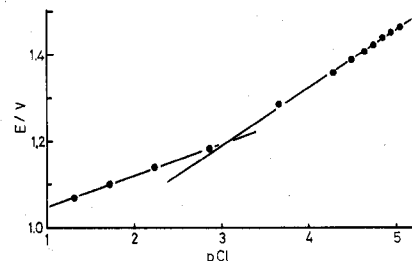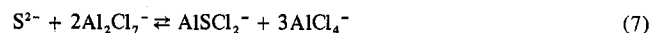

Figure 3. Plot of the acidity dependence of the potential of the Se_2/Se^{2-} couple at a vitreous carbon electrode. $[Se_2]$ 5.03×10^{-4} M, $[Se^{2-}]$ 1.1×10^{-4} M.

Results and Discussion

The titration of Na_2Se, added to an approximately neutral melt, with Al^{3+} is shown in Figure 1. The curve has the appearance of a strong acid–strong base titration, and the endpoint gives an Al^{3+} to Se^{2-} ratio of 3.04 ± 0.1:1. This means that the Se^{2-} ion is behaving as a tribase. Similar results were obtained for O^{2-}, S^{2-}, and Te^{2-} ions. When oxide or chalcogenide ions were added to basic melts (pCl on the molal scale less than 2.8), a lower basicity was indicated. Figure 2 shows the $Al^{3+}:S^{2-}$ ratio as a function of melt acidity, as determined from a series of titrations. As the melt acidity is reduced, the S^{2-} ion appears to change from being a tribase to a dibase. In acidic melts the equilibrium between S^{2-} ions and the melt is described in eq 6, while in more basic solutions

$$S^{2-} + 3Al_2Cl_7^- \rightleftarrows AlSCl + 5AlCl_4^- \qquad (6)$$
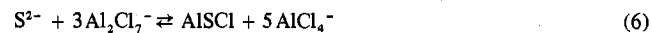
it follows eq 7. It is probable that the species $AlSCl$ and

$$S^{2-} + 2Al_2Cl_7^- \rightleftarrows AlSCl_2^- + 3AlCl_4^- \qquad (7)$$

$AlSCl_2^-$ are solvated as $Al_2SCl_5^-$ and $Al_2SCl_6^{2-}$; however, evidence for such species will only come from a spectroscopic investigation. Attempts to calculate the equilibrium constants for eq 6 and 7 were unfortunately unsuccessful due to the lack of precision in the titrations, particularly in the more basic melts. Plots similar to those of Figure 2 were obtained for Se^{2-}, Te^{2-}, and O^{2-}, except that in the latter case values could not be calculated for melts more basic than a pCl of about 1.85 since $BaCl_2$ was precipitated. Similar equilibria can also be proposed.

A plot of the acidity dependence of the Se_2 equilibrium potential on a vitreous carbon electrode in a solution of Se and Se^{2-} is shown in Figure 3. There was a problem in determining the acidity of the melt. Since both the oxidized and the reduced forms of the couple were present, neither an Al nor a Cl_2 electrode could be used to determine the acidity which had therefore to be calculated. In this calculation the basicity of the Se^{2-} had to be considered, and we decided to regard it as a tribase throughout the acidity range. Since the Se^{2-} concentration was so low, its basicity only slightly affected the calculation. The gradient of the plot in Figure 3 in the acidic region is about 130 mV, close to the value of $2.3 \times 3RT/2F$ (133 mV at 175 °C), while the slope in the basic region is 75 mV, fairly close to the value of $2.3RT/F$ (89 mV).

It can be shown that the equilibrium determining couple is Se_2/S^{2-}.[11] The above therefore suggests that in acidic melts the electrode reaction is

$$Se_2 + 2AlCl_4^- + 4e^- \rightleftarrows 2AlSeCl + 6Cl^- \tag{8}$$
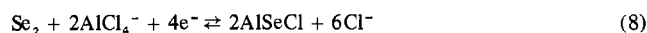
for which the Nernst expression is given by eq 9. If it is

$$E = E^\circ_1 - \frac{RT}{4F} \ln \left(\frac{[AlSeCl]^2[Cl^-]^6}{[Se_2][AlCl_4^-]^2} \right) \tag{9}$$

assumed that the concentrations of AlSeCl, Se_2, and $AlCl_4^-$ remain constant, then eq 9 can be simplified to eq 10, which

$$E = E^\circ_1{}' - \frac{3RT}{2F} \ln [Cl^-] \tag{10}$$

gives the $3RT/2F$ slope observed. In a similar way, the slope in the basic region implies the reaction detailed by equilibrium 11, for which the Nernst equation is given by eq 12. As above,
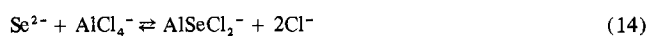
$$Se_2 + 2AlCl_4^- + 4e^- \rightleftarrows 2AlSeCl_2^- + 4Cl^- \tag{11}$$
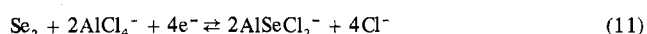
$$E = E^\circ_2 - \frac{RT}{4F} \ln \left(\frac{[AlSeCl_2^-]^2[Cl^-]^4}{[Se_2][AlCl_4^-]^2} \right) \tag{12}$$

