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Thermodynamic and Structural Investigations of Chlorides in the Systems $KCl/MgCl_2$ and $KCl/MnCl_2$

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By means of a galvanic cell, emf values were measured for the solid-state reactions nKCl + $M\mathrm{Cl}_2$ = $\mathrm{K}_nM\mathrm{Cl}_{n+2}$ for all existing compounds in the pseudobinary systems with M = Mg and Mn. Thus ΔG^r values could be calculated and, from their linear temperature dependence in the range 550–730 K, reaction entropies could be determined. Enthalpies ΔH^r were calculated using the Gibbs–Helmholtz relation; they are compared with values found by solution calorimetry at room temperature. The magnitude of the entropy term for the free enthalpy of the formation reactions is discussed for the different compounds. For the modifications of $\mathrm{K}M\mathrm{Cl}_3$ the lattice parameters for the cubic, tetragonal, and one of the orthorhombic phases were determined by X-ray photographs at varying temperatures. By DSC measurements the transition enthalpy for the tetragonal to cubic transition of $KMnCl_3$ at 659 K was found to be 0.20–0.4 kJ · mole^{-1}, compared to 4.6 kJ · mole for the transition of the stable room-temperature modification with the NH_4CdCl_3 structure to the metastable $GdFeO_3$ structure.

1. Introduction

Our previous work on ternary halides has revealed that reactions of the type

$$nA\mathrm{Cl} + M\mathrm{Cl}_2 = A_nM\mathrm{Cl}_{n+2} \quad (A = \text{alkaline metal})$$

do not always occur with a gain in (lattice) enthalpy, ΔH^r, as commonly assumed in crystal chemistry; rather, a negative free enthalpy of reaction, ΔH^r, can also be produced by a gain in entropy, ΔS^r. In order to elucidate such entropy effects we constructed a galvanic cell to measure the electromotive force E associated with the appropriate solid-state reaction in dependence on temperature. From $\Delta G = -n \cdot F \cdot E$ and $(\delta\Delta G/\delta T)_p = -\Delta S$ the entropy is obtained and, from the Gibbs–Helmholtz relation $\Delta G = \Delta H - T \cdot \Delta S$, the enthalpy. To date we have determined these state functions for the compounds of the systems NaCl–$CdCl_2$ (*1*) and $M\mathrm{Cl}_2$ (M = Ca, Sr, Ba, Pb) with KCl (*2*) and RbCl (*3*).

In this paper our investigations of ternary chlorides in the systems of KCl with $MgCl_2$ and $MnCl_2$ are presented. Of particular interest is a comparison of the compounds $KMgCl_3$ and $KMnCl_3$. Both compounds crystallize in the perovskite structure type, but recently Horowitz *et al.* (*4*) have found a low-temperature modification of $KMnCl_3$ with the NH_4CdCl_3 structure. In previous papers we have discussed the relationships between magnesium and manganese(II)

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double chlorides and bromides, particularly with regard to ΔH^r values, measured by solution calorimetry (*5, 6*) using the concept of the polarizing effect of the M^{2+} ions on the halide ions. We were anxious to find such correlations in ΔG^r, too.

2. Experimental

2.1 Material Preparation

Anhydrous $MnCl_2$ and $MgCl_2$ were prepared from $MnCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$ (Merck, p.A.). The hydrates were preliminarily treated in a vacuum oven at 100°C and then in an HCl stream for 1 day in temperature stages of ~100°C up to melting (652 and 711°C). The temperature was raised only after water was no longer detected at the exhaust of the reaction tube. Potassium chloride (Merck, p.A.) was dried at 500°C in an HCl stream.

2.2. Difference Thermal Analysis (DTA) and Thermogravimetry (TG)

The home-built DTA device was described previously (*7*). The samples (~0.5 g) were heated to melting in vacuum-sealed quartz ampoules with a gas flame, homogenized by shaking, and solidified by rapid cooling. The solids thus obtained were sufficiently homogeneous for measuring heating curves or for annealing experiments. Thermal effects could be detected down to 0.2 J for the generally used heating rate of 2 K $\cdot$ min^{-1}. TG measurements for the decomposition of hydrates were done with a Stanton Redcroft thermobalance TG 750/770 equipped with a differentiation modulus.

