could give rise to nonzero values of η, the electric field asymmetry parameter. Indeed, Semin, *et al.*,[1] observed large values of η for $(C_6H_5)_2SbCl$ and $(C_6H_5)_2SbC{\equiv}CSb(C_6H_5)_2$. For compounds of the type $(C_6H_5)_2Sb-R-Sb(C_6H_5)_2$ (*cf.* Tables II and III) the fits for the Mossbauer spectra are not improved by inclusion of nonzero η values, and the nqr spectra give η values of the same order of magnitude as found for triphenylstibine itself—presumably associated with molecular distortion resulting from packing forces. This is in accord with the observation in the preceding paragraph that the antimony nucleus sees little difference between a phenyl substituent and a methyl substituent, now expanded to include a methylene substituent. Indeed, isomer shifts and quadrupole splittings for trimethylstibine, triphenylstibine, and all of the bis(diphenylstibino)methylene compounds also are similar; IS ranges from −0.22 to −0.69 mm/sec and e^2qQ/h ranges from 486 to 530 MHz.

Although based upon very limited observations, it is interesting to note that $\eta \cong 0$ when X is attached to antimony through an aliphatic linkage and that η is large when X has considerable electron density in p orbitals, lone pairs in the case of chlorine, electrons associated with the triple bond in the case of the acetylenic group.[16] The similarity of this behavior of η to the behavior of e^2qQ/h in tin compounds of the R_3SnX type is striking.[17-19] In the tin case, when R = C_6H_5 or CH_3 and if X is a halogen, oxygen, or acetylenic linkage, e^2qQ/h has a large value (neither its sign nor the value of η can be determined from ^{119}Sn Mossbauer spectra without application of an external magnetic field), whereas if X is an ethylenic or methylenic linkage, e^2qQ/h is essentially zero.[20] Although the quadrupole splitting in the Sn^{IV} compounds has been attributed to π interaction with nonbonded p electrons on the X group,[17] it has also been proposed that inequalities in σ-bond polarities can explain the magnitude of e^2qQ/h in Sn^{IV} compounds.[19] It may well be that the η values in unsymmetrical Sb^{III} compounds and the e^2qQ/h values in Sn^{IV} compounds are influenced by common factors.

Registry No. $(C_6H_5)_2AsCH_2As(C_6H_5)_2$, 21892-63-7; *p*-$(C_6H_5)_2AsCH_2C_6H_4CH_2As(C_6H_5)_2$, 39936-99-7; $(C_6H_5)_3Sb$, 603-36-1; $(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$, 30224-53-4; $(C_6H_5)_2Sb(CH_2)_4Sb(C_6H_5)_2$, 5865-82-7; $(C_6H_5)_2Sb(CH_2)_{10}Sb(C_6H_5)_2$, 39937-02-5; $(CH_3)_3Sb$, 594-10-5; ^{75}As, 7440-38-2; ^{121}Sb, 14265-72-6; ^{123}Sb, 14119-16-5.

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[16] This is also the case for bis(diphenylantimony) oxide where $\eta = 0.90 \pm 0.05$! This value was taken from the ^{121}Sb Mossbauer spectrum of the compound which was determined on the same equipment and under the same conditions as used for the spectra reported in this paper. The other Mossbauer parameters for ^{121}Sb are IS = -1.10 ± 0.05 mm/sec and $e^2qQ/h = 21 \pm 1$ mm/sec: L. H. Bowen, J. G. Stevens, and G. G. Long, to be submitted for publication.

[17] T. C. Gibb and N. N. Greenwood, *J. Chem. Soc.*, 43 (1966).

[18] S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc. A*, 1311 (1971).

[19] R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 2145 (1969).

[20] The large positive e^2qQ/h in the stibines is due to the unshared electron pair, which, of course, is not present in the Sn^{IV} compounds.

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Potentiometric Study of the Systems $KCl-AlCl_3$ and $KCl-AlCl_3-ZnCl_2$ at 300°, Performed with a Chlorine-Chloride Electrode

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A completely sealed off chlorine-chloride electrode cell was developed. By means of this cell a $KCl-AlCl_3$ melt saturated with KCl was found to contain 51.69 ± 0.03 mol % KCl at 300°. The p*K* value for the dissociation $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$ was found to be 7.83 ± 0.02 at 300°. At very high chloride activities (*i.e.*, low pCl^-) added Zn(II) formed $ZnCl_4^{2-}$, while at somewhat lower chloride activities the buffering effect of adding 0.10 and 0.30 *F* $ZnCl_2$ to $KCl-AlCl_3$ could best be explained by the following dissociation: $ZnCl_4^{2-} \rightleftharpoons ZnCl_3^- + Cl^-$, where $ZnCl_3^-$ possibly is solvated to $AlCl_4^-$. The p*K* value of this reaction was found to be 2.15 ± 0.04 at 300°.

Introduction

It is well-known that pCl^- plays a critical role in the intricate chemical phenomena that occur in chloride molten salts, and it has become common to try to describe this role quantitatively in terms of model acid-base equilibria in which the activity coefficients of the reacting species are treated as constants, independent of system composition. In such investigations the foremost problem is to establish reliable and convenient experimental procedures for measuring pCl^-. Once definitive data have been obtained, the utility and uniqueness of model equilibria with constant activity coefficients can be critically examined. These two tasks are the central concerns of the present investigation.

