

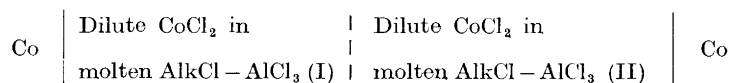
## EMF Studies in Aluminium Chloride Systems

### II. Cobalt Chloride in Mixtures of Alkali and Aluminium Chloride

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The concentration cells



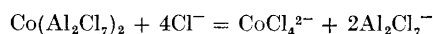
have been studied.

The emf studies support the assumption of formation of  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  in  $\text{AlCl}_3$  rich mixtures. Using this model,  $K_A$  for the bulk dissociation reaction



is evaluated for mixtures with different alkali chlorides.

The energy of the octahedral-tetrahedral transformation



has been calculated.

Molten mixtures of alkali chloride and aluminium chloride are important media for obtaining information about coordination equilibria, since there are pronounced changes in the chloride affinity and acid-base properties when the composition is varied.

Coordination equilibria of dilute solutions investigated in this media cover  $\text{UCl}_3$ ,  $\text{ThCl}_3$ ,  $\text{PrCl}_3$ , and  $\text{PuCl}_3$  in  $\text{KCl} - \text{AlCl}_3$ ,<sup>1</sup>  $\text{CoCl}_2$  in  $\text{KCl} - \text{AlCl}_3$ ,<sup>2</sup>  $\text{NiCl}_2$  in  $\text{CsCl} - \text{AlCl}_3$ .<sup>3,4</sup>

When  $X_{\text{AlkCl}}/X_{\text{AlCl}_3} > 1$  it is known that the dilute ions form simple species as  $\text{UCl}_6^{3-}$ ,<sup>1</sup>  $\text{CoCl}_4^{2-}$ ,<sup>2</sup> and  $\text{NiCl}_4^{2-}$ ,<sup>3</sup> and recently also  $\text{NiCl}_3^-$ .<sup>4</sup> In this concentration range,  $\text{Al}^{3+}$  is coordinately saturated as  $\text{AlCl}_4^-$  and additional chloride ions present form complexes with the transition ions.

The situation is considerably more complex on the  $\text{AlCl}_3$ -rich side. A statistical treatment<sup>2</sup> of the vapour pressure data of  $\text{Al}_2\text{Cl}_6$  in  $\text{NaCl} - \text{AlCl}_3$  mixtures<sup>5</sup>

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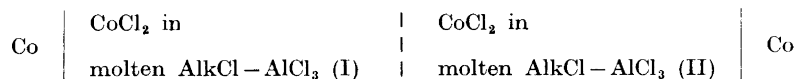
strongly suggested the presence of  $\text{AlCl}_4^-$  and  $\text{Al}_2\text{Cl}_7^-$  ions. A recent investigation<sup>6,7</sup> has further established the presence of  $\text{Al}_2\text{Cl}_7^-$  in alkali-aluminium chloride melts, the structure being a double tetrahedron sharing one corner.

For  $\text{CoCl}_2$  in  $\text{KCl}-\text{AlCl}_3$ , two coordinations distinctly different from the tetrahedral  $\text{CoCl}_4^{2-}$  were found.<sup>2</sup> The two species were proposed to be  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  and  $\text{Co}(\text{Al}_2\text{Cl}_7)(\text{AlCl}_4)$ .<sup>2</sup>

The basis for the proposal of  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  is an observed octahedral ligand field spectrum and the spectral identity with  $\text{CoCl}_2$  in pure  $\text{AlCl}_3$ . Octahedral coordination can be established by coordination of the three end chlorides of the  $\text{Al}_2\text{Cl}_7^-$ . Spectroscopic measurements of mixtures with varying  $\text{KCl}$ -content gave evidence that there is an equilibrium between the first and the second Co-complex.

The spectra gives only information about the coordination of the species and it is of interest to obtain thermodynamic data for this kind of complexation. Thermodynamic data coupled with statistical models will give clues of the bond strength of such complexes, and a check on the models proposed from the spectroscopic studies.

For this reason the electrochemical concentration cell



was studied at 300° or 400°C with the alkali chlorides  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{RbCl}$ , and  $\text{CsCl}$ .