2.3. Solution Calorimetry

The apparatus used was a home-built isoperibolic calorimeter (*8*) with a volume of 1.3 liters. Samples of 3–6 g thus yielded virtually ideal solutions (dissolution ratio 1 : 3500 moles). From the enthalpies of solution, ΔH^1, the reaction enthalpies, ΔH^r, were calculated by $\Delta H^r_{298} = \{\Delta H^1_{298}(M\mathrm{Cl}_2) + n \cdot \Delta H^1_{198}(\mathrm{KCl})\} - \Delta H^1_{298}(\mathrm{K}_nM\mathrm{Cl}_{n+2})$. Each ΔH^1 was measured at least three times; KCl was dissolved in a solution of MCl$_2$ of adequate concentration.

2.4. X-Ray Techniques

Powder patterns at room temperature were taken with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum attachment. During exposure (Cu$K\alpha$ radiation) the samples were in a He atmosphere. An Enraf–Nonius-553 Simon–Guinier camera was used for photographs at continuously varying temperatures. The samples were encapsulated in quartz tubes of 0.3-mm diameter. For the determination of cell dimensions Al_2O_3 was used as an internal standard; the calculations were done with the least-squares computer program of Warczewski (*9*) for the varied temperatures.

2.5. Electromotive Force Measurements

A detailed description of the galvanic cell is given elsewhere (*1*). The anode and cathode are graphite disks (20 mm Ø) in a Cl_2 atmosphere. For a reaction KCl + MCl$_2$ = KMCl$_3$, for example, the electrode processes are

$$\text{Anode:}\qquad \mathrm{KCl} \xrightarrow{-e^-} \mathrm{K}^+ + \tfrac{1}{2}\mathrm{Cl}_2$$

$$\text{Cathode:}\qquad \mathrm{K}^+ + M\mathrm{Cl}_2 + \tfrac{1}{2}\mathrm{Cl}_2 \xrightarrow{+e^-} \mathrm{K}M\mathrm{Cl}_3$$

The electrolytes, ACl and MCl$_2$, were prepared by compressing the substances, moisture being excluded, similar to the preparation of disks for IR spectroscopy. MCl$_2$ was mixed with KMCl$_3$ for reversibility of the cell; this mixture was prepared in the same way as for DTA measurements. The electrolytes were separated by a sintered disk of a K$^+$-conducting glass powder prepared according to a prescription of Østvold (*10*) (64.8 mole% SiO_2, 15% K_2O, 15.2% Al_2O_3, 2% TiO_2, 2% ZrO_2, 1%

Ce_2O_3). Disks of KASICON, applied for measurements on the systems of $BaCl_2$ and $SrCl_2$ (*2*) could not be used because of a reaction with the MCl_2 in the catholytes. Preliminary results given at the 7th ICTA (*11*) must therefore be corrected; the time for approaching the equilibrium potentials was generally not greater than 6 hr. Thus, the temperature dependence of the emf was measured stepwise in several temperature cycles so that at least 20 emf values were collected for every temperature. They were subjected to a linear regression analysis. The emf/T curves proved to be linear down to a temperature of 280°C. The upper limit was given by the temperatures of the lowest adjacent eutectic. In the case of $KMgCl_3$ equilibrium was established slowly; therefore measurements were made at two temperatures only, each time allowing 40 hr for equilibration.

3. Results

3.1. The Phase Diagrams

Figure 1 shows the phase diagrams of the systems $KCl/MgCl_2$ and $KCl/MnCl_2$. Three aspects are remarkable and shall be discussed in detail:

(a) The absence of the compound K_2MnCl_4, previously (*13*) shown to be absent by DTA and X-ray measurements, was now confirmed by emf measurements. A galvanic cell with electrolytes of 30 against 35 mole% $MnCl_2$, for example, yielded an emf of zero. Attempts to prepare K_2MnCl_4 by dehydration of $K_2MnCl_4 \cdot 2H_2O$ (*14*) resulted in the formation of K_4MnCl_6 and $KMnCl_3$ ($GdFeO_3$ type).

