at 50-kbar pressure were unsuccessful. Comparison of the solid-state chemistry of Ni, Pd, and Pt, indicates that $5d^8$ Pt cannot occupy an octahedral site, whereas d^8 Ni and d^8 Pd are known to occupy octahedral sites. This is consistent with the failure to observe a phase transition for rhodium-substituted platinum diselenide.

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Registry No. $PdSe_2$, 60672-19-7; $RhSe_2$, 12038-76-5; $PtSe_2$, 12038-26-5.

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Chloro Complexes in Molten Salts. 6. Potentiometric and Vapor Pressure Study of the System $KCl–AlCl_3$ in the Temperature Range 275–350 °C

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By potentiometric measurements with chlorine/chloride electrodes (and aluminum electrodes) the solubility of KCl in $KCl–AlCl_3$ melts was examined in the temperature range 275–350 °C. A plot of $-pK_s$ (where K_s is the solubility product of K^+ and Cl^- in molar concentrations) vs. the inverse absolute temperature in the above temperature range gave an almost linear plot. From this plot $\Delta S°$ and $\Delta H°$ (for dissolution of KCl in $KAlCl_4$) were calculated to be 46.8 (11) J/(deg mol) and 19.7 (6) kJ/(mol), respectively. It was furthermore found that for up to a mole fraction of $AlCl_3$ of 0.524 62 in the temperature range from 275 to 350 °C, the potentiometric results were best explained by a combination of two reactions: $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ and $Al_2Cl_7^- \rightleftarrows Al_2Cl_6 + Cl^-$ (model 1) or $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$ and $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$ (model 2). However, combined potentiometric and vapor pressure measurements could better be explained by three reactions (model 3): (i) $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$, (ii) $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$, and (iii) $2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6 + 2Cl^-$. The p*K* values (based on molar concentrations) for reaction (i) were found to be 8.15 (1), 7.80 (2), 7.47 (2), and 7.15 (3) at 275, 300, 325, and 350 °C, respectively. Possible values for reaction (ii) were found to be 7.6 (4), 7.3 (6), 7.1 (7), and 7.1 (11) and for reaction (iii) 15.4, no value found, 14.0, and 12.1 at 275, 300, 325, and 350 °C, respectively. From the temperature dependence of reaction (i) it was found that in the temperature range 275–350 °C the values of $\Delta S°$ and $\Delta H°$ were 0.9 (22) J/(deg mol) and 86.0 (12) kJ/mol, respectively.

Introduction

An exact value for the equilibrium constants for the acid–base reactions in molten chloroaluminates at different temperatures is of the utmost importance when one is dealing with examination of chloro complexes of dilute metal salts dissolved in these melts. Very accurate values of the equilibrium constants for the solvents are necessary in order to get the correct values for the dilute systems.

In the present paper a more detailed examination than performed earlier[1] for the $KCl–AlCl_3$ system is presented. In a fairly small range around 50–50 mol % $KCl–AlCl_3$ one equilibrium (i.e., $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$) is sufficient to explain the acid–base reactions of the melt itself reasonably well.[1,2] However, if very accurate measurements are performed or if a larger range is examined, the above model is quite inadequate.

The closely related system $NaCl–AlCl_3$ has been examined potentiometrically by several authors.[3-5] The measurements have been performed mostly by use of aluminum electrodes but also chlorine/chloride electrodes in an open system have been used.[3] Boxall et al.[5] examined the potentiometric measurements for this system over a fairly large compositional range (50–70 mol % $AlCl_3$) in terms of the species Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, and Al_2Cl_6. In order to obtain agreement between the calculated and measured values at high $AlCl_3$ composition, the activity coefficients were adjusted to vary as required by a regular solution. Fannin et al.[4] did not take the change in activity coefficients into consideration even when they were working in a large compositional range; on the other hand, they included on the acidic side the existence of $Al_3Cl_{10}^-$ in order to obtain better agreement between measured and calculated values. The existence of a higher polymeric aluminum species than $Al_2Cl_7^-$ and Al_2Cl_6 in $KCl–AlCl_3$ (and in $NaCl–AlCl_3$) is supported by Raman spectroscopic evidence.[6-8] The existence of $AlCl_4^-$ and $Al_2Cl_7^-$ is well supported by the Raman spectra as is the existence of Al_2Cl_6. However, at higher contents of $AlCl_3$, the bands which cannot be ascribed to any of the above species appear.

Experimental Section

The chemicals in the present work were prepared in the same way as in previous work dealing with $KCl–AlCl_3$ solvents.[1,9] Similarly, the experimental technique concerning the potentiometric measurements was the same as described in previous work.[1,9,10] A concentration cell made of Pyrex glass (without a pressure equilibrium connecton tube between the two chambers[10]) was used for the potentiometric measurements. The electrode material was either glassy carbon (V10 from Carbone Lorraine) for the chlorine/chloride electrodes or pure aluminum (99.999%, Atomergic Chemetals Corp.) for the aluminum electrodes.