The equation for the emf of this cell has been presented in the preceding paper.<sup>8</sup> Neglecting the transport of  $\text{Al}^{3+}$  because of the large size of the  $\text{Al}-\text{Cl}$  species, the emf is obtained from Ref. 8 (eqn. (8)):

$$\Delta E = E_{\text{II}} - E_{\text{I}} = \frac{R'T}{F} \int_{\text{I}}^{\text{II}} \left( \frac{1}{2} d \log a_{\text{CoCl}_2} - t_{\text{Alk}} d \log a_{\text{AlkCl}} \right) \quad (1)$$

$\Delta E$ : Change in electromotive force

$R'$ :  $R \ln 10$

$T$ : Temperature, K

$F$ : Faraday constant

$a$ : Activity

$t_{\text{Alk}}$ : External electrochemical transport number of  $\text{Alk}^+$

In the concentration range studied,  $X_{\text{AlkCl}} < 0.549$ , the transport number of  $t_{\text{Cl}}$  can be considered negligible with respect to  $t_{\text{Alk}}$ <sup>8</sup> giving

$$\Delta E = \frac{R'T}{F} \int_{\text{I}}^{\text{II}} \left( \frac{1}{2} d \log a_{\text{CoCl}_2} - d \log a_{\text{AlkCl}} \right) \quad (2)$$

The previous paper<sup>8</sup> also gave the emf dependence on different realistic statistical models of the melt. We will return to this in the discussion.

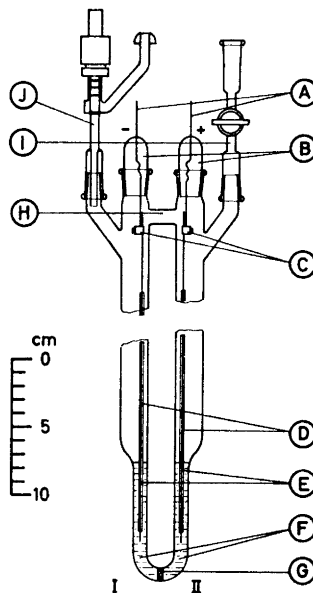
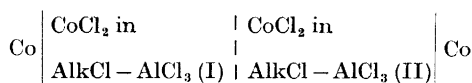


Fig. 1. Apparatus for studying the electrochemical cell



A: Pt-leads. B: Pyrex caps. C: Connection between Pt-leads and Co-electrode. D: Co-electrodes. E: Protective quartz tubes. F: Salt melts. G: Quartz diaphragm. H: Connecting tube. I: Side arm. J: Side arm with Delmar-Urrey valve.

## EXPERIMENTAL

*Apparatus.* The concentration cell apparatus is shown in Fig. 1. The apparatus below the ground joints is made of quartz and the upper part of pyrex.

Pt-leads (A) are sealed into pyrex caps (B) and joined to the cobalt electrodes (D) at (C). The lower part of the electrodes are melted into tight fitting quartz tubes (E) so that only the last 10 mm are freely submerged into the melt. The tight fit in the quartz tubes is obtained by gradually melting the electrode in the tubes so that the space is completely filled. The lower 10 mm of the quartz tube is then removed giving a non-oxidized metal for submerging into the melt (F). This protection tube of quartz prevents attack of the electrodes, especially on the surface between melt and gas. A minute amount of melt is sucked up by the capillary forces between the electrode and the protective quartz tube. However, this melt does not seem to be exchanged by the bulk melt, since no color changes take place in this melt when  $X_{\text{AlCl}_3} \geq 0.50$ .

The two cell compartments are separated by a quartz frit (G) with pore size 5–15  $\mu$ . A connection tube (H) between the two half cells prevents possible pressure differences between the two sides.

Two side arms are used for loading the cell. The right hand side arm (I) is used for initial loading of the cell, evacuating and filling with inert atmosphere. The left hand arm (J) contains a Delmar-Urrey needle valve stopcock (Delmar Scientific Lab., Maywood, Ill.) facilitating addition of alkali chloride to the left half cell without exposing the cell atmosphere to air.

The emf was measured by a precision potentiometer (Thermo-Electric Free Potentiometer, Diesselhorst Pattern, Type 3589, R. H. Tinsley and Co., London) and a mirror galvanometer with resistance 24  $\Omega$  (W. G. Pye and Co., Cambridge).

The desired temperature of the cell was maintained by dipping the cell into a  $\text{NaNO}_3 - \text{NaNO}_2$  bath keeping the temperature constant within  $\pm 1^\circ\text{C}$  by a dip heater, stirrer and contact thermometer. The temperature was measured by a Pt/Pt10Rh thermocouple. The thermocouple was calibrated against the melting point of Ag and Sn.

*Chemicals.* The metal electrodes were obtained as 1 mm wire, Matthey spectrographically standardized (Johnson, Matthey & Co., London) Detectable elements in ppm: Si, 3; Fe, Mg, 2; Al, Cu, Ca, Ag < 1.

Table 1. Emf for concentration cells with Co electrodes containing dilute amounts of  $\text{CoCl}_2$ .