The particular acid-base phenomenon chosen for study was the buffering action of solute $ZnCl_2$ in $KCl-AlCl_3$ melts. The existence of this buffering action has been known for some years, and it proved very useful in investigations that led to the discovery of some of the novel low oxidation states of tellurium,[1] but its quantitative aspects have never been studied.

In the present paper we describe a relatively simple concentration cell with chlorine electrodes and report the pCl^- dependence on composition of the molten system $KCl-AlCl_3-ZnCl_2$ at low $ZnCl_2$ concentration and $KCl:AlCl_3$ mole ratios neighboring unity. Then, using these data, we

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[1] N. J. Bjerrum, *Inorg. Chem.*, 9, 1965 (1970); 10, 2578 (1971); 11, 2648 (1972).

investigate model acid-base equations with constant activity coefficients.

Acid-base equilibria in the closely related system, NaCl-$AlCl_3$, have been studied previously, mainly with aluminum electrodes[2-5] but also with a chlorine-chloride electrode in an open system.[2] In the neighborhood of the equivalence point, the model equilibrium

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \quad (1)$$

with constant activity coefficients represents the dependence of pCl^- on the NaCl:$AlCl_3$ ratio quite successfully. Furthermore, the physical existence of $AlCl_4^-$ and $Al_2Cl_7^-$ complexes is supported by Raman measurements.[6-8] However, at low NaCl:$AlCl_3$ mole ratios, the above model is quite inadequate and there is also spectroscopic evidence for higher polynuclear complexes.[8]

Although there are no data on the acid-base equilibria of $ZnCl_2$ in three-component MCl-$AlCl_3$-$ZnCl_2$ systems (M = Li, Na, K, Rb, Cs), there have been several Raman investigations of the two-component MCl-$ZnCl_2$ system.[9-12] These studies support the view that $ZnCl_4^{2-}$ predominates at high MCl:$ZnCl_2$ mole ratios while the strong tendency of zinc to form chloride-bridged polymers comes into play at low values of this ratio. The details of the picture are by no means clear, however, and investigators have asserted the possibility of interpreting some of the Raman bands in terms of the low coordination number entities $ZnCl_3^-$ and molecular $ZnCl_2$.

Experimental Section

Materials and Measurements. $AlCl_3$ and $ZnCl_2$ were made from pure metals (99.999%) and HCl gas (electronic grade from Matheson). KCl (Baker Analyzed) was purified by first passing HCl gas over the solid and then the melt, next flushing with pure N_2, and finally filtering the melt.[13,14] The chlorine gas used was from Fluka (>99.9%).

The electrode cells were made of Pyrex. Chlorine was added under a known pressure to the cells, which were then sealed vacuum tight. This seal-off made the construction of the cells more difficult but gave several advantages with respect to their subsequent handling. For example, an experiment could be discontinued for a period and then started again. An empty Pyrex cell is shown in Figure 1. It is equipped with two necks (A) made of 300-mm lengths of 8-mm tubing with standard-taper joints on top. The cell compartment (C) consists of a 110-mm length of 18-mm tubing and has 3 × 35 mm glassy carbon rods (E) (Carbone Lorraine Type V 10) fused into the bottom. Such a vacuum-tight seal between glassy carbon and Pyrex can be achieved by applying a vacuum to the cell while the glass tube being sealed is heated with a torch. A similar process of sealing Pyrex to glassy carbon has been previously reported by Gupta.[15]

A sintered disk (D) from Radiometer separates the two cell compartments. Before a cell was used, the sintered disk was tested for leaks under a water pressure of about 300 mm. The disk was considered to be satisfactory if the flow did not exceed 0.2 cm^3 of water over a 12-hr period. In order to get the same pressure over the melt in both compartments they were connected by a tube (B) with inside diameter of about 1 mm.

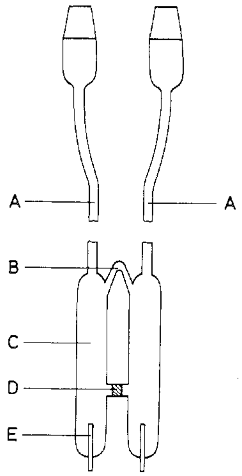

Figure 1. Electrode cell of Pyrex: A, neck; B, connection tube to equilibrate the pressure; C, cell compartment; D, fritted disk; E, carbon rods.

The materials that made up a melt were weighed in a nitrogen-filled glove-box and added to the cell. The weight of material was chosen so that the melt barely covered the sintered disk (D).

Because the dissolution of KCl in KCl-$AlCl_3$ mixture is rather slow, the charged cell was placed in a special furnace, which was gently rocked over an extended period of time (16-24 hr) in such a way that no mixing occurred between the two cell compartments. After this treatment the cell was transferred to an aluminum-block furnace where the final measurements were made. In this furnace the measured cell potential did never vary more than 0.1 mV hr^{-1} and usually the variation was of the order of 0.02 mV.

As a precaution against a wrong initial melt composition, stoichiometric amounts of KCl and $AlCl_3$ were always added to one of the cell chambers and compared with a saturated solution. On the basis of this measurement a correction for the melt composition was made. This correction amounted to 0-10 mg of KCl or $AlCl_3$ compared with a total amount of 10.5 g of $KAlCl_4$ in the melt. In order to make the correction a preliminary value of the equilibrium quotient for reaction 1 as well as a preliminary value for the chloride ion activity in the saturated melt had to be known. When the final values were obtained, we found that they did not change the corrections significantly.