(b) For the compound $KMnCl_3$ we found only one phase transition at 386 ± 2°C, both in heating and cooling curves. A quantitative DSC measurement (Prof. Eysel, Hei-

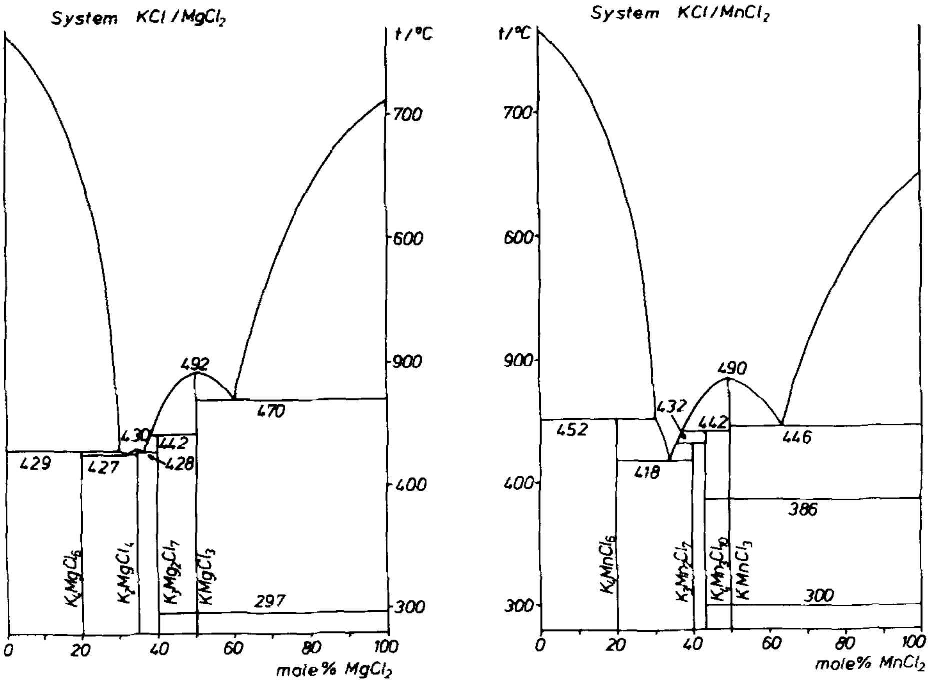


FIG. 1. The systems $KCl/MgCl_2$ (*12*) and $KCl/MnCl_2$ (*13*).

delberg, DSC II, DuPont) yielded only an approximate value of 0.17–0.40 kJ · mole^{-1} because of a drift in the baseline. A small step in the baseline at 300°C indicates a second transition, which was not found by the DTA measurements.

Phase transitions reported by Croft (*15*) at ~450°C and Horowitz *et al.* (*4*) at 430–450°C could not be confirmed when strictly stoichiometric $KMnCl_3$ was used. However, slight stoichiometric deviations yielded thermal effects of the adjacent eutectic at 446°C (excessive $MnCl_2$) or the peritectics at 442 and 432°C, if too little $MnCl_2$ was used. In particular, such deviations were encountered for $KMnCl_3$ samples prepared from $KMnCl_3 \cdot 2H_2O$. It is difficult to prepare pure samples of the dihydrate due to its incongruent solubility.

Measurements with $KMgCl_3$ yielded two transitions: one at 297°C and a small effect at 224°C.

(c) According to Horowitz *et al.* (*4*), the *stable* room-temperature modification of $KMnCl_3$, crystallizing with the NH_4CdCl_3 structure, is formed very slowly so that it cannot be detected by DTA. The best way of preparation therefore is the dehydration of $KMnCl_3 \cdot 2H_2O$ at 120°C. (This temperature was found by a thermogravimetric decomposition.) To obtain a starting material of correct composition the dihydrate was prepared by exposing $KMnCl_3$ to ambient air for a few days.