Exp. (Fig. No.)	Half cell with const. composition (II)		Half cell with varying composition (I)		Electromotive force $E = E_{II} - E_I$		Temp. °C		
	Electrolyte Amount g in the $\text{AlCl}_3$ containing melt	Dissolved $\text{CoCl}_2$ Initial g Final g	Electrolyte Mol % AlkCl in the $\text{AlCl}_3$ containing melt	Dissolved $\text{CoCl}_2$ Initial g Final g	$\left(\frac{dE}{dX}\right)_{\text{AlkCl}}$ for $X_{\text{AlkCl}} = 0.40$ V	$E_{50}$ : E linearly extrapolated to $X_{\text{AlkCl}} = 0.50$ V		$\Delta E_{\text{jump}} = E_{\text{sat}} - E_{50}$ V	
2a	7.000	0.0070	35.0 → 53.2 KCl	0.0071	0.0170	0.28	0.010	0.855	300
2b <sup>a</sup>	7.003	0.0070	35.0 → 50.4 KCl	0.0070	0.0103	0.25	0.005	—	300
2c	6.999	0.0070	35.0 → 52.5 KCl	0.0070	0.0079	0.27	0.013	0.840	300
2d <sup>b</sup>	7.003	0.0014	35.0 → 52.3 KCl	0.0014	0.0020	0.28	0.018	0.867	300
2e	6.995	0.0018	45.0 → 52.3 KCl	0.0019	0.0022	0.25	0.024	0.861	300
3a	7.004	0.0016	35.0 → 51.7 LiCl	0.0017	0.0022	0.24	0.005	0.153	300
3b	6.992	0.0022	35.0 → 50.9 NaCl	0.0021	0.0036	0.25	0.010	0.365	300
3d	7.002	0.0030	35.0 → 54.1 RbCl	0.0032	0.0035	0.59	0.032	1.042	400
3e	7.006	0.0032	35.0 → 54.6 CsCl	0.0029	0.0035	0.53	0.030	1.147	400

<sup>a</sup> Crack of the cell on the side of constant composition.<sup>b</sup> Repeated in Fig. 3 as 3c.

Aluminium chloride was made from 99.99 % aluminium (Vigeland Bruk, Vigeland, Norway) and HCl at 450°C. HCl was made by interaction of *p.a.* H<sub>2</sub>SO<sub>4</sub> (Merck, Darmstadt) with *p.a.* NaCl (Merck, Darmstadt). The HCl was cooled in a trap filled with dry ice-acetone to condensate out possible water and organic vapours. After reaction the aluminium chloride was sublimed through a porous quartz frit and sealed into a quartz ampule. The KCl *p.a.* (Merck, Darmstadt) was dehydrated by slow heating and melting under vacuum.

*Procedure.* The quartz cell was carefully dried by flame heating under vacuum and was then filled with dry N<sub>2</sub> (H<sub>2</sub>O content < 5 ppm) and transferred to a dry box (H<sub>2</sub>O content < 25 ppm).

Desired amounts of aluminium chloride and alkali chloride were melted together in sealed ampules which previously had been evacuated. The salt mixture was filled into the cell together with the cobalt chloride using the dry box.

The cell was then reevacuated and filled with dry N<sub>2</sub> and transferred to the salt bath.

The concentration of the left half cell was changed by adding alkali chloride through the Delmar-Urrey valve and shaking the cell. The right half was kept at 45 mol % AlkCl. This was a compromise between having a fairly low vapour pressure of aluminium chloride and avoiding being too close to the composition AlkAlCl<sub>4</sub>, where small concentration changes have a marked influence on the emf.

It was not practical to have mixtures with higher AlCl<sub>3</sub> content than 65 mol % AlCl<sub>3</sub> because of the high vapour pressure of AlCl<sub>3</sub> above that composition. At 65 mol % AlCl<sub>3</sub>, losses through evaporation still corresponded to less than 0.5 mol % and it was possible to transfer the evaporated AlCl<sub>3</sub> back to the melt by a combination of heating and tapping the cell walls so that accumulated concentration changes did not occur.

The emf was read when a constant potential was obtained, usually after 30 min.

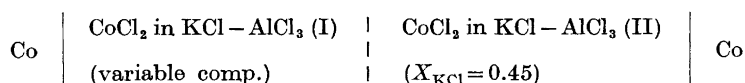
After each experiment was completed, the melt was analyzed on the basis of total amount of cobalt chloride.

A serious problem by working with these melts is their corrosive nature. Attempts to study the Fe/Fe<sup>2+</sup> couple were unsuccessful because of the dissolution of Fe. Metallic Co and Ni withstood attack fairly well, provided that the melts are absolutely anhydrous. For instance, by keeping Co wire in an anhydrous molten mixture of 55 mol % AlCl<sub>3</sub> and 45 mol % KCl at 700°C for more than 24 h results in a dissolution of Co of only 1 × 10<sup>-3</sup> weight % or about 0.05 mg in a 5 g melt. It was, however, not possible to avoid some dissolution of the Co-wire under the actual experimental conditions, probably due to introduction of traces of water when adding KCl or by the shaking of the melts (see Table 1).