The furnace and its regulation have been described in detail in connection with a method for determination of densities of molten

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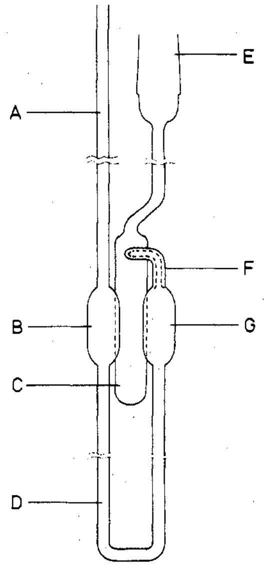

Figure 1. Quartz cell for vapor pressure measurements: A, stem (which can be connected to vacuum pump); B, reservoir for manometer tin; C, salt melt compartment; D, manometer tube; E, standard taper joint removed after filling of C; F, capillary connection between G and space above melt; G, reservoir for manometer tin.

salts.[11] The chromel–alumel thermocouples (from Pyrotenax) were calibrated at the freezing points of pure tin, lead, and zinc to within ±0.5 °C. The measured temperatures at 275, 300, 325, and 350 °C are probably correct to within ±0.7 °C (the regulation of the furnace is ca. ±0.1 °C).

The apparatus for the vapor pressure measurements consisted of a quartz cell (shown in Figure 1) and a furnace. The furnace was made from a quartz tube (length 750 mm) with a Kanthal wire winding and a surrounding water-cooled glass jacket. A Eurotherm Type LP-PID-FC regulator was used to control the furnace.

The procedure for filling the apparatus was as follows. First small pieces of tin were added through the stem (A). The tin was then melted under vacuum (less than 20 μ) using a Bunsen burner and was then allowed to solidify. The materials that made up the initial melt (with a mole fraction of KCl of approximately 0.52) were introduced through the standard taper joint (E). This was, of course, carried out in a glovebox. The cell was now taken out of the glovebox and a vacuum hose attached to the stem (A) and the standard taper joint was sealed off and removed under vacuum. The quartz cell was mounted in a stainless steel holder of the type described previously.[11] The cell was placed in such a way in the holder that the tip of the stem (A) was outside the furnace, providing access for the attachment of a vacuum hose. In order to obtain a uniform temperature of the melt the quartz tube (C) containing the melt material was surrounded by a thick-walled aluminum cylinder secured to the stainless steel holder. A chromel–alumel thermocouple was placed in a small hole in this cylinder. A stainless steel rule secured to the stainless steel holder was used to measure the difference in height in the manometer branch (D).

After the cell was filled and placed in the holder, the vacuum hose attached to the stem (A) was filled with dry nitrogen and the material in compartment C was melted, allowed to mix completely, and then allowed to solidify. In order to get rid of the dissolved gases in the material the tin was melted and allowed to solidify in reservoirs B and G and a vacuum was again applied to the system. The melt material was carefully heated to a little above the melting point (ca. 250 °C) and the melt exposed to vacuum. Although the vapor pressure above this initial melt is very small at the given composition and temperature, the melt was only exposed to vacuum for a few minutes. The vapor pressure of this initial melt after the degassing procedure was less than 0.2 mmHg in the temperature range 275–350 °C. After the initial measurements, the melt was allowed to solidify and the cell was again taken into the glovebox. Here an addition of $AlCl_3$ could be made to the cell so that the melt (after mixing) had an excess of $AlCl_3$ (i.e., a mole fraction of $AlCl_3$ higher than 0.500). The degassing procedure was now repeated except that only the mixed solid salt, but not the melt, was exposed to a vacuum to avoid evaporation of $AlCl_3$. This procedure was repeated several times with the same melt composition and it was found that the measured pressure above the melt (at the same temperature) did not change, indicating that a stable condition had been reached. As we shall see later on, about 4 mmHg of the measured pressure is in this case due to gases other than Al_2Cl_6, the most likely gas being N_2 since the materials were mixed under N_2 pressure.

General Considerations

The formality C' is defined as the initial molar amount of one of the added substances (in the present work either KCl or $AlCl_3$) dissolved in 1 L of the melt. The excess formality of KCl or $AlCl_3$, C'_{excess}, is defined as the difference in formality between KCl and $AlCl_3$ or $AlCl_3$ and KCl, respectively. All melts with more than 50 mol % KCl are called basic. A more informative expression for the acidity/basicity of the melt is the pCl^-, defined as the negative logarithm of the chloride concentration (in molar units). The densities of the KCl–$AlCl_3$ system were obtained from the work by Morrey and Carter.[12]

It has previously[1,13] been shown that close to 1:1 composition in the KCl–$AlCl_3$ system (from ca. 47 to ca. 52 mol % KCl) the potential for the chlorine/chloride concentration cell used (with electrode process $Cl_2 + 2e^- \rightleftarrows 2Cl^-$) can generally be given as

