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EMF-MEASUREMENTS IN GALVANIC CELLS WITH RUBIDIUM CHLORIDE AS SOLID ELECTROLYTE

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ABSTRACT

With a galvanic cell the e.m.f. for solid-state reactions $nRbCl+MCl_2=Rb_nMCl_{n+2}$ was measured. With the relation $\Delta G_R=-nF(e.m.f.)$ the free enthalpies for these reactions were obtained, as well as the reaction-enthalpies and -entropies by the temperature dependence of ΔG_R. Results for the following compounds are given: $Rb_{2.07}Ba_{0.965}Cl_4$; $RbSr_2Cl_5$ and $RbSrCl_3$; $RbCaCl_3$; $RbMgCl_3$; $Rb_2Mg_3Cl_7$; Rb_2MgCl_4 and Rb_3MgCl_5.

INTRODUCTION

The free (Gibbs) enthalpy ΔG_R for the formation of ternary chlorides according to the equation

$$n\ RbCl + MCl_2 = Rb_nMCl_{n+2}$$

can be determined by measuring the e.m.f. (E) of a galvanic cell with chlorine electrodes and RbCl resp. MCl_2 as solid electrolytes, separated by a Rb^+-conducting diaphragm. The relation to be used is $\Delta G_R= -n\cdot F\cdot E$ (n= transported charge; F= Faraday constant). By also running temperature cycles the dependence of E from T was found to be linear: $E = a+b\cdot T$. Thus, with the Gibbs-Helmholtz-relation $\Delta G_R=\Delta H_R-\Delta S_R\cdot T$ all thermodynamic functions can be obtained.

In the last few years systems with NaCl (ref. 1,2) and KCl (ref. 3-5) were investigated; here results of measurements on RbCl-systems with the chlorides of the earth alkaline metals Ba, Sr, Ca and Mg are presented.

EXPERIMENTAL

The general design of the cell and the experimental procedures were described previously (ref. 2).

For the formation of $RbCaCl_3$ e.g., the special design is:
$(C+Cl_2)/RbCl(s)/Rb^+$-conduct.diaphragm/$(CaCl_2+RbCaCl_3)(s)/(C+Cl_2)$

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The electrodes ($C+Cl_2$) are graphite discs in a Cl_2-atmosphere; the diaphragm is a disc of sintered glass powder, prepared according to a prescription of Østvold (ref. 6): 75 mole percent SiO_2; 20 Rb_2O; 5Al_2O_3.

The cell reaction producing the e.m.f. can be separated into the two electrode reactions:

Anode: $RbCl=1/2\ Cl_2+Rb^++e^-$

Cathode: $Rb^++CaCl_2+1/2\ Cl_2+e^-=RbCaCl_3$

The time for approaching the equilibrium potentials at the electrodes depends on the temperature, the conductivity of the substances and on the preparations of the whole sandwich. Five hours are required especially when changing temperature. So the temperature dependence of the e.m.f. was measured stepwise in several temperature cycles. The e.m.f. vs. T-curves proved to be linear, down to a temperature of 350°C.

RESULTS

The system $RbCl-BaCl_2$

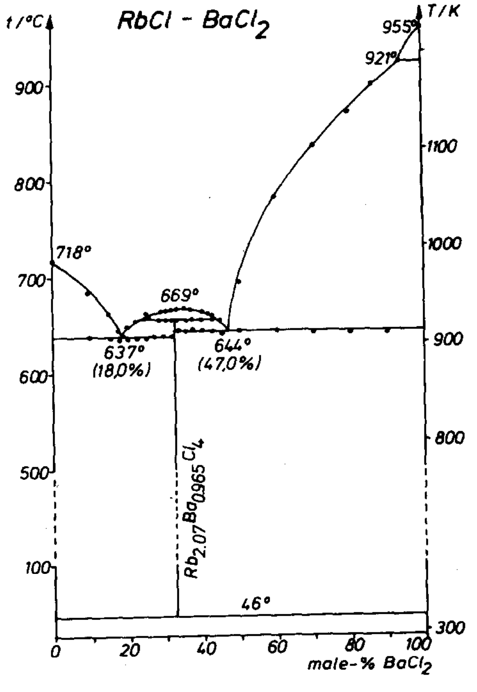
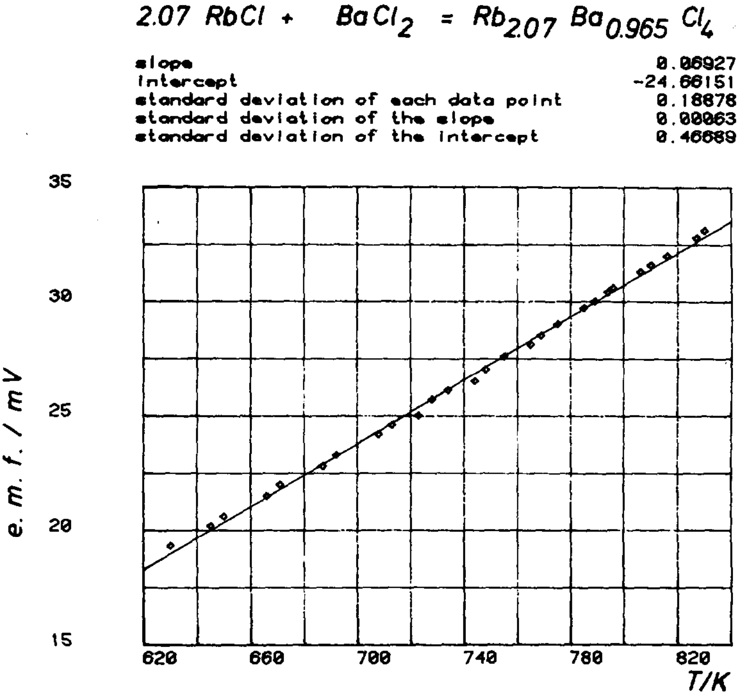