To check the reversibility of the electrodes, *n* in the Nernst equation was determined by successively adding 1 mg CoCl<sub>2</sub> at a time to 6 g melt mixtures 4 times and at last 4 mg. The value of *n* was found to be 2.2. A small dissolution of the Co wire was also observed. This corresponded to 1 mg during the run. However, assuming that this amount dissolves linearly with time, *n* = 2.0 was obtained.

## RESULTS

Fig. 2 and the first part of Table 1 give results for the cell.



For experiments 2a, the electrodes were not melted in a quartz tube (Fig. 1), and the dissolution of Co was much higher than for later experiments. In experiments 2a - 2c, 7 mg of CoCl<sub>2</sub> were initially dissolved. In later experiments this was reduced to about 2 mg, in order that the CoCl<sub>2</sub> added should have a negligible effect on the bulk chloride concentration in the AlkCl - AlCl<sub>3</sub> melt. The change in bulk chloride concentration due to addition of CoCl<sub>2</sub> is then about 0.04 mol %.

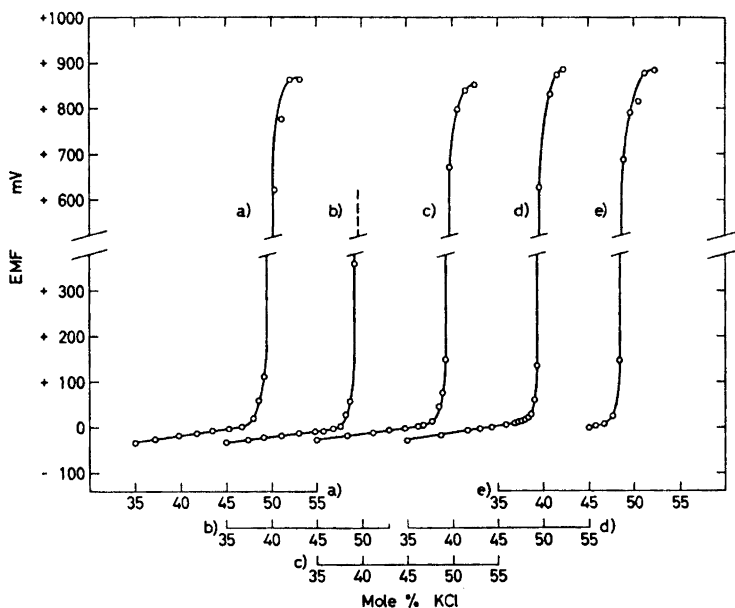
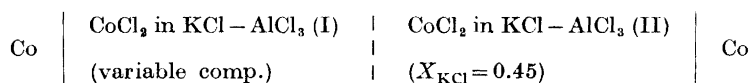


Fig. 2. Emf at 300°C for the cells



with varying contents of  $\text{CoCl}_2$  dissolved. Approximate  $\text{CoCl}_2$  content per 7 g initial melt: a, b, c: 0.007 g; d, e: 0.002 g. Further details in Table 1.

A very steep increase in emf is observed between 48 and 51 mol % KCl. The position of the near-vertical part of the emf curve can be used as an estimation on the reproducibility of composition of the bulk melt. For experiments 2a – 2d the mean deviation in the position of this nearly vertical curve is  $\pm 0.1$  mol %. For experiment 2e, a mishap made it impossible to return all evaporated  $\text{AlCl}_3$  to the melt. As judged from the position of the near vertical part, the composition is 0.8 mol % lower in  $\text{AlCl}_3$  than given in Fig. 2e.

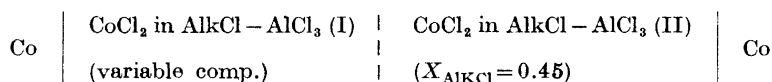
The reproducibility in emf can be estimated from the deviation from zero when the composition in both cells is equal ( $X_{\text{KCl}} = 0.45$ ) and from the total value of the potential jump around  $X_{\text{KCl}} = 0.50$ .

The deviations from zero for equal bulk composition were found to be  $\pm 0.005$  V.  $\Delta E$  (Table 1), which was the change in emf between the mixtures saturated with KCl and emf when extrapolating the linear part for  $X_{\text{KCl}} < 0.45$  to  $X_{\text{KCl}} = 0.50$ , was found to be  $0.848 \pm 0.008$  V when 7 mg  $\text{CoCl}_2$  was added and  $0.864 \pm 0.003$  V when 2 mg  $\text{CoCl}_2$  was added. Judging from these results, the standard deviation in emf is estimated to 0.005 V or 0.6 % of the total potential jump around 50 mol % KCl.