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

(at constant T) since the chlorine pressure and hence the chlorine activity are the same in both cell compartments. t_i, z_i, and μ_i are the transference number, charge, and chemical potential for the ith ion, respectively, and I and II refer to the two cell compartments. Within the experimental uncertainty this can be reduced to[1]

$$\Delta E = -\frac{RT}{F}\ln\frac{[Cl^-]_{\mathrm{II}}}{[Cl^-]_{\mathrm{I}}} \qquad (2)$$

where $[Cl^-]_{\mathrm{I}}$ and $[Cl^-]_{\mathrm{II}}$ are the chloride activities in the respective two cell compartments. In order to obtain a stable reference, cell compartment II is usually saturated with KCl. Since the solubility of KCl in $KAlCl_4$ is rather temperature dependent,[14] it is important to have a good temperature control of the furnace. If one is working with aluminum electrodes where the electrode process can be written as $AlCl_4^- + 3e^- \rightleftarrows Al + 4Cl^-$, the electrode potential can similarly (within the experimental uncertainty) be reduced to

$$\Delta E = -\frac{4RT}{3F}\ln\frac{[Cl^-]_{\mathrm{II}}}{[Cl^-]_{\mathrm{I}}} \qquad (3)$$

Quite generally the potential for any electrode cell measuring the chloride activity in KCl–$AlCl_3$ in the composition range ca. 47 to ca. 52 mol % KCl can be expressed as

$$\Delta E = \frac{m}{n}\frac{RT}{F}\ln\frac{[Cl^-]_{\mathrm{II}}}{[Cl^-]_{\mathrm{I}}} \qquad (4)$$

where m and n are the number of chloride ions and number of electrons involved in the electrode processes, respectively.

The pCl^- of the melt can be given as

$$pCl^- = -(Fn/(mRT \ln 10))\Delta E + pCl_{\mathrm{II}}^- \qquad (5)$$

where pCl_{II}^- is the pCl^- in the saturated melt (i.e., in cell compartment II). It is now well-known[1-8] that in basic KCl–$AlCl_3$ (except close to the 1 to 1 composition) the only aluminum complex present is $AlCl_4^-$. Therefore, in the basic region and according to the definition of $C'_{KCl(\text{excess})}$, the pCl^- of the melt is equal to $C'_{KCl(\text{excess})}$. This provides an opportunity to check eq 5 since $-(Fn/(mRT \ln 10))\Delta E$ plotted against $C'_{KCl(\text{excess})}$ should give a straight line with the slope of unity

Table I. Values of Mole Fraction and Cell Potentials for Molten KCl–$AlCl_3$ in the Temperature Range 275–350 °C

mole fraction of KCl	$-\Delta E$, mV			
	275 °C	300 °C	325 °C	350 °C
0.4753_8	646.5	646.7	647.0	647.4
0.4782_0	639.6	637.6	637.4	635.2
0.4791_0	637.9	637.4	637.0	637.3
0.4797_1	634.9	634.9	633.6	633.2
0.4838_8	625.0	623.8	622.3	621.2
0.4886_0	608.1	606.2	604.7	601.5
0.4915_8	594.1	591.0	588.3	583.5
0.4951_9	567.9	562.4	558.5	555.1
0.5099_9	17.85	28.66	39.49	
0.5101_0	19.70	29.89	41.52	
0.5110_3	15.14			
0.5110_6	15.12	25.53	36.27	46.08
0.5113_4		33.60[a]		
0.5116_3	12.45			
0.5124_0	9.97	21.22		
0.5128_6	9.65[a]	22.65[a]	36.88[a]	52.30[a]
0.5130_2		15.46		
0.5131_8	6.61	17.28		
0.5139_8		13.31	24.93	
0.5144_6		15.50[a]		
0.5148_1		8.61	18.34	
0.5150_3		10.01	20.79	
0.5152_7		5.89		
0.5162_7		7.05		
0.5155_3			15.65	
0.5156_5		6.23	15.86	
0.5158_8		4.68	14.78	
0.5160_5		8.02[a]		
0.5170_1		3.72	13.15	23.83
0.5172_5				21.13
0.5197_1			4.22	16.18
0.5231_4				6.65

[a] Measured with an aluminum electrode; the other measurements were made with a chlorine/chloride electrode.

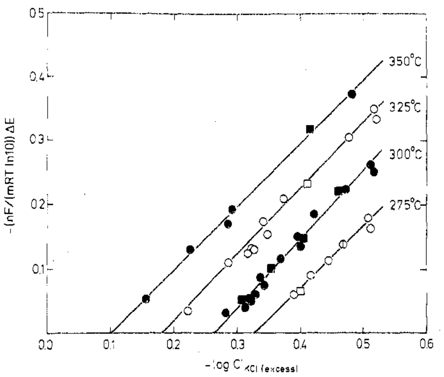

Figure 2. Plots used to check eq 5 for the KCl–$AlCl_3$ system at 275 °C (open circles and open squares), 300 °C (filled circles and filled squares), 325 °C (open circles and open squares), and 350 °C (filled circles and filled squares). Open and filled circles indicate measurements obtained with chlorine/chloride electrodes; open and filled squares indicate measurements obtained with aluminum electrodes. The open circle divided by a vertical line represents a coincidence of two open circles.

and the intercept at the abscissa (where $-\Delta E = 0$) will give pCl_{II}^- at the chosen temperature.