Further additions of KCl, $AlCl_3$, or $ZnCl_2$ could be made to the cell by breaking off the tip of the neck in the glove-box, adding the material, and finally resealing the cell under $^1/_2$ atm of chlorine. The uncertainty in the weighings was much smaller here since only a few clean crystals were weighed at a time and the spatula was weighed before and after the additions.

The aluminum-block furnace consisted of an inner cylindrical core of aluminum with a diameter of 140 mm and a length of 430 mm. This core had an axial hole (diameter 63.5 mm) through which a stainless steel tube (inside diameter 60.5 mm) was pressed. The block was heated by three Thermocoax elements. The main heater was wound in a helical groove around the middle of the block. The end elements (with outside diameter 1.5 mm) were placed in grooves in the ends of the cylinder. The free ends of the stainless steel tube were heated by two more heating coils, kept in series with the main heating elements. The aluminum block was suspended inside a water-cooled cylindrical housing (diameter 240 mm, length 540 mm). Six small (8-mm diameter) vertical holes were drilled through the block, so that it could be cooled by compressed air if necessary. The insulating material between the block and the outer furnace shell consisted of asbestos. A separately heated cylindrical furnace (outer diameter 120 mm and length 320 mm) could be placed on top of the main furnace to extend its length. The extension was necessary when cells with long necks were used.

The temperature of the main furnace was controlled by an Eurotherm regulator, Type LP96/CR, PID (proportional, integral, and differential regulation), with digital setting (DHS) and with fast cycling (FC). The temperature-sensing element was a platinum resistance thermometer. The top and bottom heating elements were controlled by a simple regulator, Type LP96/MK2/PID/FC, that regulated on the temperature difference measured by thermocouples placed on the middle and end parts of the furnace. The furnace tem-

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(2) B. Tremillon and G. Letisse, *J. Electroanal. Chem. Interfacial Electrochem.*, **17**, 371, 387 (1968).

(3) G. Torsi and G. Mamantov, *Inorg. Chem.*, **10**, 1900 (1971).

(4) A. A. Fannin, Jr., L. A. King, and D. W. Seegmiller, *J. Electrochem. Soc.*, **119**, 801 (1972).

(5) L. G. Boxall, H. L. Jones, and R. A. Osteryoung, private communication.

(6) G. Torsi, G. Mamantov, and G. M. Begum, *Inorg. Nucl. Chem. Lett.*, **6**, 553 (1970).

(7) H. A. Oye, E. Rytter, P. Klaeboe, and S. J. Cyvin, *Acta Chem. Scand.*, **25**, 559 (1971).

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(11) S. R. Mayer, S. C. Ewans, and G. Y.-S. Lo, *J. Electrochem. Soc.*, **113**, 158 (1966).

(12) R. B. Ellis, *J. Electrochem. Soc.*, **113**, 485 (1966).

(13) H. A. Laitinen, W. S. Ferguson, and R. A. Osteryoung, *J. Electrochem. Soc.*, **104**, 516 (1957).

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(15) N. K. Gupta, *Rev. Sci. Instrum.*, **42**, 1368 (1971).

perature could be kept within ±0.1° in the range 100–500°. The temperature variation over the middle 200 mm was less than 0.3°. The temperature of the furnace was measured by a calibrated chromel-alumel thermocouple connected to a Type DM 2022S digital voltmeter from Digital Measurements Ltd. with a built-in standard cell. The same instrument was also used for the potentiometric measurements.

Results and Discussion

General Considerations. The formality is defined as the initial molar amount of one of the added substances (in the present work either KCl, AlCl$_3$, or ZnCl$_2$) dissolved in 1 l. of the melt. The excess formality of KCl or AlCl$_3$ is defined as the difference in formality between KCl and AlCl$_3$ or AlCl$_3$ and KCl, respectively. The densities of the buffered KAlCl$_4$ solutions was calculated assuming ideal mixtures of ZnCl$_2$ and KCl-KAlCl$_4$. This assumption is reasonable as the amounts of ZnCl$_2$ added were small compared to the amounts of KCl-KAlCl$_4$. The density of ZnCl$_2$ and of KCl-AlCl$_3$ was obtained, respectively, from the work of Smith and Smith[16] and of Morrey and Carter.[17] All deviations given in this work are with a 95% confidence probability. A micropolarization test[18] of the electrodes in the concentration cell, carbon$_\text{I}$, Cl$_2$|Cl$^-$(KCl-AlCl$_3$-ZnCl$_2$)$_\text{I}$|sintered disk| Cl$^-$(KCl$_\text{satd}$-AlCl$_3$)|Cl$_2$, carbon$_\text{II}$, with an applied voltage of ±20 mV and a sweep rate of 5 mV/sec showed no hysteresis. Furthermore the electrodes had completely recovered within the experimental uncertainty of ±0.1 mV within about 30 sec after an applied potential of 20 mV, which lasted 1 min, had been taken away. The internal resistance of the cells were usually in the range 100–500 Ω. On basis of this the electrode was considered to be reversible. The potential of the cell is then generally given by[19]

$$\Delta E = \frac{1}{F}\int_\text{I}^\text{II}\sum_i t_i(-z_i^{-1}\ \mathrm{d}\mu_i + z_{\text{Cl}^-}{}^{-1}\ \mathrm{d}\mu_{\text{Cl}^-})$$
$$\text{(at constant } T\text{)} \qquad (2)$$

since the chlorine pressure and hence the chlorine activity are the same in both cell compartments due to the connecting tube (B) (Figure 1). t_i, z_i, and μ_i are the transference number, charge, and chemical potential for the ith ion, respectively.