this can be reduced to eq 13. That the experimental slope

$$E = E^\circ_2{}' - \frac{RT}{F} \ln [Cl^-] \tag{13}$$

observed is slightly less than the 89 mV predicted is probably due to a small degree of dissociation of the $AlSeCl_2^-$ into free Se^{2-} ions, which can be written as equilibrium 14 with the

$$Se^{2-} + AlCl_4^- \rightleftarrows AlSeCl_2^- + 2Cl^- \tag{14}$$

equilibrium constant K_1 (see eq 15). If this dissociation is

$$K_1 = \frac{[AlSeCl_2^-][Cl^-]^2}{[Se^{2-}][AlCl_4^-]} \tag{15}$$

taking place, eq 13 no longer holds and has to be modified as shown by eq 16, where $[Se^{2-}]_t$ is the total concentration of

$$E = E^\circ_2 - \frac{RT}{4F} \ln \left(\frac{[Se^{2-}]_t{}^2}{[Se_2][AlCl_4^-]^2} \right) -$$
$$\frac{RT}{4F} \ln \left(\frac{[Cl^-]^4}{\left[1 + \frac{[Cl^-]^2}{K_1[AlCl_4^-]} \right]^2} \right) \tag{16}$$

selenide added. By considering the value of the potential at two pCl values, K_1 is determined to be 4.5×10^{-4} mol kg^{-1}.

Very similar data were obtained for the S_2/S^{2-} couple; however, in this case the precision of the measurements was not as great, and a calculation of the association constant as outlined above for Se^{2-} was not attempted. No measurements of the Te/Te^{2-} and O_2/O^{2-} potentials were made.

From the point of intersection of the two straight lines of Figure 3, it is possible to calculate the equilibrium constant for equilibrium 17. At the point of intersection the right-hand

$$AlSeCl_2^- \rightleftarrows AlSeCl + Cl^- \tag{17}$$

sides of eq 9 and 12 can be equated and the resulting equation simplified to give eq 18, which can be further reduced to eq

$$E^\circ_1 - E^\circ_2 = \frac{RT}{2F} \ln \left(\frac{[AlSeCl][Cl^-]}{[AlSeCl_2^-]} \right) \tag{18}$$
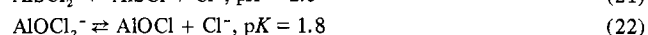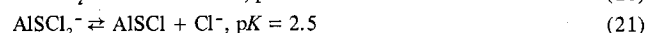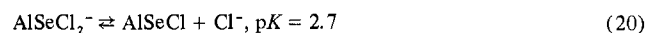
19. The value of E°_1 was calculated from the slope in the

$$E^\circ_1 - E^\circ_2 = \frac{RT}{2F} \ln K_2 \tag{19}$$

acidic region and eq 9, while E°_2 was obtained from the slope in the basic region and eq 16. Using this information K_2 was calculated.

From these results it can readily be shown that the possible dissociation of AlSeCl into Se^{2-} is in fact negligible in the acidic range and has no effect on the slope in agreement with the experimental values.

The calculated pK (molal scale) for the equilibrium in eq 17 and the values determined for similar equilibria for AlSCl and AlOCl are shown in eq 20–22. The pK value for AlSCl

$$AlSeCl_2^- \rightleftarrows AlSeCl + Cl^-, \ pK = 2.7 \tag{20}$$

$$AlSCl_2^- \rightleftarrows AlSCl + Cl^-, \ pK = 2.5 \tag{21}$$

$$AlOCl_2^- \rightleftarrows AlOCl + Cl^-, \ pK = 1.8 \tag{22}$$

was determined in the same way as for AlSeCl except that no allowance was made for the dissociation of $AlSCl_2^-$ into free S^{2-}. It is reasonable to assume that this dissociation will be very similar to that of $AlSeCl_2^-$ and, therefore, the pK shown for eq 21 is probably too large. The value for AlOCl is taken for Gilbert et al.,[12] who used titration techniques to determine its value. From these pKs it can be concluded that the tribase strength increases in order $Se^{2-} < S^{2-} < O^{2-}$ and it is reasonable to assume that the tribase strength of Te^{2-} will be similar to or less than that of Se^{2-}.

From these results it can be concluded the O^{2-}, S^{2-}, Se^{2-}, and Te^{2-} ions all behave as trichloro bases in acid melts and dichloro bases in basic melts. The relative strength of the tribases are in the order Te^{2-}, $Se^{2-} < S^{2-} < O^{2-}$.

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