In all calculations the variation in the activity coefficients has been neglected. This can be justified by the fact that the solvent was $KAlCl_4$ and that the concentrations of solute species, i.e., Cl^-, $Al_2Cl_7^-$, Al_2Cl_6, and higher complexes, were small compared to the concentrations of K^+ and $AlCl_4^-$. Furthermore, it was clear from the observations made during the course of this work that only very small (if any) variations occurred in the activity coefficients. This is in complete agreement with previous calculations on the same system.[1]

Results and Discussion

Determination of the Solubility of KCl in $KAlCl_4$ at Different Temperatures. From what has been said under General Considerations it should be clear that in order to determine the pCl^- in a given melt it is necessary to know the chloride concentration in the saturated melt used in the reference compartment. In Table II are given the values of $-(Fn/(mRT \ln 10))\Delta E$ obtained from the measurements with KCl mole fractions somewhat higher than 0.500 (values for the measured $-\Delta E$'s are given in Table I) as a function of the negative logarithm of the excess formality of KCl at different temperatures. A plot, as discussed in connection with eq 5, of the values in Table II is given in Figure 2. From this figure it can be seen that the measuremenns obtained with chloride/chloride electrodes (open and filled circles) agree well with the measurements obtained with the aluminum electrodes (open and filled squares). The straight lines in Figure 2 are drawn by use of a least-squares method. The weighted average of the slopes for all the lines shown in this figure is found to be 0.97 (2) (i.e., 0.97 ± 0.02). The difference between this number and 1.00 might be explained as due to differences in activity coefficients in going from a lower chloride concen-

Table II. Values Used To Obtain the Solubility of KCl in $KAlCl_4$ in the Temperature Range 275–350 °C[a]

275 °C		300 °C		325 °C		350 °C	
$-\log C'_{KCl(excess)}$	$-Fn\Delta E/(mRT \ln 10)$	$-\log C'_{KCl(excess)}$	$-Fn\Delta E/(mRT \ln 10)$	$-\log C'_{KCl(excess)}$	$-Fn\Delta E/(mRT \ln 10)$	$-\log C'_{KCl(excess)}$	$-Fn\Delta E/(mRT \ln 10)$
0.3902	0.0608	0.2825	0.0327	0.2221	0.0356	0.1560	0.0538
0.4010[b]	0.0665[b]	0.3081	0.0529[b]	0.2871	0.1108	0.2267	0.1309
0.4169	0.0917	0.3128	0.0412	0.3174	0.1245	0.2856	0.1709
0.4449	0.1145	0.3192	0.0548	0.3238	0.1336	0.2917	0.1927
0.4670	0.1390	0.3225	0.0518	0.3271	0.1319	0.4148	0.3172[b]
0.4681	0.1392	0.3299	0.0620	0.3415	0.1752	0.4809	0.3727
0.5068	0.1811	0.3369	0.0880	0.3480	0.1545		
0.5115	0.1641	0.3435	0.0757	0.3733	0.2101		
		0.3539	0.1022[b]	0.4102	0.2331		
		0.3688	0.1170	0.4762	0.3056		
		0.3999	0.1360	0.5160	0.3498		
		0.4056	0.1494[b]	0.5206	0.3327		
		0.3947	0.1520				
		0.4214	0.1866				
		0.4607	0.2216[b]				
		0.4716	0.2245				
		0.5114	0.2628				
		0.5160	0.2520				

[a] Also used to check eq 5. [b] Measured with an aluminum electrode; the other measurements were made with a chlorine/chloride electrode.

Table III. Composition of Saturated Melts in the Temperature Range 275–350 °C

temp, °C	pCl^-	mole fraction X_{KCl}[a]	variance × 10^7	$[K^+]$, M	$[Cl^-]$, M
275	0.331 (2)[b]	0.51507 (9)	0.30	7.970	0.467
300	0.255 (3)	0.51809 (11)	1.23	7.952	0.556
300	0.251 (4)[c]	0.51829 (16)[c]			
325	0.181 (3)	0.52166 (17)	1.49	7.946	0.659
350	0.103 (3)	0.52608 (17)	0.77	7.957	0.789

[a] Other component $AlCl_3$. [b] I.e., 0.331 ± 0.002. [c] Calculations based only on measurements with aluminum electrodes.