Method of Investigation. On basis of previous measurement in MCl-AlCl$_3$ systems it is reasonable to assume that the ions present in KCl-AlCl$_3$-ZnCl$_2$ are K$^+$, AlCl$_4^-$, Cl$^-$, Al$_2$Cl$_7^-$, and Zn$_x$Cl$_y$$^{2x-y}$ and that of these only K$^+$, AlCl$_4^-$, and Cl$^-$ make a contribution to the current since Al$_2$Cl$_7^-$ and Zn$_x$Cl$_y$$^{2x-y}$ ions have a low mobility and are present only in small concentrations. Under these circumstances eq 2 can be expressed in activities as

$$\Delta E = \frac{RT}{F}\int_\text{I}^\text{II} \mathrm{d}\ln\,[\text{Cl}^-] - t_{\text{K}^+}\,\mathrm{d}\ln\,[\text{K}^+] +$$
$$t_{\text{AlCl}_4^-}\ \mathrm{d}\ln\,[\text{AlCl}_4^-] + t_{\text{Cl}^-}\ \mathrm{d}\ln\,[\text{Cl}^-] \qquad (3)$$

Unfortunately no data are available for the transference numbers in this equation but since the two electrode solutions consist mainly of K$^+$ and AlCl$_4^-$ ions, it is reasonable to neglect variations with composition in the transference numbers for K$^+$ and AlCl$_4^-$. The concentrations of the chloride ions are by comparison rather small and vary a great deal. A reasonable assumption here is that t_{Cl^-} is proportional to the concentration and hence the activity of Cl$^-$. This can be expressed in the following way

$$\Delta E = \frac{RT}{F}\int_\text{I}^\text{II} -\mathrm{d}\ln\,[\text{Cl}^-] - t^0{}_{\text{K}^+}\,\mathrm{d}\ln\,[\text{K}^+] +$$
$$t^0{}_{\text{AlCl}_4}\ \mathrm{d}\ln\,[\text{AlCl}_4^-] - k[\text{Cl}^-]\ \mathrm{d}\ln\,[\text{Cl}^-] \qquad (4)$$

where $t^0{}_{\text{K}^+}$ and $t^0{}_{\text{AlCl}_4}$ are the transference numbers in pure KAlCl$_4$ and k is a constant for which $t_{\text{Cl}^-} = k[\text{Cl}^-]$ at a low concentration of chloride ions. An integration of this expression gives

$$\Delta E = -\frac{RT}{F}\ln\frac{[\text{Cl}^-]_\text{II}}{[\text{Cl}^-]_\text{I}} - \frac{RT}{F}t^0{}_{\text{K}^+}\ln\frac{[\text{K}^+]_\text{II}}{[\text{K}^+]_\text{I}} +$$
$$\frac{RT}{F}t^0{}_{\text{AlCl}_4}\ \ln\frac{[\text{AlCl}_4^-]_\text{II}}{[\text{AlCl}_4^-]_\text{I}} + \frac{RT}{F}k([\text{Cl}^-]_\text{II} - [\text{Cl}^-]_\text{I}) \qquad (5)$$

In order to evaluate the last three therms in this equation we have to know the values of the transference numbers in KAlCl$_4$ and the value of k. These values are not known, but if we assume that the mobilities of the ions considered are inversely proportional to their ionic radii (an assumption which fit reasonably well for a number of molten salts where the anions and cations are well defined[20]), we can probably get an idea about the sizes of the three terms. By assuming that the ionic radii for K$^+$, AlCl$_4^-$, and for Cl$^-$ are 1.33, 3.30, and 1.81 Å, respectively, the values for the three terms, in the order written, will be −3.8, +1.9, and 4.0 mV for the KCl-AlCl$_3$ system and −0.8, +0.2, and +0.4 mV for the KCl-AlCl$_3$-0.3 F ZnCl$_2$ system. These values are small compared to the maximum $|\Delta E|$ values which were obtained in these systems, furthermore the three terms cancel each other partially. On basis of this and on basis of the uncertainty in the calculations we decided to neglect the last three terms in the calculation of the chloride activity in the melt.

In the calculations mentioned above, the variation in the activity coefficients has been neglected. Due to lack of data it is impossible to make an exact calculation of this change. However, the size of the change cannot be very large. If we assume that KAlCl$_4$ is a regular solution, the activity coefficient for KAlCl$_4$ can be calculated from $RT \ln \gamma = kN_2{}^2$, where γ is the activity coefficient for KAlCl$_4$, k is a constant, and N_2 is the mole fraction of the other component, *i.e.*, KCl or KAl$_2$Cl$_7$. The value of k is usually less than ±3 kcal mol^{-1}.[21] If a value of ±3 kcal is used, it is found that in the present measurement the maximum variation in the activity coefficient is ±2.2% on the acidic side and ±1.0% on the basic side. There are, however, indications that in the present case it is quite a bit smaller, but since we have no reliable data, we have neglected this variation. We can now return to the potential of the cell, which is given by

$$\Delta E = -\frac{RT}{F}\ln\frac{[\text{Cl}^-]_\text{II}}{[\text{Cl}^-]_\text{I}} \qquad (6)$$

which, at 300°, becomes

$$\text{pCl}^- = \frac{-\Delta E}{113.0} + \text{pCl}^-{}_\text{II} \qquad (7)$$

where pCl$^-{}_\text{II}$ is the pCl$^-$ in the saturated melt.