A correction for the unequal amounts of  $\text{CoCl}_2$  in the two half cells because

of the dissolution of the electrodes and from additions of KCl was not found necessary as these corrections were within  $\pm 0.003$  V.

Fig. 3 and Table 1 give results for the cells



where AlkCl is LiCl, NaCl, KCl, RbCl, and CsCl, respectively.

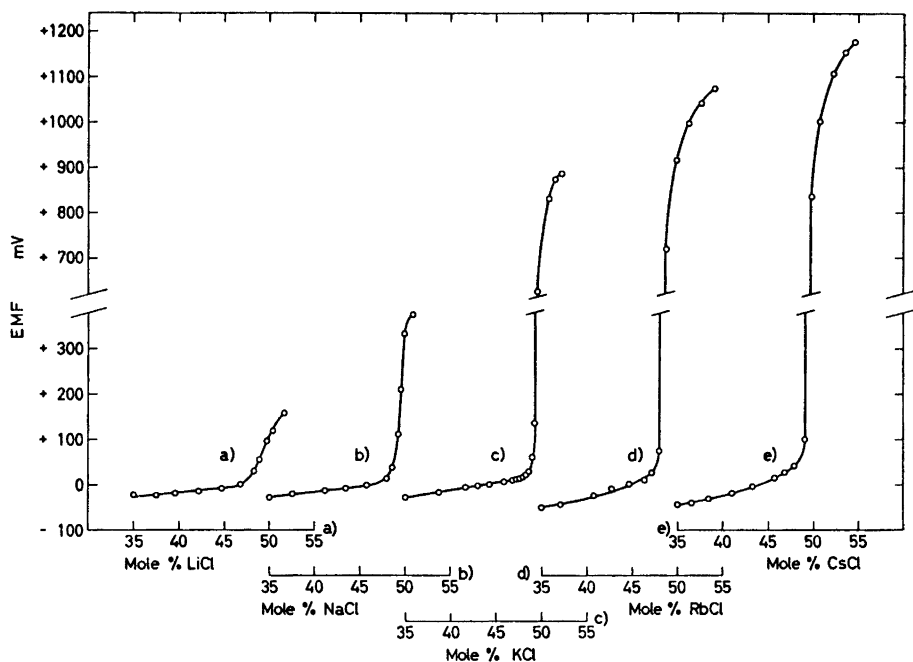
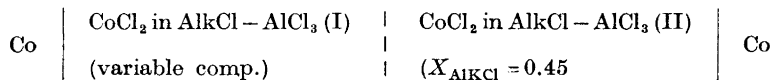


Fig. 3. Emf as function of composition for the cells



Alkali chloride and temperature: a, LiCl; b, NaCl; c, KCl; 300°C; d, RbCl; e, CsCl; 400°C.

#### DISCUSSION

*The model: Dissolved  $\text{Co}^{2+}$  ions.* We will first use the results to test different statistical-thermodynamic models for structural entities in these melt systems.

A possible model for dissolved  $\text{CoCl}_2$  in  $\text{AlCl}_3$ -rich melts may be the assumption of dissolved  $\text{Co}^{2+}$  ions, the interaction with the melt being independent of

bulk melt composition. By assuming a Temkin model<sup>9</sup> modified in the way that neutral species are counted among the negative ions,<sup>8</sup> the emf is then (simply given as, Ref. 8, eqn. (11)):

$$dE = \frac{RT}{2F} d \ln X'_{\text{Co}} \quad (3)$$

Hence only a change in emf due to the experimental changes in the composition, *i.e.* diluting the  $\text{Co}^{2+}$  ion by adding AlkCl, should then be observed.  $X'$  refers to cation fraction or modified anion fraction where neutral species are counted with.

Assuming a constant number of moles of  $\text{CoCl}_2$ ,  $a_0$ , an initial number of moles of AlkCl,  $n_0$ , and adding  $dn_{\text{AlkCl}}$  mol AlkCl in (I), the change in emf according to this model is for  $a_0 \ll n_0$ :

$$\frac{2FdE}{RT} = \ln \left( \frac{a_0}{n_0} \right) - \ln \left( \frac{a_0}{n_0 + dn_{\text{AlkCl}}} \right) = \ln \left( 1 + \frac{dn_{\text{AlkCl}}}{n_0} \right) \simeq \frac{dn_{\text{AlkCl}}}{n_0} = dX_{\text{AlkCl}} \quad (4)$$

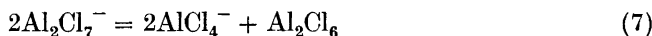
$$\frac{dE}{dX_{\text{AlkCl}}} = \frac{RT}{2F}: 0.025 \text{ V at } 300^\circ\text{C and } 0.029 \text{ V at } 400^\circ\text{C} \quad (5)$$

This is only 10 % of the slope observed in mixtures with LiCl, NaCl, KCl at  $300^\circ\text{C}$  and 5 % of the slope of those with RbCl and CsCl at  $400^\circ\text{C}$ . A model based on the simple dissolution of  $\text{CoCl}_2$  is hence totally inconsistent with the experimental results.