tration (ca. 0.3 M) to higher chloride concentration (ca. 0.5 M). However, the standard error is so large that there is reason to expect that the difference is due to uncertainty in the measurements. This way of reasoning is in agreement with the results obtained for the analogous $KCl-FeCl_3$ system[10] where the weighted average of the slopes obtained for the same temperature range and for about the same concentration range was found to be 1.01 (1). Therefore, in Table III the pCl^- and the composition of the saturated melt at the measured temperatures are calculated as before[10] on the basis of straight lines with fixed slopes of unity. In Table III the molar concentrations of potassium and chloride ions are given together with the variances. These variances (called the experimental variances) are calculated from the deviations in mole fractions between the measured data points and the calculated straight lines. Since these calculated values are given at several temperatures, it is obvious to plot them in such a way that an extrapolation is easy. Since the melts are saturated, the product of the concentration of potassium ions $[K^+]$ and chloride ions $[Cl^-]$ should be constant at constant temperature, i.e.

$$[K^+][Cl^-] = K_s \qquad (6)$$

K_s (the solubility product constant) can now be calculated from Table III and $-pK_s$ plotted vs. the inverse absolute temperature. Such a plot is shown in Figure 3. On the basis of a regression analysis of the weighted data the equation for the line shown in Figure 3 was found to be $-pK_s = -1030\ (34)/T + 2.45\ (6)$. This equation can for example be used to calculate the composition of the melt at the eutectic temperature of 250 °C found by Fischer and Simon.[14] Their value for the mole fraction of KCl at the eutectic temperature is 0.51_0 which compares well with a value of 0.5120 (3) found by using the above equation and assuming that the temperature given by Fischer and Simon is correct.

If the pCl^- values for the saturated melt at 300 °C in this work (Table III) are compared with the values for the similar system in the earlier work,[1] it is seen that there is a considerable deviation between the given values. However, the old value is based on only four measurements with the same cell, obtained in a rather limited range. Furthermore, it should be noted that this error has only had a marginal influence on previous calculations involving chloro complexes in molten $KCl-AlCl_3$ melts (i.e., ref 9).

From the plot given in Figure 3, $\Delta S°$ and $\Delta H°$ for the dissolution process $KCl(s) \rightleftarrows K^+(soln) + Cl^-(soln)$, where the solvent is $KAlCl_4$, can be calculated to be 46.8 (11) J/(deg mol) and 19.7 (6) kJ/mol, respectively. For the analogous reaction for the $KCl-FeCl_3$ system and for the same temperature range, $\Delta S°$ and $\Delta H°$ can be calculated from the original measurements obtained by Andreasen and Bjerrum[10] to be 40.8 (19) J/(deg mol) and 15.3 (11) kJ/mol, respectively. Since no direct calorimetric investigations seem to have been performed on these systems, the best quantity with which to compare the obtained $\Delta H°$ values is the heat of fusion of KCl (where the solvent is KCl); calorimetrically the heat of fusion of KCl has been found to be 26.5 kJ/mol.[15] This value is considerably higher than the value found for the dissolution of KCl in $KAlCl_4$ or $KFeCl_4$. Apparently these solvents, perhaps due to the larger size of the anion (compared with the Cl^-), reduce the energy necessary to break down the crystal lattice.

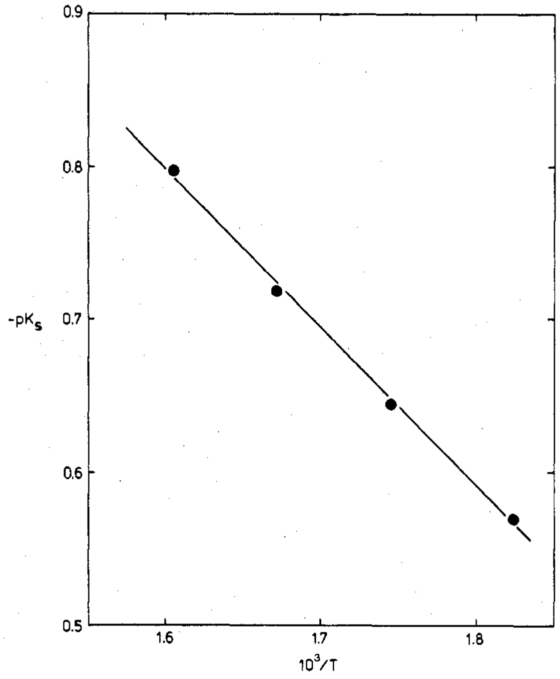

Figure 3. $-pK_s$ (K_s is the solubility product for K^+ and Cl^- ions) as a function of the inverse absolute temperature ($\times 10^3$). The straight line is drawn from a least-squares calculation using weighted values.