The transition to the high-temperature modification was found by DSC (Prof. Eysel) at 267°C with a transition enthalpy of 4.60 kJ · mole^{-1}. However, as described by Horowitz (*4*), this temperature can vary between 150 and 270°C, probably due to kinetic effects. By solution calorimetry the solution enthalpy of the NH_4CdCl_3-type $KMnCl_3$ was found to be −35.5 ± 0.1 kJ · mole^{-1}. This leads to a $\Delta H^{\mathrm{r}}_{298}$ (calor) = −20.7 kJ · mole^{-1}. Together with the ΔH^{r} value for the $GdFeO_3$-type $KMnCl_3$ of −16.4 kJ · mole^{-1} (*6*) a transition enthalpy of +4.3 kJ · mole^{-1} results: that is a sufficient conformity.

The dehydration of $KMgCl_3 \cdot 6H_2O$ both in an HCl stream and by boiling with $SOCl_2$ results in the formation of $KMgCl_3$ with the $GdFeO_3$ structure.

If $KMnCl_3$ is treated with absolute alcohol, an incongruent dissolution process occurs: $MnCl_2$ is partially dissolved and a residue of K_4MnCl_6 remains (experimental conditions: 20 g $KMnCl_3$ is stirred for 4 hr with 500 ml absolute ethanol). Both modifications of $KMnCl_3$ react in this way. This reaction is a convenient method to prepare pure K_4MnCl_6, which melts incongruently with a difference of ~200°C between peritectic and liquidus temperature. ($KMgCl_3$ under the same conditions leaves a residue of KCl.) This reaction proceeds through the solution phase as proven by the fact that an alcoholic solution of $MnCl_2$ stirred with solid KCl also yields K_4MnCl_6.

3.2. Crystal Structures

3.1.1. The Compounds $KMgCl_3$ and $KMnCl_3$

Both compounds crystallize from the melts in the cubic perovskite structure type. With decreasing temperature they undergo several phase transitions which can be explained with group–subgroup relations generated by octahedra tilting (Glazer (*16*), Aleksandrov (*17*)).

Midorikawa *et al.* (*18*) had found by measurements of the thermal expansion and of the temperature dependence of birefringences that $KMgCl_3$ undergoes four phase transitions between room temperature and its melting point:

$$\text{monocl} \xrightarrow{142^\circ\text{C}} \text{orthorhomb } (D_{2h}^{16}) \xrightarrow{212^\circ\text{C}} \text{orthorhomb } (D_{2h}^{17}) \xrightarrow{224^\circ\text{C}} \text{tetrag } (D_{4h}^{5}) \xrightarrow{296^\circ\text{C}} (O_h^1)$$

Earlier Brynestad *et al.* (*19*) had found by X-ray investigations on $KMgCl_3$ single crystals an orthorhombic structure ($GdFeO_3$ type; D_{2h}^{16}) at room temperature.

For $KMnCl_3$ the first investigation in 1965 on crystal powders (*15*) alleged a tetragonal structure at room temperature with a transition to a cubic cell at 485°C. We could correct this finding in 1977 (*6*): the room-temperature structure is orthorhombic ($GdFeO_3$ type) and the phase transition to the cubic form occurs at 386°C. The orthorhombic structure was confirmed later by Horowitz *et al.* (*4*). In Table I the results of our dynamic high-temperature measurements on crystal powders with Al_2O_3 as an internal standard (*9*) are compiled. The transition from the orthorhombic to the tetragonal structure were indicated by the disappearance during heating of the orthorhombic reflex (031), the transition to the cubic structure by the disappearance of the tetragonal reflexes (201) and (220). The stability range for the second orthorhombic phase of $KMgCl_3$—space group D_{2h}^{17}—from 212 to 224°C could not be verified by X-ray measurements due to their low sensitivity; neither could the monoclinic room-temperature phase be observed by powder investigations because the cell dimensions—$\beta = 90°$, $a = c$—are pseudotetragonal.

3.3. Electromotive Force Measurements

In this chapter the results of the emf measurements are compiled. For each reaction the formula of the regression line over all measured emf/T points is given and then the Gibbs–Helmholtz relations with temperature-independent ΔH^r and ΔS^r values are calculated. The ΔH^r values are compared with those found by solution calorimetry at 298 K (ΔH_{298}^r (calor.)). Additionally, the functions for the formation of the compounds from KCl and MCl_2 are calculated. ΔG_T^r is given for the temperature $T = 650$ K. The range of error is assessed from the standard deviations of each series and from the differences between the measurements of different samples for the same reaction.