Determination of the Solubility of KCl at 300°. In order to determine the pCl$^-$ of the saturated melt it was necessary to determine the solubility of KCl. At high chloride concentration (*i.e.*, low pCl$^-$) it is safe to assume that AlCl$_4^-$ is the only aluminum complex in the melt, since the coordina-

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[16] W. E. Smith and G. P. Smith, *J. Chem. Eng.*, 13, 123 (1968).

[17] J. R. Morrey and D. G. Carter, *J. Chem. Eng.*, 13, 94 (1968).

[18] D. J. G. Ives and G. J. Janz, "Reference Electrodes," D. J. G. Ives and G. J. Janz, Ed., Academic Press, New York, N. Y., 1961, p 18.

[19] E. A. Guggenheim, "Thermodynamics," North-Holland Publishing Co., Amsterdam, 1967, p 324.

[20] G. J. Janz, Ed., "Molten Salts Handbook," Academic Press, New York, N. Y., 1967, pp 206-211.

[21] See ref 20, pp 344, 345.

tion number for aluminum with respect to chloride cannot exceed 4. A dimeric complex might be present at high chloride concentrations but the data obtained so far give no indication of this. Therefore an addition of KCl gives rise to a corresponding amount of chloride ions. Thus, when $-\Delta E/113.0$ is plotted against the negative logarithm of the excess formality of KCl, one should obtain a straight line with a slope of unity whose intercept at the abscissa ($-\Delta E = 0$) equals pCl^-_{II}. Such a plot is shown in Figure 2. The temperature is 300°. A straight line is obtained with a slope of $+1.02 \pm 0.11$. The large uncertainty is due to the small number of points. The intercept at the abscissa gives a pCl^- value of 0.284 ± 0.007, which corresponds to a composition of 51.69 ± 0.03 mol % KCl. This value fits well with the phase diagram for $KCl-AlCl_4$ by Fischer and Simon.[22]

pCl^- Behavior and Model Equilibria for the $KCl-AlCl_3$ System. If the electrodes discussed above are used for a large compositional range and the pCl^-, calculated from the cell voltage, is plotted against the mole fraction of KCl, an S curve is obtained similar in shape to the S curve found for the $NaCl-AlCl_3$ system.[2] As already mentioned, this curve has been shown to be due to the acid-base reaction $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$. Hence it was possible to use the $KCl-AlCl_3$ system as a test for the experimental and mathematical methods prior to applying them to the more complicated problem of the behavior of $KCl-AlCl_3-ZnCl_2$ melts.

In calculations on the $KCl-AlCl_3$ system only the last five measurements in Table Ia were used because in the first seven measurements in Table Ia very little of the dimeric complex $Al_2Cl_7^-$ was present. These data were fitted to model reactions of the form

$$nAlCl_4^- \rightleftharpoons Al_nCl_{4n-m}{}^{(n-m)-} + mCl^- \qquad (8)$$

where n and m are integers. For each reaction (*i.e.*, for each n and m) the best pK was obtained by a least-squares method in which the deviation was minimized and n and m were varied within the range 1-6. A survey of the best model reactions is shown in Table IIa in the order of increasing polymerization. A so-called F test ($F = v_1/v_2$ where v is the variance) was applied to the results. This test gave the model involving $Al_2Cl_7^-$ a probability of 99% compared with a 1% probability for the next best model, which involved $Al_3Cl_{11}{}^{2-}$. On this basis, the equilibrium $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ was considered to be the correct one.

The variance for an equilibrium involving $Al_2Cl_7^-$ is 8.8×10^{-8}. This variance is somewhat larger than the variance found for the same system at high chloride activities. The excess variance can be explained by a change in activity as well as by a change in the last three terms in (3). Furthermore, the composition of the melt is slightly more uncertain in this high-pCl^- range due to transportation of $AlCl_3$ in the vapor phase from one of the chambers to the other. This transportation can be divided into two parts, one which takes place when the cell is heated after an addition of $AlCl_3$ and the other which takes place between the melt surfaces. A correction cannot be made for the first transportation, whereas the other is easy to correct for since a steady decrease of the cell voltage, which corresponds to 0.5-2.5 mg of $AlCl_3$/hr depending of the composition of the melt, is observed. Because the time in which the cell is heated is small (about 10 min), the uncertainty due to the first transportation is probably small.

Plots of the measurements compared with some of the best fits are shown in Figure 3. This shows that the equilib-

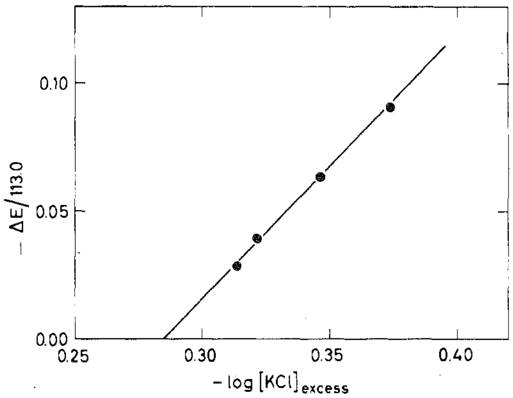

Figure 2. Plot used to obtain the pCl^- of a $KCl-AlCl_3$ melt saturated with KCl at 300°.