*The model:  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$ .* According to spectral indications<sup>2</sup>  $\text{Co}^{2+}$  was supposed to exist mainly as  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  in aluminium chloride-rich melt partly being converted to  $\text{Co}(\text{Al}_2\text{Cl}_7)(\text{AlCl}_4)$  near 50 mol % aluminium chloride. Similar to the previous model we will assume the interaction of  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  with the melt to be independent on composition of the bulk melt. Using again a modified Temkin model, the emf of the cell is given according to Ref. 8 (eqn. (15)):

$$\frac{2FdE}{RT} = d \ln X'_{\text{Co}(\text{Al}_2\text{Cl}_7)_2} - 2d \ln X'_{\text{Al}_2\text{Cl}_7^-} \quad (6)$$

The concentration of the cobalt species exhibits relatively small changes in the concentration range  $0.35 < X_{\text{AlkCl}} < 0.48$ .<sup>2</sup> Therefore the emf will mainly reflect the concentration change in  $\text{Al}_2\text{Cl}_7^-$ . The concentration of  $\text{Al}_2\text{Cl}_7^-$  is determined from the bulk composition and the dissociation equilibrium



$$\frac{X'_{\text{Al}_2\text{Cl}_6}(X'_{\text{AlCl}_4})^2}{(X'_{\text{Al}_2\text{Cl}_7^-})^2} = K_A \quad (8)$$

Neglecting the amount of  $\text{CoCl}_2$  the following stoichiometric relations are valid:

$$X_{\text{AlkCl}} = n_{\text{Cl}} + n_{\text{Al}_2\text{Cl}_7^-} + n_{\text{AlCl}_4} \quad (9)$$

$$1 - X_{\text{AlkCl}} = 2n_{\text{Al}_2\text{Cl}_6} + 2n_{\text{Al}_2\text{Cl}_7^-} + n_{\text{AlCl}_4} \quad (10)$$



where  $n$  denotes number of moles in 1 mol of  $\text{AlkCl}-\text{AlCl}_3$  mixture. Total number of anionic and neutral species:

$$\sum n = n_{\text{Al}_2\text{Cl}_7} + n_{\text{AlCl}_4} + n_{\text{AlCl}_3} + n_{\text{Cl}} = X_{\text{AlkCl}} + n_{\text{Al}_2\text{Cl}_7} \quad (11)$$

Introducing  $X'_1 = n_i/\sum n$  (modified Temkin model<sup>8</sup>) and neglecting  $n_{\text{Cl}}$  in eqn. (9) and  $n_{\text{Al}_2\text{Cl}_7}$  in eqn. (11), the following relation between  $K_A$  and  $X'_{\text{Al}_2\text{Cl}_7}$  is obtained from eqns. (8–11):

$$K_A = \frac{1/X_{\text{AlkCl}} - (2 + X'_{\text{Al}_2\text{Cl}_7})}{2(X'_{\text{Al}_2\text{Cl}_7}/(1 - X'_{\text{Al}_2\text{Cl}_7}))^2} \quad (12)$$

When the dissociation constant for  $\text{Al}_2\text{Cl}_7^-$  is very small,  $K_A \simeq 0$ , then eqn. (12) is simplified to:

$$X'_{\text{Al}_2\text{Cl}_7} = \frac{1}{X_{\text{KCl}}} - 2 \quad (13)$$

By means of eqns. (6) and (12), and knowing the amount of  $\text{Co}^{2+}$  present as  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  it is now possible to calculate the change in emf as function of composition assuming different  $K'_A$ s.

The fraction of  $\text{Co}^{2+}$  existing as  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  is only known for the system  $\text{KCl}-\text{AlCl}_3$  and in Fig. 4a is shown the calculated emf for this system, using the values  $K_A = 1, 10^{-1}, 0$ .