3.3.1. Magnesium Compounds

$KMgCl_3$. Reaction $KCl + MgCl_2 = KMgCl_3$. Samples: 60 and 80 mole% $MgCl_2$. Measurements were performed at 652 and 782 K after allowing 40 hr for equilibration.

$\mathrm{emf/mV} = 90.50 + 0.1731\ T/K$

$\Delta G^r/\mathrm{kJ \cdot mole^{-1}} = -8.73 - 0.0167\ T/K$

$\Delta H^r = -8.7 \pm 0.1\ \mathrm{kJ \cdot mole^{-1}}$

$\Delta H_{298}^r(\mathrm{calor}) = -9.90\ \mathrm{kJ \cdot mole^{-1}}$ (*5*)

$\Delta S^r = 16.7 \pm 0.2\ \mathrm{J \cdot K^{-1} \cdot mole^{-1}}$

$\Delta G_{650}^r = -19.6 \pm 0.9\ \mathrm{kJ \cdot mole^{-1}}$

TABLE I

LATTICE PARAMETERS (IN Å) FOR $KMgCl_3$ AND $KMnCl_3$ FROM SIMON–GUINIER PHOTOGRAPHS AT VARYING TEMPERATURES

	Temperature (°C)	Z	Space group	a	b	c
$KMgCl_3$	330	1	$Pm3m(O_h^1)$	4.998(1)	—	—
	250	2	$P4/mbm(D_{4h}^5)$	7.024(2)	—	5.007(1)
	150	4	$Pnma(D_{2h}^{16})$	7.005(2)	9.974(2)	7.001(2)
	20	4	$Pnma(D_{2h}^{16})$	6.967(2)	9.917(2)	6.967(2)
$KMnCl_3$	480	1	$Pm3m(O_h^1)$	5.084(1)	—	—
	320	2	$P4/mbm(D_{4h}^5)$	7.126(1)	—	5.007(1)
	260	4	$Pnma(D_{2h}^{16})$	7.109(2)	10.149(2)	7.108(2)
	20	4	$Pnma(D_{2h}^{16})$	7.075(1)	10.014(2)	7.022(1)

$K_3Mg_2Cl_7$. Reaction 0.5KCl + $KMgCl_3$ = $K_{1.5}MgCl_{3.5}$. Samples: 41.5 and 45 mole% $MgCl_2$. Stepwise measurements; 610–710 K; 27 and 49 points, respectively.

emf/mV = 31.56 + 0.0365 T/K

ΔG^r/kJ · mole^{-1} = −1.52 − 0.0018 T/K

For the reaction 1.5KCl + $MgCl_2$ = $K_{1.5}MgCl_{3.5}$:

ΔG^r/kJ · mole^{-1} = −10.25 − 0.0185 T/K

ΔH^r = −10.2 ± 0.2 kJ · mole^{-1}

ΔH^r_{298}(calor) = −7.95 kJ · mole^{-1} (*5*)

ΔS^r = 18.5 ± 0.3 J · K^{-1} · mole^{-1}

ΔG^r_{650} = −22.3 ± 0.4 kJ · mole^{-1}

K_2MgCl_4. Reaction 0.5KCl + $K_{1.5}MgCl_{3.5}$ = K_2MgCl_4. Sample: 36 mole% $MgCl_2$. Stepwise measurements; 610–700 K; 33 points.

emf/mV = 0.28 + 0.0361 T/K

ΔG^r/kJ · mole^{-1} = −0.01–0.0017 T/K

($\Delta H^r \approx$ 0 kJ · mole^{-1})

For the reaction 2KCl + $MgCl_2$ = K_2MgCl_4:

ΔG^r/kJ · mole^{-1} = −10.26 − 0.0202 T/K

ΔH^r = −10.3 ± 0.3 kJ · mole^{-1}

ΔH^r_{298}(calor) = −7.75 kJ · mole^{-1} (*5*)

ΔS^r = 20.2 ± 0.5 J · K^{-1} · mole^{-1}

ΔG^r_{650} = −23.4 ± 0.5 kJ · mole^{-1}

K_4MgCl_6. Reaction 2KCl + K_2MgCl_4 = K_4MgCl_6. Sample: 25 mole% $MgCl_2$. Stepwise measurements; 590–690 K; 100 points.