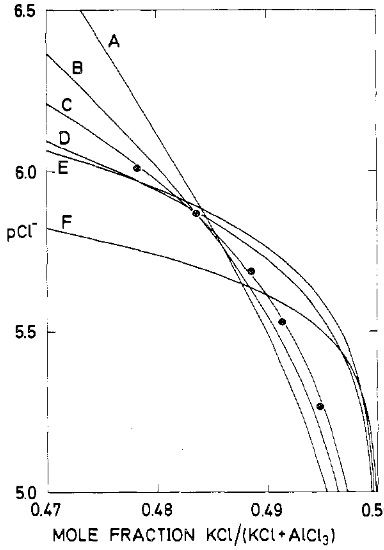

Figure 3. Measured pCl^- values (filled circles) as a function of mole fraction of $(KCl)/(KCl + AlCl_3)$ in a $KCl-AlCl_3$ melt at 300° compared with calculated values (full lines) for a series of reaction schemes which were in reasonably good agreement with the experimental data. All the calculated values have been minimized in order to obtain the best fit. The third species, aside from Cl^- and $AlCl_4^-$: A, $Al_4Cl_{15}{}^{3-}$; B, $Al_3Cl_{11}{}^{2-}$; C, $Al_2Cl_7^-$; D, $Al_4Cl_{14}{}^{2-}$; E, $Al_3Cl_{10}^-$; F, $Al_4Cl_{13}^-$.

Table I. Values of Cell Potential and Composition of Molten Electrolyte at 300°

Part a		Part b		Part c	
0.00 F $ZnCl_2$		0.10 F $ZnCl_2$		0.30 F $ZnCl_2$	
$-\Delta E$, mV	Mole fraction of (KCl)/(KCl + $AlCl_3$)	$-\Delta E$, mV	Mole fraction of (KCl)/(KCl + $AlCl_3$)	$-\Delta E$, mV	Mole fraction of (KCl)/(KCl + $AlCl_3$)
647.1	0.4782_5	174.2	0.5062_2	212.4	0.5147_3
631.1	0.4836_5	148.4	0.5067_5	196.5	0.5159_1
610.7	0.4886_6	132.4	0.5073_0	181.5	0.5168_8
592.8	0.4914_1	103.5	0.5082_9	165.7	0.5178_4
563.0	0.4948_7	86.9	0.5091_5	144.3	0.5188_8
109.0	0.5022_0	30.9	0.5154_2	129.0	0.5196_9
49.1	0.5066_3	6.9	0.5213_6	127.4	0.5196_5
28.9	0.5100_7	4.3	0.5219_1	92.0	0.5217_3
10.3	0.5137_9	3.4	0.5222_6	85.4	0.5222_6
7.2	0.5146_9			20.0	0.5312_2
4.4	0.5155_6			16.1	0.5325_0
3.2	0.5158_5			14.7	0.5323_7
				10.3	0.5338_8
				5.8	0.5351_8

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(22) W. Fischer and A. L. Simon, *Z. Anorg. Allg. Chem.*, **306**, 1 (1960).

Table II. Comparison between Some of the Best Models for the Equilibria

[ZnCl$_2$], *F*	Higher complex	p*K*	Variance, *v*	$F = v/v_{min}$	% probability (for two best models)
		Part a			
0.000	$Al_2Cl_7^-$	7.83 ± 0.02	8.8×10^{-8}	1.00	99
0.000	$Al_3Cl_{11}^{2-}$	8.57 ± 0.08	1.6×10^{-6}	17.8	1
0.000	$Al_4Cl_{15}^{3-}$	9.26 ± 0.20	5.7×10^{-6}	65.1	
		Part b			
0.100	$ZnCl_3^-$	2.24 ± 0.10	9.4×10^{-9}	1.00	70
0.100	$Zn_2Cl_6^{2-}$	3.12 ± 0.25	28.5×10^{-9}	3.02	
0.100	$Zn_3Cl_{10}^{4-}$	1.72 ± 0.21	13.9×10^{-9}	1.47	30
0.100	$Zn_4Cl_{13}^{5-}$	2.45 ± 0.42	30.7×10^{-9}	3.25	
0.100	$Zn_6Cl_{20}^{8-}$	1.75 ± 0.62	27.7×10^{-9}	2.93	
		Part c			
0.300	$ZnCl_3^-$	2.14 ± 0.04	6.8×10^{-8}	1.10	43
0.300	$Zn_2Cl_6^{2-}$	3.56 ± 0.12	13.2×10^{-8}	2.14	
0.300	$Zn_3Cl_{10}^{4-}$	2.45 ± 0.15	11.9×10^{-8}	1.93	
0.300	$Zn_4Cl_{13}^{5-}$	3.71 ± 0.13	6.2×10^{-8}	1.00	57
0.300	$Zn_6Cl_{20}^{8-}$	3.79 ± 0.23	9.7×10^{-8}	1.57	

rium involving $Al_2Cl_7^-$ gives much the best fit. The p*K* value for $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ was found to be 7.83 ± 0.02. This value is considerably higher than the value 7.1 given by Torsi and Mamantov.[23]

pCl$^-$ Behavior and Model Equilibria for the KCl-AlCl$_3$-ZnCl$_2$ System. Next we consider a system to which $ZnCl_2$ has been added. In Table Ib, c the values of ΔE as a function of mole fraction of (KCl)/(KCl + AlCl$_3$) for 0.10 and 0.30 *F* ZnCl$_2$ are shown. Since the solubility of ZnCl$_2$ is rather small at high pCl$^-$, measurements were only done in a limited pCl$^-$ range. A plot of the corresponding pCl$^-$ as a function of (KCl)/(KCl + AlCl$_3$) compared with a similar plot for pure KCl-AlCl$_3$ is shown in Figure 4. This figure illustrates the buffering effect of adding ZnCl$_2$ to the melt.

