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THERMAL ANALYSIS BY EMF-MEASUREMENTS ON SOLID ELECTROLYTES- THE SYSTEM RbCl WITH EARTH ALKALINE METALCHLORIDES

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ABSTRACT

Measurement of the temperature dependence of the e.m.f. of a galvanic cell with solid electrolytes can be a useful tool for studying solid state reactions. This was done for the following compounds and reactions:

a) $Rb_{2.07}Ba_{0.965}Cl_4$: to prove the uneven stoichiometry;
b) $RbSrCl_3$: is formed at high temperature;
c) $Rb_3Mg_2Cl_7$: decomposes at high temperature;
d) Rb_2MgCl_4: has a reconstructive phase transition.

The results are compared with those of classical DTA.

INTRODUCTION

In the preceding paper thermodynamic functions for solid state reactions $nRbCl+MCl_2=Rb_nMCl_{n+2}$ (M=earth alkaline metal) were presented, measured electrochemically with a galvanic cell of the type $(C+Cl_2)/RbCl(s)/Rb^+$-conduct.diaphragm/$(CaCl_2+RbCaCl_3)(s)/(C+Cl_2)$. The free enthalpy of reaction was obtained by the relation $\Delta G_R=-n \cdot F \cdot E$ (E=e.m.f.), and by its temperature dependence the reaction-enthalpies and -entropies could be determined, too. The latter measurements were done by stepwise changing the temperature to allow time for approaching equilibrium.

In this paper measurements for studying special solid state reactions are described. For determining reaction temperatures e.m.f. vs. T-curves were measured continuously, too, neglecting a certain thermal lag. Analogous investigations on systems with NaCl and KCl were presented previously (ref. 1).

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EXPERIMENTAL

The set-up of the cell and the experimental procedures were described previously (ref. 1,2).

For DTA-measurement a home-built cell (ref. 3) was used; the samples (~0.5g) were melted in vacuum-sealed quartz tubes, homogenized by shaking and solidified by rapid cooling. They were annealed for several days, when necessary.

RESULTS

The stoichiometry of the 2:1 phase in the system $RbCl/BaCl_2$

By investigations of the system $KCl/BaCl_2$ (ref. 4) we found that the long known 2:1-phase has an uneven stoichiometry, $K_{2.08}Ba_{0.96}Cl_4$. This composition was elucidated with DTA-measurements together with crystal-chemical considerations: the crystal structure is related to the cubic Th_3P_4-type, the K^+ and Ba^{2+} occupying the Th-sites. Because the sum of the cations is greater than three (3.04) the structure is only pseudocubic.

In the system $RbCl/BaCl_2$ an analogous compound exists. Its

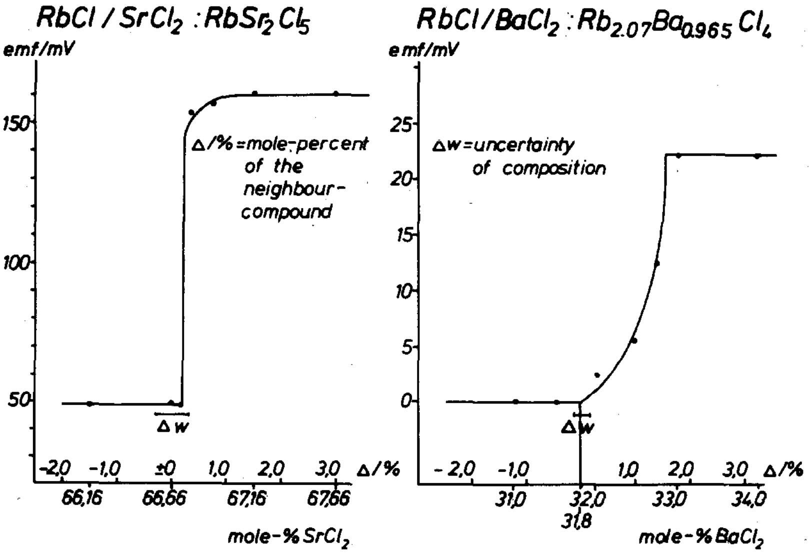

Fig. 1. Elucidation of uneven stoichiometry by e.m.f.-measurements.

composition, $Rb_{2.07}Ba_{0.965}Cl_4$, is based on the observation that a sample with 32.0 mole-% $BaCl_2$ still gives a thermal effect in the DTA-curve at 644°C due to the eutectic at 47.0 mole-%.

E.m.f.-measurements of all samples containing free $BaCl_2$ should yield a constant value caused by the formation of the ternary compound. Theoretically it should drop down to zero exactly at the real composition of the compound. But, experiments have shown (fig. 1) that for mixtures with less than 2% $BaCl_2$ (relating to 98% of the compound) the e.m.f. values are diminished - there is no longer equilibrium between the two components in each part of the sample. The same was found for $RbSr_2Cl_5$, a compound with even stoichiometry. But nevertheless, e.m.f.-measurements can be used for finding uneven stoichiometry with an only small range of error.