A correction for dilution by adding  $\text{KCl}$  has been performed (eqn. (4)). The calculated values are compared with the experimentally obtained results

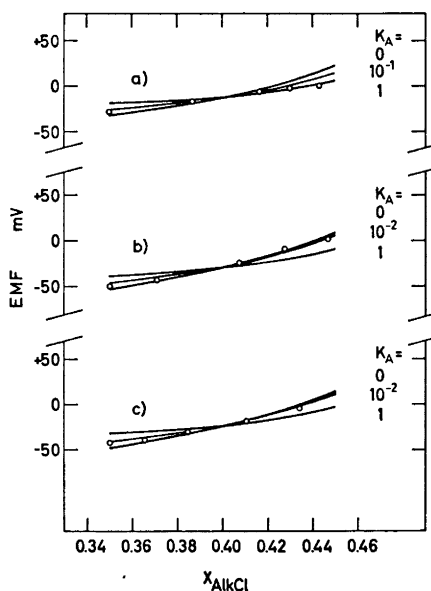


Fig. 4. Calculated change in emf assuming the species  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  present for different values of  $K_A$  for the dissociation  $2\text{Al}_2\text{Cl}_7^- = 2\text{AlCl}_4^- + \text{Al}_2\text{Cl}_6$  as compared with experimental values. Calculated and experimental emf set equal for  $X_{\text{AlkCl}} = 0.40$ . a,  $\text{KCl}-\text{AlCl}_3$ : 300°C. b,  $\text{RbCl}-\text{AlCl}_3$ : 400°C. c,  $\text{CsCl}-\text{AlCl}_3$ : 400°C.

(expt. 2d) by arbitrarily setting the calculated emf equal to the experimental for  $X_{\text{KCl}} = 0.40$ .

In the composition range  $0.35 < X_{\text{KCl}} < 0.45$  it is seen that the dissociation constant for  $\text{Al}_2\text{Cl}_7^-$ ,  $K_A = 10^{-1}$ , gives a reasonably good fit.

The equilibrium value for  $K_A$  for the system  $\text{KCl} - \text{AlCl}_3$  are found somewhat larger than calculated for the system  $\text{NaCl} - \text{AlCl}_3$ ,<sup>2</sup>  $K_A \simeq 2.5 \times 10^{-2}$  and from Raman spectra of  $\text{KCl} - \text{AlCl}_3$ ,<sup>7</sup>  $K_A = 0.8 \times 10^{-2}$ .

In the systems  $\text{RbCl} - \text{AlCl}_3$  and  $\text{CsCl} - \text{AlCl}_3$  it is reasonable to assume the fractions of  $\text{Co}^{2+}$  being present as  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  are still larger than for the  $\text{KCl} - \text{AlCl}_3$  system. Since the fraction was quite close to 1 in the  $\text{KCl} - \text{AlCl}_3$  system it may be justifiable to set it equal to 1 in mixtures with  $\text{RbCl}$  and  $\text{CsCl}$  in the concentration range  $0.35 < X_{\text{AlKCl}} < 0.45$ . Making this assumption, the change in emf in  $\text{RbCl} - \text{AlCl}_3$  and  $\text{CsCl} - \text{AlCl}_3$  is given in Fig. 4, b and c, using eqns. (6) (12), and (4), and compared with the experimental when the two are set equal for  $X_{\text{AlKCl}} = 0.40$ . The following values for  $K_A$  have been used: 1,  $10^{-2}$ , 0. (For these systems  $K_A \leq 10^{-2}$  gives a reasonably good fit.)

None of the models fit well for  $X_{\text{AlKCl}} > 0.45$ . This may be due to the fact that the second dissociation equilibrium

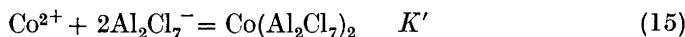


is neglected.

This will tend to make  $X_{\text{Al}_2\text{Cl}_7^-}$  larger and hence the change in emf smaller. A complete fit may be obtained by choosing a proper value for  $K_B$  and not neglecting  $X'_{\text{Cl}}$ .

*Octahedral-tetrahedral transformations.* We will now examine the coordination change around 50 mol %  $\text{AlCl}_3$ .

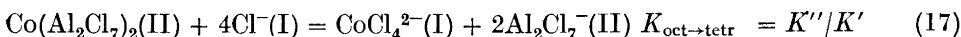
On the aluminium chloride side (II)  $\text{Co}(\text{Al}_2\text{Cl}_7)_2$  is considered to be the dominant complex species formed by the complex equilibrium



Similarly on the alkali chloride side (I)



Combining the two equilibria we get for the octahedral-tetrahedral transformation:



The change in emf of the cell is given as Ref. 8, eqn. (22)):

$$\frac{2F}{RT} \Delta E = \ln K_{\text{oct} \rightarrow \text{tetr}} + \ln \frac{X'^{\text{II}}_{\text{Co}(\text{Al}_2\text{Cl}_7)_2} (X'^{\text{I}}_{\text{Cl}})^4}{X'^{\text{I}}_{\text{CoCl}_4} (X'^{\text{II}}_{\text{Al}_2\text{Cl}_7})^2} \quad (18)$$