In mixtures of pure KCl-AlCl$_3$ the pCl$^-$ variation between 1 and 5 is very sensitive to melt composition, but when ZnCl$_2$ is added, the variation is less sensitive to composition, at least in the pCl$^-$ range of 1-2. Furthermore the figure illustrates the fact that ZnCl$_2$ takes up additional chloride ions giving a smaller chloride ion concentration (*i.e.*, higher pCl$^-$) than corresponding unbuffered solutions.

In interpreting this buffer action the first problem is to make sure that $ZnCl_4^{2-}$ is actually present. The best way to do this is to calculate the average coordination number for Zn(II) at fairly low pCl$^-$. This can easily be done because we know how many chloride ions have been added in excess of KAlCl$_4$ and we can measure the chloride activity. The difference between those two numbers must be due to chloride ions bound to Zn(II). Of course at high pCl$^-$ a correction must be made for the presence of $Al_2Cl_7^-$.

Such a plot of the average coordination number of Zn(II) is shown for the 0.10 and 0.30 *F* ZnCl$_2$ in Figure 5. From this figure it can be seen that at low pCl$^-$ (close to the saturation point, dashed line) the average coordination number is very close to 4 for both concentrations of Zn(II). The only way to explain this is to say that only $ZnCl_4^{2-}$ is present because if additional species were present, the average coordination number would change with the total concentration of Zn(II).

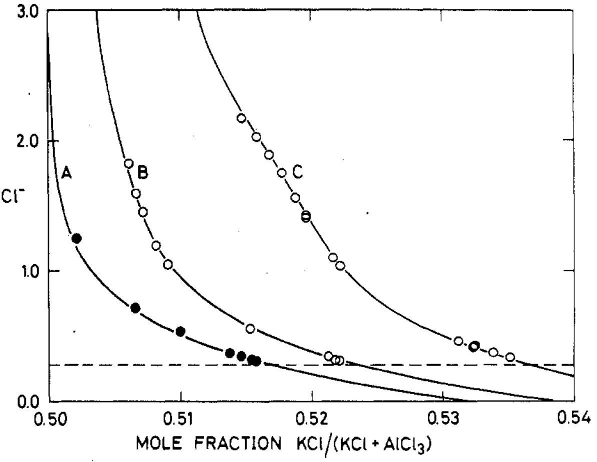

Figure 4. A comparison between the pCl$^-$ as a function of mole fraction of (KCl)/(KCl + AlCl$_3$): A, measured for a KCl-AlCl$_3$ system (filled circles); B, KCl-AlCl$_3$-0.10 *F* ZnCl$_2$ system (open circles); C, KCl-AlCl$_3$-0.30 *F* ZnCl$_2$ system (open circles). All the measurements were done at 300°. The full line shows the best fit calculated on the basis of an equilibrium (A) between Cl$^-$, $Al_2Cl_7^-$, and $AlCl_4^-$ with a p*K* of 7.83 and (B and C) between Cl$^-$, $ZnCl_3^-$, and $ZnCl_4^{2-}$ with a p*K* of 2.14. The dashed line shows the limiting pCl$^-$ (due to saturation with KCl).

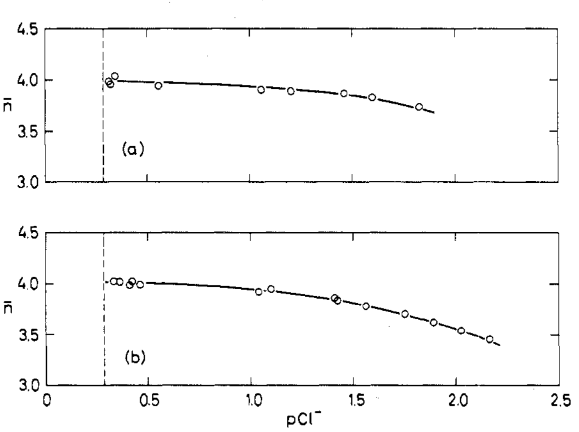

Figure 5. Average coordination number for Zn(II) as a function of pCl$^-$: (a) 0.10 *F* Zn(II); (b) 0.30 *F* Zn(II). The dashed line shows the limiting pCl$^-$ (due to saturation with KCl).