The formation of $RbSrCl_3$ at higher temperature

In the system $RbCl/SrCl_2$ (ref. 5) a compound $RbSrCl_3$ is formed from ($RbCl+RbSr_2Cl_5$) when heating this mixture up to ~350°C. At

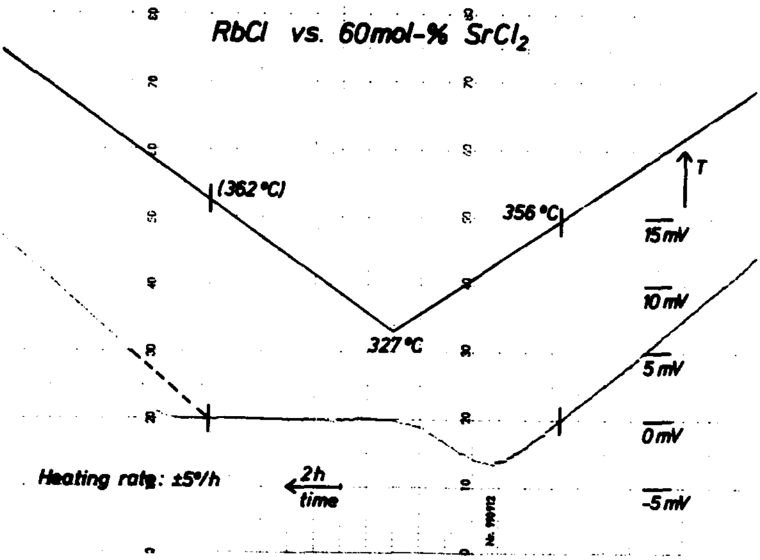

Fig. 2. E.m.f. vs. T-curve for $RbSrCl_3$(60 mole-% $SrCl_2$)

the temperature of formation ΔG_R and also the relating e.m.f. must be zero. So this temperature can be determined by continuously measured e.m.f. vs. T-curves (fig. 2). Below this temperature a metastable state exists with negative e.m.f.- (and positive ΔG_R-) values. As fig. 2 shows, the equilibrium values are approached in 6 hours when cooling and in 3 hours when heating.

The temperature of formation was found to be 356°C from cooling curves and from stepwise measured (e.g. heating rate = 0) e.m.f. vs. T-curves. A heating curve gave a somewhat higher temperature of 362°C due to a certain thermal lag. By DTA-measurements (heating rate 2°/min) a higher termperature - 370°C - was found caused by superheating.

The compound Rb_3MgCl_5 (ref. 6) has analogous properties; it is formed at 386°C according to e.m.f. measurements (preceding paper); but DTA gave temperatures of 361°C (cooling curve) resp. 398°C (heating curve).

The phase transition of Rb_2MgCl_4

Rb_2MgCl_4 has a phase transition at ~420°C from the K_2NiF_4-type with $NiCl_{4/2}Cl_2$-octahedra (D-Rb_2MgCl_4) to the K_2SO_4-type with isolated tetrahedra (H-Rb_2MgCl_4) (ref. 6). In the e.m.f. vs. T-curve of a sample with 38 mole-% $MgCl_2$ the transition temperature is to be seen as a pronouced kink (fig. 3).

A regression analysis of the e.m.f.-values for the reaction

$0.5RbCl+Rb_{1.5}MgCl_{3.5}$=H-$Rb_2MgCl_4$

measured in the temperature range 710-732 K gave the linear relation $E(mV)=-326.6+0.5451T$ and $\Delta G_R(kJ/mole)=15.76-0.0263T$. The condition for equilibrium is that ΔG_R for the D-Rb_2MgCl_4 ($\Delta G_R(kJ/mole)=-0.9-0.0027T$; paper Seifert/Thiel) must be equal to ΔG_R for H-Rb_2MgCl_4. It is fulfilled for T=708 K (435°C). From both equations the enthalpy of transition (ΔH_T) and also the entropy (ΔS_T) can be derived: $\Delta H_T=17\ kJ\cdot mole^{-1}$ $\Delta S_T=24\ J\cdot K^{-1}\cdot mole^{-1}$. It is a strongly endothermal reaction with a large gain in entropy.