emf/mV = 36.69 − 0.0459 T/K

ΔG^r/kJ · mole^{-1} = −7.08 + 0.0089 T/K

For the reaction 4KCl + $MgCl_2$ = K_4MgCl_6:

ΔG^r/kJ · mole^{-1} = −17.34 − 0.0113 T/K

ΔH^r = −17.3 ± 0.5 kJ · mole^{-1}

ΔS^r = 11.3 ± 0.7 J · K^{-1} · mole^{-1}

ΔG^r_{650} = −24.7 ± 0.7 kJ · mole^{-1}

The value of ΔH^r_{298} previously measured by solution calorimetry (*5*) must be corrected. A redetermination yielded the following values for solution enthalpy:

K_4MgCl_6	−66.0 ± 0.5 kJ · mole^{-1}
$MgCl_2$	−156.4 ± 0.2 kJ · mole^{-1}
KCl in $MnCl_2$ solution	+17.9 ± 0.1 kJ · mole^{-1}
ΔH^r_{298}(calor)	−18.8 ± 6 kJ · mole^{-1}

3.3.2. Manganous Compounds

$KMnCl_3$. Reaction KCl + $MnCl_2$ = $KMnCl_3$. Samples: 70 and 80 mole% $MnCl_2$. Stepwise measurements; 610–715 K; 120 points.

emf/mV = 124.39 + 0.1631 T/K

ΔG^r/kJ · mole^{-1} = −12.0 − 0.0156 T/K

ΔH^r = −12.0 ± 0.3 kJ · mole^{-1}

ΔH^r_{298}(calor) = −15.53 kJ · mole^{-1}

ΔS^r = 15.6 ± 0.5 J · K^{-1} · mole^{-1}

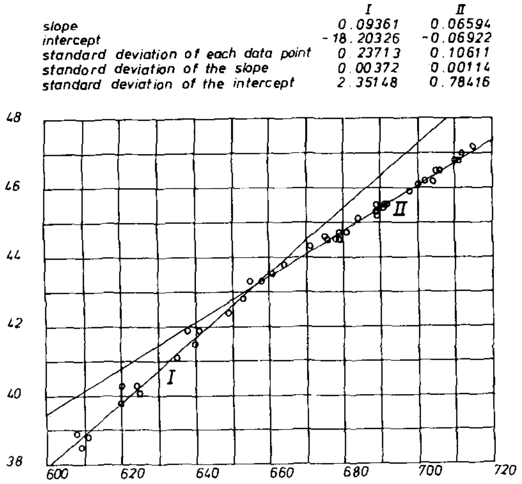
ΔG^r_{650} = −22.1 ± 0.2 kJ · mole^{-1}

The phase transition at 659 K could not be detected as a kink of the emf-vs-*T* curve.

$K_4Mn_3Cl_{10}$. Reaction 0.33KCl + $KMnCl_3$ = $K_{1.33}MnCl_{3.33}$. X-Ray photographs showed that this compound could not be obtained pure even after extended annealing. Therefore a sample was prepared from $KMnCl_3$ in the galvanic cell by a coulometric titration: by applying a direct current 0.2 mole% KCl was transferred into the $KMnCl_3$ disk.

For this reaction a kink at the transition point of $KMnCl_3$ (659 K) could be observed because of the small charge factor $n = 0.33$ in the relation $\Delta G = -n \cdot F \cdot E$. This can be seen in Fig. 2.

Measurements below 659 K (608–655 K; 15 points):



	I	II
slope	0.09361	0.06594
intercept	-18.20326	-0.06922
standard deviation of each data point	0.23713	0.10611
standard deviation of the slope	0.00372	0.00114
standard deviation of the intercept	2.35148	0.78416

FIG. 2. Computer plot of emf vs T for the reaction $0.33KCl + KMnCl_3 = K_{1.33}MnCl_{3.33}$. (I—tetragonal $KMnCl_3$; II—cubic $KMnCl_3$.)