Model Equilibria for the $KCl-AlCl_3$ System Based on the Potentiometric Measurements. If the pCl^- values calculated from all the concentration cell measurements (at constant *T*) are plotted against the mole fraction of KCl, it is well-known that an S-shaped curve is obtained.[3-5] The shape of this curve has been shown to be due primarily to the acid–base reaction

$$2AlCl_4^-(soln) \rightleftarrows Al_2Cl_7^-(soln) + Cl^-(soln) \qquad (7)$$

with equilibrium constant K_1. As mentioned in the Introduction smaller amounts of aluminum-containing species other than $AlCl_4^-$ and $Al_2Cl_7^-$ have been considered to be involved. Our approach has been first to look at two interrelated equilibria and then if possible at three interrelated equilibria. Since the $KCl-AlCl_3$ system on the acidic side has a fairly high vapor pressure, the most likely new species to be included in another equilibrium is Al_2Cl_6 and in the following way:

$$Al_2Cl_7^-(soln) \rightleftarrows Al_2Cl_6(soln) + Cl^-(soln) \qquad (8)$$

The equilibrium constant associated with this equation will be called K_2. Since as mentioned in the Introduction, higher complexes (for example $Al_3Cl_{10}^-$ which is the most likely higher complex after $Al_2Cl_7^-$) have been suggested on the basis of Raman spectra for the melt, another possibility for the second reaction would be

$$3Al_2Cl_7^-(soln) \rightleftarrows 2Al_3Cl_{10}^-(soln) + Cl^-(soln) \qquad (9)$$

with equilibrium constant K_3. If we are looking only at two interrelated equilibria at the same time, the most likely possibilities are the ones given in Table IV (model 1 and model 2). As can be seen from this table by examining the values of the variances, both methods give comparable fits. Furthermore, the obtained variances are rather similar to the experimental variances given in Table III. On the basis of these criteria only, there is no reason to include a third

Table IV. Comparison between Two Different Two-Equilibria Models for the System KCl-$AlCl_3$ at Different Temperatures

		275 °C		300 °C		325 °C		350 °C	
equilibrium	model no.	pK	variance × 10^7	pK	variance × 10^7	pK	variance × 10^7	pK	variance × 10^7
$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$	1	8.13 (1)[a]		7.78 (2)		7.46 (2)		7.13 (3)	
$Al_2Cl_7^- \rightleftarrows Al_2Cl_6 + Cl^-$		7.16 (8)	0.74	6.86 (11)	1.30	6.59 (13)	1.68	6.42 (23)	3.62
$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$	2	8.15 (1)		7.80 (2)		7.47 (2)		7.15 (3)	
$3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$		7.6 (4)	0.58	7.3 (6)	1.13	7.1 (7)	1.46	7.1 (11)	3.39

[a] I.e., 8.13 ± 0.01.

Table V. Values of Mole Fraction and Vapor Pressure for Molten KCl-$AlCl_3$ in the Temperature Range 275-350 °C

mole fraction of KCl	vapor pressure, mmHg[a]			
	275 °C	300 °C	325 °C	350 °C
0.4991_3	$0._7$	$0._7$	$0._6$	$0._9$
0.4946_3	$1._2$	$1._7$	$2._1$	$2._4$
0.4898_8	$3._3$	$3._7$	$5._2$	$6._0$
0.4846_3	$6._3$	$7._8$	$10._8$	$14._6$
0.4799_4	$9._9$	$12._9$	$17._4$	$22._2$
0.4748_4	$16._1$	$21._1$	$28._6$	$39._0$
0.4698_0	$25._3$	$34._9$	$49._5$	$64._9$
0.4650_4	$38._7$	$54._4$	$76._1$	*b*

[a] With the pressure due to dissolved gases, mainly N_2, substrated, the pressures of the dissolved gases were found to be $3._4$, $3._4$, $4._0$, and $4._7$ mmHg for the temperatures 275, 300, 325, and 350 °C, respectively. [b] Higher than $86._8$.

Table VI. Comparison between pK_4 Values[a] Obtained by Different Methods

temp, in °C	from potentiometry, lower limit[c] for pK_4	from vapor pressure using Henry's law		from vapor pressure using Raoult's law,[b] pK_4
		pK_4	lower limit[c]	
275	⩾16.5	15.4	⩾12.6	(15.1)
300	⩾15.4	*d*	⩾13.1	(14.6)
325	⩾14.6	14.0	⩾12.3	(13.9)
350	⩾13.1	12.1	⩾8.4	(13.2)

[a] I.e., for reaction $2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6(soln) + 2Cl^-(soln)$ assuming the pK values (pK_1 and pK_3) calculated for model 2, Table III, to be correct. [b] Raoult's law probably rather approximate for the present case. [c] 95% confidence. [d] No minima found here.