A second way to get information about this phase transition is to consider the formation reaction of Rb_3MgCl_5 from RbCl and both modifications of Rb_2MgCl_4. For the reaction

RbCl+H-Rb_2MgCl_4=Rb_3MgCl_5

we found in the range 695 K < T < 730 K (423-457°C) e.m.f.-values obeying the equation $E(mV)=24.72-0.0193T$ which gives

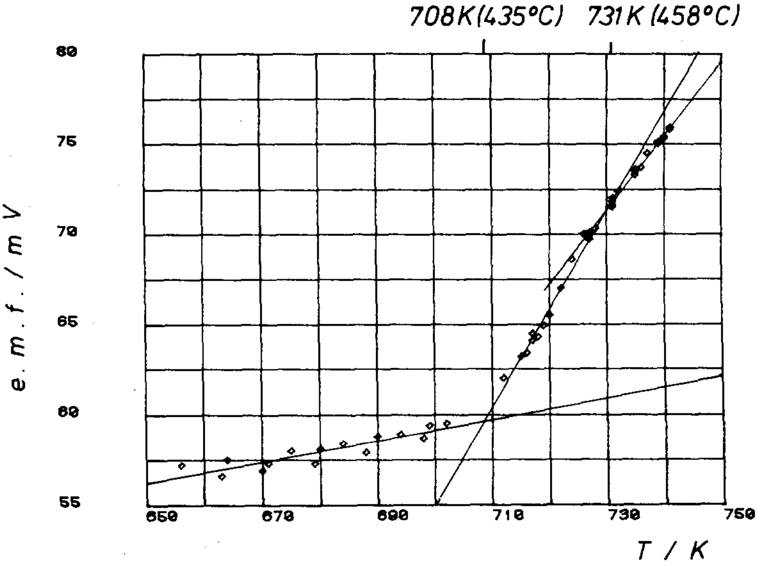

Fig. 3. E.m.f. vs. T-curve for Rb_2MgCl_4 (38 mole-% $MgCl_2$)

ΔG_R(kJ/mole)=-2.4+0.0019T. Together with ΔG_R(kJ/mole)= 21.0-0.0319T for the temperature range 659-694 K, a transition temperature was calculated of 694 K (421°C) and a ΔH_T=23 kJ·mole^{-1}.

The transition temperatures found as crossing points of the two e.m.f. vs. T-curves differ by 14°C, but they lie between those found by DTA from cooling- (415°C) and heating curves (443°C) respectively. The enthalpies determined on both ways differ by 6 kJ; but that is typical for this method: One gets only bad enthalpies (and not very good entropies) if the temperature range available for making measurements is small!

The decomposition of $Rb_3Mg_2Cl_7$ at higher temperature

For $Rb_3Mg_2Cl_7$ DTA-measurements gave the following temperatures of decomposition: 431°C from cooling curves (ref. 6) and 465°C from heating curves.

To determine this temperature by e.m.f.-measurements, too, in addition to the e.m.f.-value for the formation of $Rb_3Mg_2Cl_7$ at deep temperature (E(I)) the reaction $RbCl+RbMgCl_3$=H-Rb_2MgCl_2 was investigated in the range $728 < T(K) < 742$.

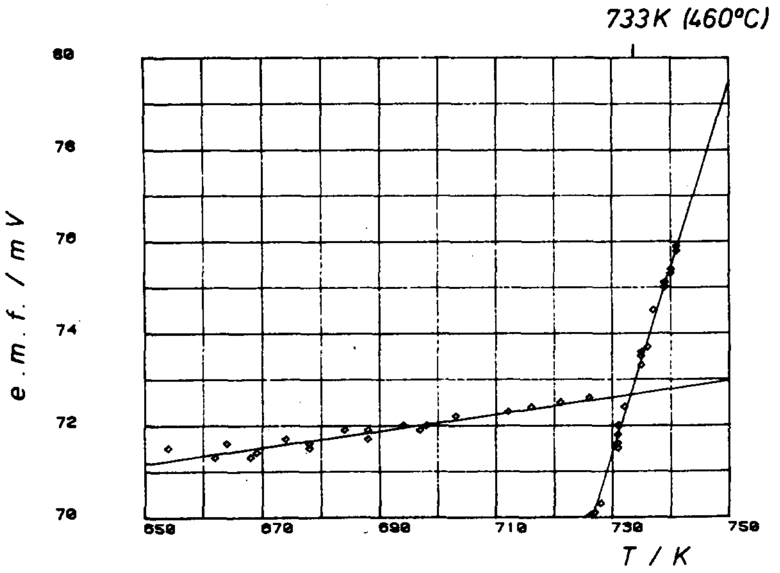

Fig. 4. E.m.f. vs. T-curve for $Rb_3Mg_2Cl_7$ (45 mole-% $MgCl_2$)

RESULTS: E(II) (mV)=-223.7+0.4042T and ΔG_R(kJ/mole)=21.6-0.0390T This reaction is strongly endothermal with an entropy-gain of nearly 40 $J \cdot K^{-1} \cdot mole^{-1}$.

The reaction temperature could be obtained as the crossing point of the E(I)- and E(II)-lines, that gives 733 K or 460°C (fig. 4) and as a kink in the e.m.f. vs. T-curve for the formation of H-Rb_2MgCl_4 from $Rb_3Mg_2Cl_7$ and $RbMgCl_3$ (fig. 3, right-hand) respectively yielding 731 K (458°C). Again these values lie between those from DTA-measurements.

Thus it can be concluded that in the case of solid state reactions with a tendency for undercooling or superheating e.m.f. vs. T-measurements give more reliable equilibrium temperatures than DTA.

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