As in the case of pure KCl-AlCl$_3$ a general reaction scheme of the following form was set up

$$n_1 ZnCl_4^{2-} \rightleftarrows Zn_{n_1}Cl_{4n_1-m_1}{}^{(2n_1-m_1)-} + m_1 Cl^- \qquad (9)$$

where n_1 was allowed to vary between 1 and 6 and m_1 was allowed to vary between 1 and $2n_1$. The latter means that the higher complex will either have a negative charge or be without charge. A survey of the five best models out of a

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(23) G. Torsi and G. Mamantov, *Inorg. Chem.*, 11, 1439 (1972).

total of 42 for both 0.10 and 0.30 *F* $ZnCl_2$ is shown in Table IIb, c. These models have been selected so that the probability on the basis of an *F* test for the model with the highest variance should be higher than 5% as compared with the model with the lowest variance either for the 0.1 *F* $ZnCl_2$ or for the 0.3 *F* $ZnCl_2$ solutions. From this table it can be seen that on the basis of the *F* test it is not possible to distinguish between the best models even if the model involving $ZnCl_3^-$ is the only one with a reasonably high probability at both concentrations. However, if we include the stipulation that for a given model the p*K* values calculated for each concentration should agree, we find that only one model will fit these criteria, namely, the equilibrium $ZnCl_4^{2-} \rightleftarrows ZnCl_3^- + Cl^-$ with an average p*K* value of 2.15 ± 0.04. Furthermore the variance for this system is smaller than the variance found at high pCl^- for the KCl-$AlCl_3$ system but larger than the variance of 3×10^{-9} found at low pCl^- for the KCl-$AlCl_3$ system (last four measurements in Table Ia) where the reaction mechanism is unambiguous. This is a behavior which one would expect.

In view of the unexpected degree of success with which the polymers $Zn_3Cl_{10}^{4-}$ and $Zn_4Cl_{13}^{5-}$ represent the data, respectively, at 0.10 and 0.30 *F* $ZnCl_2$ it would have been interesting to include n_1 values higher than 6 in the above model fitting, but unfortunately this would have required excessive computer time. The ambiguity in choosing a preferred model on the basis of mathematical data fitting is obviously accentuated by the small variation in the degree of zinc coordination provided by the data, as illustrated in Figure 5. If the data had covered a wider range, the probability of the reaction $ZnCl_4^{2-} \rightleftharpoons ZnCl_3^- + Cl^-$ would certainly have been vastly enhanced. However, as matters stand, we are left with trying to predict the total behavior of a function from an imperfect knowledge of only its first few derivatives. Physically there seems to be no way to get around this problem because of the low solubility of $ZnCl_2$ at high pCl^- values. However, the present measurements have not been performed all the way up to the saturation point of $ZnCl_2$.

It is noteworthy that the model equation

$$2ZnCl_4^{2-} \rightleftharpoons Zn_2Cl_7^{3-} + Cl^-$$

proved thoroughly inadequate as a representation of the data. This equation has been proposed[24,25] as the best representation of the structural situation in MCl-$ZnCl_2$ mixtures rich in MCl but it is a very poor representation of the buffering action of $ZnCl_2$ in KCl-$AlCl_3$ mixtures.

If we suppose that the structural reality behind the buffering action of $ZnCl_2$ is correctly represented by $ZnCl_4^{2-} \rightleftharpoons ZnCl_3^- + Cl^-$, we can reconcile this behavior with that in MCl-$ZnCl_2$ through the additional supposition that $ZnCl_3^-$ is four-coordinate with the fourth chloride forming a bridge to aluminum so as to give an entity such as $Cl_3ZnClAlCl_3^{2-}$. Such an entity would, of course, be impossible in MCl-$ZnCl_2$ melts while perhaps being favored in the present case because of the high concentration of chloroaluminate species. The fact that this concentration is so high and, therefore, so slightly affected by solvation reactions obviously precludes the possibility of detecting solvation reactions by means of activity measurements.

Registry No. KCl, 7447-40-7; $AlCl_3$, 7446-70-0; $ZnCl_2$, 7646-85-7; $AlCl_4^-$, 17611-22-2; $ZnCl_4^{2-}$, 15201-05-5.

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Reactions of the Difluoramine-Potassium Fluoride Adduct, $HNF_2 \cdot KF$, with Sulfinyl and Perfluoroalkylsulfinyl Fluorides. Preparation of Perfluoroalkyl Perfluoroalkylthiosulfonates

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The reaction of $HNF_2 \cdot KF$ with sulfinyl fluoride gave $FS(O)NF_2$ which was isolated and had sufficient stability to be characterized by spectroscopic methods. Attempts to prepare $CF_3S(O)NF_2$ and $C_2F_5S(O)NF_2$ resulted in the formation of N_2F_4 and the perfluoroalkyl perfluoroalkylthiosulfonate esters $CF_3SO_2SCF_3$ and $C_2F_5SO_2C_2F_5$. Efforts to synthesize additional thiosulfonate esters led to the characterization of $C_2F_5S(O)Cl$, ^{19}F nmr spectral identification of $C_2F_5SO_2SCF_3$ and $CF_3SO_2SC_2F_5$, and spectroscopic characterization of the previously reported $C_2F_5SO_2F$.

Introduction

In surveying the field of fluorinated sulfur-nitrogen compounds, the dearth of compounds which contain the difluoroamino moiety bound to sulfur became apparent. With the exception of CF_3SNF_2,[2] the known difluoroamino derivatives of this class of compounds are limited to cases in which sulfur is present in its maximum oxidation state.[3] Photolytic or thermal reactions of N_2F_4 for the preparation of sulfur(IV) difluoroamino compounds were not useful since oxidation of sulfur occurred with SF_4 derivatives or

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(2) E. C. Stump and C. D. Padgett, *Inorg. Chem.*, 3, 610 (1964).

(3) S. M. Williamson, *Progr. Inorg. Chem.*, 7, 39 (1966).