equilibrium. However, since the vapor pressure above the melt in the acidic part of the range where we have been working (i.e., 50.0–52.5 mol % $AlCl_3$) is rather high (values are given in Table V) and $AlCl_3$ in the examined temperature range is present in the vapor phase as Al_2Cl_6, it is obvious that model 2 in Table IV is not a good model. However, since the Raman spectra can only be explained by assuming at least one higher polymer, the obvious choice would be to combine models 1 and 2 into three interrelated equilibria where the last equilibrium is given by

$$2Al_3Cl_{10}^-(soln) \rightleftarrows 3Al_2Cl_6(soln) + 2Cl^-(soln) \quad (10)$$

so that the solvent is described by eq 7, 9, and 10 (model 3). The equilibrium constant associated with eq 10 will be called K_4. Calculations based on this model show that it is not possible to obtain three defined equilibrium constants. In other words, mathematically no more than two equilibria seem to be necessary. If three equilibria are introduced, the two last reactions (i.e., eq 9 and 10) are strongly correlated and K_4 will go to the calculation limit of 10^{-25}. One possibility for getting an idea about the value of K_4 would be to assume that the equilibrium constants associated with eq 7 and 9 obtained for model 2 are correct and that the found variances in Table II are due to the reaction given by eq 10. Unfortunately, in this case it is only possible to obtain the lower limit (95% confidence) for the equilibrium constant. This limit is given in Table VI calculated for the different measured temperatures. In order to obtain more information the vapor pressure of the system was included in the calculations.

Vapor Pressure Measurements and Model Equilibria for the KCl–$AlCl_3$ System. In Table V are given the vapor pressures over molten KCl–$AlCl_3$ in the temperature range 275–350 °C. The values given in this range have been corrected for dissolved gases, mainly N_2. This correction was found by an extrapolation of the logarithm of the measured pressure vs. the mole fraction of KCl, X_{KCL}, down to $X_{KCl} = 0.5000$. In contrast to the compositions with excess $AlCl_3$, it is still possible at this composition to use the degassing procedure under vacuum described in the Experimental Section. It was found that the pressure was less than 0.2 mmHg even at 350 °C. Unfortunately, there are no literature values with which to compare the obtained vapor pressures. The values of Linga, Motzfeldt, and Øye[16] were obtained at much higher temperatures and only at basic compositions.

As a first approximation the very simple proposal can be made that the vapor pressure above the melt is proportional to the species fraction of Al_2Cl_6 present in the melt (Raoult's law extended over the whole range for the $AlCl_3$–$KAlCl_4$ system). From model 1 the compositions where the vapor pressures have been measured (within the range given by the potentiometric measurements), i.e. at mole fractions of KCl of 0.4991_3, 0.4946_3, 0.4898_8, 0.4846_3, 0.4799_4, and 0.4748_4, the vapor pressures can then be calculated to be, at 300 °C, 0.1, 2.6, 9.3, 21.3, 35.9, and 55.8 mmHg, respectively. The vapor pressures calculated in this manner should be compared with the measured vapor pressures of $0._7$, $1._7$, $3._7$, $7._8$, $12._9$, and $21._1$ mmHg, respectively. From this it can be seen that the calculated vapor pressures are much higher than the measured vapor pressure (this is also the case at the other temperatures) in contrast to the behavior in the analogous KCl–$FeCl_3$ system.[10] This could be taken as an indication of the presence of $Al_3Cl_{10}^-$ (or another polymeric species as suggested by the Raman spectra[6-8]) together with Al_2Cl_6, since this would lower the vapor pressure of the system; the problem is that there is no special reason to expect Raoult's law to be correct over the whole phase diagram and especially not at low concentrations of Al_2Cl_6.

However, it is obvious (since the activity coefficients are not expected to change in the examined range) to assume that there is proportionality between vapor pressure and concentration (i.e., Henry's law). One way to use accurate vapor pressure measurements would then be to vary systematically the values for the equilibrium constants for the reactions given by eq 9 and 10 (i.e., K_3 and K_4) until the best proportionality is obtained between vapor pressures and concentrations. The equilibrium constant for the reaction associated with eq 7 is seen from Table IV to be rather independent of the subsequent reactions. Unfortunately, the vapor pressure measurements obtained by the present experimental setup are not good enough for such a calculation. The only possibility left is to keep the equilibrium constants, K_1 and K_3, constant (with values taken from model 2) and allow the equilibrium constant

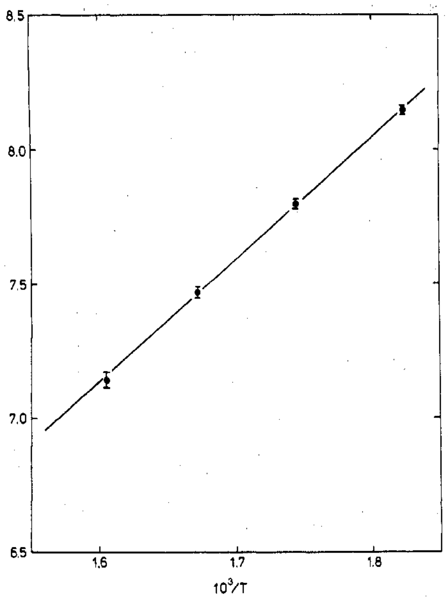

Figure 4. pK_1 values (from model 2, Table IV) as a function of the inverse absolute temperature ($\times 10^3$). The straight line is drawn from a least-squares calculation using weighted values. The shown limits are based on standard errors.

associated with eq 10 (i.e., K_4) to vary. If Henry's law is correct, there should be a linear relationship between the calculated concentrations of Al_2Cl_6 and the found vapor pressure. The values of K_4 which gives the best (least-squares) linear relationships between the calculated molar concentration of Al_2Cl_6 in the melt and the found vapor pressures are given in Table VI together with the lower limit based on a 95% confidence.