$$\text{emf/mV} = -18.20 + 0.0936\ T/K$$

$$\Delta G^r/\text{kJ} \cdot \text{mole}^{-1} = 0.59 - 0.0030\ T/K$$

Measurements above 659 K (660–715 K; 30 points):

$$\text{emf/mV} = -0.07 + 0.0659\ T/K$$

$$\Delta G^r/\text{kJ} \cdot \text{mole}^{-1} = 0.00 - 0.0021\ T/K$$

Transition temperature
$(\Delta G^r(I) = \Delta G^r(II)) = 655$ K (382°C)

Transition enthalpy
$(\Delta H^r(II) - \Delta H^r(I)) = +0.6$ kJ · mole^{-1}

(By DSC measurements (p. 4) a value of 0.17–0.40 kJ · mole^{-1} was found.) For the reaction $1.33KCl + MnCl_2 = K_{1.33}MnCl_{3.33}$ (below 659 K):

$$\Delta G^r/\text{kJ} \cdot \text{mole}^{-1} = -11.4 - 0.0186\ T/K$$

$$\Delta H^r = -11.4 \pm 0.3\ \text{kJ} \cdot \text{mole}^{-1}$$

$$\Delta S^r = 18.6 \pm 0.6\ \text{J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1};$$

$$\Delta G^r_{650} = -23.5 \pm 0.3\ \text{kJ} \cdot \text{mole}^{-1}.$$

$K_3Mn_2Cl_7$. Reaction $0.17KCl + K_{1.33}MnCl_{3.33} = K_{1.5}MnCl_{3.5}$. Sample: 41.5 mole% MnCl. Stepwise measurements; 640–700 K; 27 points.

$$\text{emf/mV} = 0.59 + 0.0594\ T/K$$

$$\Delta G^r/\text{kJ} \cdot \text{mole}^{-1} = -0.01 - 0.0010\ T/K$$

$$(\Delta H^r \approx 0)$$

For the reaction $1.5KCl + MnCl_2 = K_{1.5}MnCl_{3.5}$:

$$\Delta G^r/\text{kJ} \cdot \text{mole}^{-1} = -11.4 - 0.0196\ T/K$$

$$\Delta H^r = -11.4 \pm 0.04\ \text{kJ} \cdot \text{mole}^{-1}$$

$$\Delta H^r_{298}(\text{calor}) = -12.64\ \text{kJ} \cdot \text{mole}^{-1}\ (5)$$

$$\Delta S^r = 19.6 \pm 0.8\ \text{J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

$$\Delta G^r_{650} = -24.1 \pm 0.4\ \text{kJ} \cdot \text{mole}^{-1}$$

K_4MnCl_6. Reaction $2.5KCl + K_{1.5}MnCl_{3.5} = K_4MnCl_6$. Samples: 25 and 36 mole% $MnCl_2$. Stepwise measurements; 638–690 K; 18 points.

$$\text{emf/mV} = 39.90 - 0.0372\ T/K$$

$$\Delta G^r/\text{kJ} \cdot \text{mole}^{-1} = -9.63 + 0.0090\ T/K$$

For the reaction $4KCl + MnCl_2 = K_4MnCl_6$:

$$\Delta G^r/\text{kJ} \cdot \text{mole}^{-1} = -21.0 - 0.0106\ T/K$$

$$\Delta H^r = -21.0 \pm 0.8\ \text{kJ} \cdot \text{mole}^{-1}$$

$$\Delta H^r_{298}(\text{calor}) = -25.1\ \text{kJ} \cdot \text{mole}^{-1}\ (5).$$

4. Discussion of the Results of the Electromotive Force Measurements

For the systems $KCl/MgCl_2$ and $KCl/MnCl_2$ three groups of compounds must be considered which are also found in other ACl/MCl_2 systems:

1. The perovskites $AMCl_3$.
2. The compounds A_2MCl_4 (K_2NiF_4 type) and the related compounds $A_3M_2Cl_7$ and $A_4M_3Cl_{10}$, which were found for the first time in the system $KCl/MnCl_2$ in 1965 (*13*). In all these structures MCl_6 octahedra are connected through four coplanar corners forming $(MCl_{4/2}Cl_2)_\infty$ layers which are held together by the A^+ ions. In $A_3M_2Cl_7$ two layers are condensed to double layers, while in $A_4M_3Cl_{10}$ triple layers are formed.