Introducing a modified Temkin model,<sup>8</sup> and neglecting the dilution by addition of alkali chloride

$$\frac{2F}{RT} \Delta E = \ln K_{\text{oct} \rightarrow \text{tetr}} + \ln \frac{(X'^{\text{I}}_{\text{Cl}})^4}{(X'^{\text{II}}_{\text{Al}_2\text{Cl}_7})^2} \quad (19)$$

We are here interested in the change in emf from a composition where  $\text{Co}^{2+}$  being mainly octahedral to a composition where it is tetrahedral. We will use the composition change:  $0.45 \rightarrow X_{\text{AlkCl}} \rightarrow 0.515$ .

For  $X_{\text{KCl}} = 0.45$ ,  $X^{\text{III}}_{\text{Al,Cl}}$ , can to a good approximation be given from eqn. (13) even if  $K_A$  is not extremely small:

$$X^{\text{III}}_{\text{Al,Cl}} = \frac{1}{X_{\text{KCl}}} - 2 \quad (20)$$

Similarly  $K_B$  (eqn. (14)) can be assumed small enough so that  $X^{\text{I}}_{\text{Cl}}$  is given from eqns. (9–11) neglecting  $n_{\text{Al,Cl}}$ , and  $n_{\text{Al,Cl}}$ :

$$X^{\text{I}}_{\text{Cl}} = 2 - \frac{1}{X^{\circ}_{\text{KCl}}} \quad (21)$$

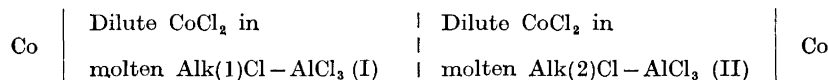
Using eqns. (20–21) and the experimentally determined  $\Delta E$ , the resulting values of  $K_{\text{oct} \rightarrow \text{tetr}}$  are given in Table 2.

Table 2. Octahedral – tetrahedral transformation for  $\text{Co}^{2+}$  in  $\text{AlkCl} - \text{AlCl}_3$  melts.

AlkCl	Change in composition $X_{\text{AlkCl}}$	Temp. °C	$\Delta E$ V	$\log K_{\text{oct} \rightarrow \text{tetr}}$ eqn. (19)	$\Delta G^{\circ}_{\text{oct} \rightarrow \text{tetr}}$ kcal
LiCl	0.45 → 0.515	300	0.165	6.5	–17.0
NaCl	0.45 → 0.509	300	0.379	11.2	–29.4
KCl <sup>a</sup>	0.45 → 0.515	300	0.881	19.1	–50.0
RbCl	0.45 → 0.515	400	1.004	18.7	–57.5
CsCl	0.45 → 0.515	400	1.068	19.7	–60.6

<sup>a</sup> Average expt. 2d and 2e.

#### Studies of cells of the type <sup>11</sup>



where  $X_{\text{Alk(1)Cl}} = X_{\text{Alk(2)Cl}}$  give an emf of approximately 0 when  $X_{\text{AlkCl}} < 0.5$  and a jump around 50 mol %. This jump is equal to the difference in emf for the corresponding cells with only one alkali ion. This is an indication that the junction potential is the same for the two types of cells and that the stability of the octahedral configuration is quite insensitive to the bulk alkali ion.  $K'$  is hence expected to be approximately constant. The change in  $\Delta E$ , from mixtures with LiCl to CsCl, is then due to the change in  $K''$ . The stability of the tetrahedral configuration increases sharply in mixtures with LiCl to NaCl to KCl. A much less pronounced increase is observed when having

RbCl and CsCl. Actually a small decrease of  $K$  for the octahedral–tetrahedral transformation is seen from KCl to RbCl but this is expected due to the temperature increase from 300 to 400°C. When calculating  $\Delta G^{\circ}_{\text{oct} \rightarrow \text{tetr}} = RT \ln K$  a steady increase is observed from LiCl to CsCl (Table 2).

The increase of the tetrahedral stability with decreasing ionic strength of the cation is in accordance with what one would expect from electrostatics for the reaction:



A bonding of  $\text{Cl}^{-}$  to  $\text{Co}^{2+}$  means that bonds to the alkali ions have to be broken, which will be easier when the ion strength of the bulk alkali cation is weaker.

More information on the electrostatics of the octahedral tetrahedral transformation can be obtained when comparing different transition ions in these media. One is then able to separate out the energetics of the transition ion complex from the electrostatics of the melt.

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