Finally, it is interesting to note that if we assume Raoult's law to be valid for the present case—something which is rather unlikely—it is possible (from the equation $N_{Al_2Cl_6} = P_{Al_2Cl_6}/P°_{Al_2Cl_6}$, where $N_{Al_2Cl_6}$ is the species fraction of Al_2Cl_6 in the melt and $P_{Al_2Cl_6}$ and $P°_{Al_2Cl_6}$ are the measured vapor pressure and the vapor pressure of liquid $AlCl_3$, calculated from ref 17, at the given temperature, respectively) to calculate some values of K_4, which are not very different from the values obtained from Henry's law. As before K_1 and K_3 are taken from model 2, Table IV, but now K_4 is varied not to obtain the best linear relationship between the measured pressure and the calculated species fraction concentration of Al_2Cl_6 but to obtain a slope of $P°_{Al_2Cl_6}$. It can be seen that the pK_4 values obtained by this method (given in Table VI) are not much different from the values based on Henry's law. Raoult's law values are given in parentheses to indicate the uncertainty in the basic assumption behind the calculations. The conclusion from the present examination of the vapor pressures and the results shown in Table VI is that it is a reasonable guess to assume that the acid/base properties and the vapor pressures of the solvent can be described by eq 7, 9, and 10 with the equilibrium constants taken from model 2, Table IV, and the pK_4 values based on Henry's law, Table VI, but better measurements or other measurements are needed in order to say something more definite. In this connection it is worthwhile to mention that from recent potentiometric measurements on the NaCl–$AlCl_3$ system at 175 °C it is possible without any prior restrictions to calculate the equilibrium constants for eq 7, 9, and 10. An extrapolation of the present equilibrium constants (model 3) down to 175 °C will give values of pK_1, pK_3, and pK_4 higher than the similar pK values obtained for the NaCl–$AlCl_3$ system at 175 °C in agreement with the tendency of MCl (M = Li, Na, K, Rb, Cs) melts to be more basic (i.e., higher activity coefficients for Cl^-) as the size of the cation is increased. Since this effect seems to be found for pK_1 for the MCl–$AlCl_3$ system,[2] it is expected also to be found for pK_3 and pK_4. It should also be emphasized that for many applications the most important thing is not whether models 1, 2, and 3 are used to describe the solvent but whether a good or bad agreement is obtained between the measured and calculated pCl^- values for the solvent. From this point of view the three given possibilities are almost equally good.

Not many results are available in the literature for comparison with the values given in Tables IV and VI. Torsi and Mamantov[2] found for eq 7 (no second reaction was taken into consideration) pK values of 7.5, 7.1, 6.4, and 5.8 at 275, 300, 350, and 400 °C, respectively. It is clear that there is a considerable deviation between these values and the present values (where they can be compared). For the same reaction, but only at 300 °C, Barner and Bjerrum[1] found the pK to be 7.83 (2) later corrected to 7.78–7.81 (95% confidence limits).[9] It can be seen that the latter value agrees well with the present measurements.

If we compare the pK_1 and pK_2 values for the aluminum system (Table IV or calculated from model 3) with the values for the same reactions for the analogous KCl–$FeCl_3$ system,[10] it can be seen that the values obtained are in complete agreement with the notion that $AlCl_3$ is a stronger Lewis acid than $FeCl_3$. The equilibrium constants for the aluminum system are always smaller (at the same temperature) than the corresponding constants for the iron system.

In Figure 4 a plot has been made of pK_1 vs. the inverse absolute temperature. Since it is not clear whether the pK values given for eq 9 and 10 are correct, the pK values for these reactions have not been plotted in Figure 3. It can be seen from this figure that there is a linear relation between pK_1 and the inverse absolute temperature. As before $\Delta H°$ and $\Delta S°$ can be calculated from such a plot. For the shown reaction $\Delta H°$ and $\Delta S°$ were found by a weighted least-squares method to be 86.0 (13) kJ/mol and 0.9 (22) J/(deg mol), respectively. By comparison, the corresponding values calculated for the reaction $2FeCl_4 \rightarrow Fe_2Cl_7^- + Cl^-$ were found to be 68.4 (3) kJ/mol and 1.7 (6) J/(deg mol), respectively.[10]

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Registry No. KCl, 7447-40-7; $AlCl_3$, 7446-70-0.

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