Inside the layers the coordination is the same as in the perovskite structure. (For $Rb_3Mn_2Cl_7$ the structure was refined by single-crystal techniques (*20*) in 1978.)

3. The compound A_4MCl$_6$ with isolated octahedra.

To emphasize the significance of the entropy for the formation of double chlorides the energy terms ΔG^r, ΔH^r and $-(T \cdot \Delta S^r)$ for a standardized temperature $T = 650$ K are compiled in Table II for these three groups of compounds:

1. Group 1 contains all compounds KMCl$_3$ and RbMCl$_3$, crystallizing in the cubic perovskite structure or in distorted versions of it. With smaller M^{2+} ions the "hexaagonal variants" are formed. While ΔH^r is mainly determined by the ionic size and by polarizibility, the entropy term seems to depend on the structures of the mother compounds MCl$_2$: $CdCl_2$ type for M = Mg, Mn; distorted SnO_2 type for $CaCl_2$; fluorite type for $SrCl_2$; and the $PbCl_2$ type. All compounds are formed with an entropy increase, but the first four listed in Group 1 exist only due to the gain in lattice enthalpy. In contrast the Sr and Pb compounds are unstable at room temperature with regard to a disproportionation to RbCl and RbM_2Cl$_5$; at higher temperature they are formed due to a gain in entropy.

TABLE II

ENERGY TERMS (IN kJ · mole^{-1}) FOR THE FORMATION OF DOUBLE CHLORIDES AT $T = 650$ K

Compound	ΔG^r	ΔH^r	$-(T \cdot \Delta S^r)$
Group 1: reaction ACl + MCl$_2$ = AMCl$_3$			
$KMgCl_3$	−19.6	−8.7	−10.9
$KMnCl_3$	−22.1	−12.0	−10.1
$KCaCl_3$ (*21*)	−18.7	−12.4	−6.3
$RbCaCl_3$ (*3*)	−29.2	−23.1	−6.1
$RbSrCl_3$ (*3*)	−8.6	+5.4	−14.0
$RbPbCl_3$ (*21*)	−13.9	+4.9	−18.8
Group 2: successive reactions starting with KMCl$_3$			
$\frac{1}{2}K_3Mg_2Cl_7$	−2.7	−1.5	−1.2
↓			
K_2MgCl_4	−1.1	0.0	−1.1
$\frac{1}{3}K_4Mn_3Cl_{10}$	−1.4	0.0	−1.4
↓			
$\frac{1}{2}K_3Mn_2Cl_7$	−0.7	0.0	−0.7
Group 3: reaction 3KCl + KMCl$_3$ = K$_4M$Cl$_6$			
K_4MgCl_6	−5.1	−8.6	+3.5
K_4MnCl_6	−5.8	−9.0	+3.2

2. Due to the close relationship between the K_2NiF_4 and perovskite types the gain in lattice enthalpy is zero or nearly zero by the processes explained above: In going from the perovskite to the K_2NiF_4 structure type, connections between adjacent octahedra have to be broken in one direction to obtain two-dimensional $(M\text{Cl}_{4/2}\text{Cl}_2)_n$ layers. This process brings about a small but significant gain in entropy.

3. For the compounds K$_4M$Cl$_6$ the formation from KMCl$_3$ is considered because of the nonexistence of K_2MnCl_4. The entropy is decreasing; the existence of the compound is only due to the gain in lattice enthalpy.

One of the main problems concerning our investigations is the question whether it is permissible to extrapolate the ΔG^r-vs-T curves to room temperature, or in other words, if the condition $\Delta c_p = 0$ holds over this temperature range. If we compare the ΔH^r values from the emf measurements with those from solution calorimetry at $T = 298$ K we sometimes find deviations up to 3 kJ · mole^{-1}. These deviations may stem in part from uncertainties in the measurements. Small errors in the measurements would have the greatest effect on ΔH^r values, since a short line between 600 and 700 K has to be extrapolated to 0 K. However, the significance of $\Delta c_p = 0$ should also be investigated by direct c_p measurement of the double chlorides and their parent substances.

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