Fig. 1. System $RbCl/BaCl_2$

This system was studied with DTA, the first time by Hoffman (ref. 7) who found a congruently melting 2:1-compound. A re-examination yielded the phase diagram shown in fig. 1: A compound with uneven stoichiometry, $Rb_{2.07}Ba_{0.965}Cl_4$, melts at 655°C, probably forming two non-miscible fluid phases up to 669°C. The non-stability below 46°C couldn't be found by DTA but only by e.m.f. vs. T-measurements. This was proved by X-ray photographs of one-year-old samples.

Like the equivalent compound $K_{2.08}Ba_{0.96}Cl_4$ (ref. 5) it has a pseudo-cubic structure which derives from the Th_3P_4-type. By a high-temperature X-ray pattern at ~ 550°C a lattice constant a = 9.595 Å was found.



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slope                                          0.06927
intercept                                    -24.66151
standard deviation of each data point          0.18878
standard deviation of the slope                0.00063
standard deviation of the intercept            0.46689
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Fig. 2. Computer plot e.m.f. vs. T

For the e.m.f.-measurements two samples were used, with 60 and 90mole-% $BaCl_2$. Fig. 2 shows a computer plot of the regression analysis (for the 90%-sample). The equation for the temperature-dependence of $\Delta G_R = \Delta H_R - \Delta S_R \cdot T$ gives the enthalpy and entropy, both of which are temperature-independent as a concequence of the linearity ΔG vs. T.

RESULTS:

60% $BaCl_2$: $E(mV) = -22.29 + 0.0781T$

90% $BaCl_2$: $E(mV) = -24.66 + 0.0693T$

$\bar{E}(mV) = -23.48 + 0.0737T$

Deviations: $(\pm 1.2)(\pm 0.005)$

$\Delta G_R(kJ/mole) = 4.69 - 0.0147T$

$\Delta G_R(298K) = 0.3 kJ \cdot mol^{-1} (\pm 0,6)$ $\Delta G_R = 0$ at $319 \pm 30K (46^{o}C)$

$\Delta H_R = 4.7 kJ \cdot mol^{-1} (\pm 0.3)$ $\Delta S_R = 14.7 J \cdot K^{-1} (\pm 1)$

It is remarkable that the compound is formed endothermally, i.e. it 'lives from a gain in entropy'.

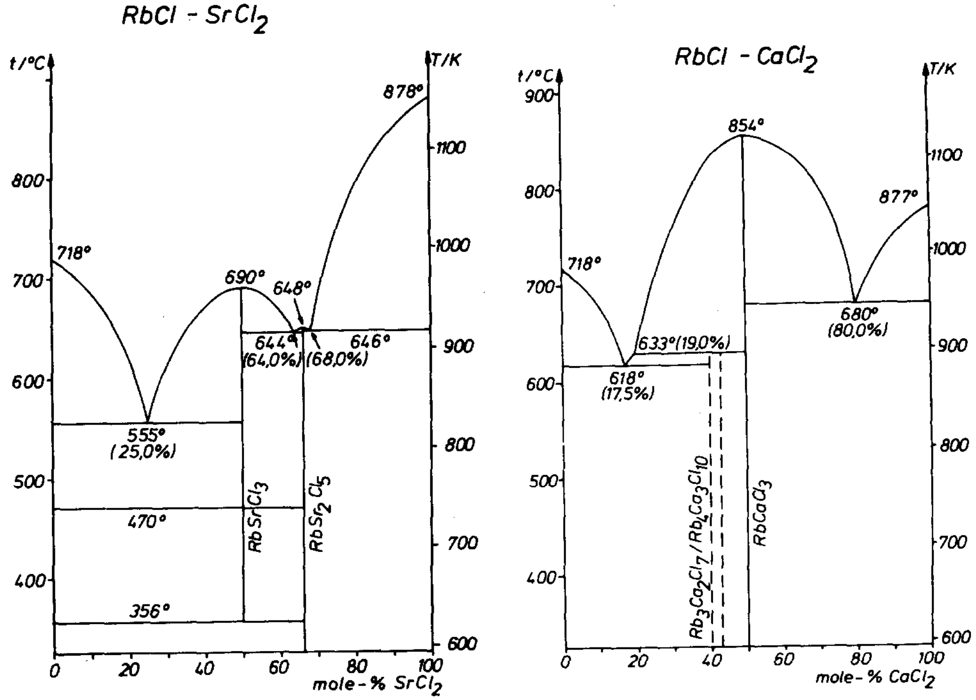

Fig. 3. The systems $RbCl/SrCl_2$ and $RbCl/CaCl_2$

The system $RbCl/SrCl_2$

Earlier we found (ref.8) two congruently melting compounds (fig. 3). The one, $RbSrCl_3$, is stable only at temperatures higher than 356°C and has a structure transition at 470°C.

For the e.m.f.-measurements we used samples with 70 and 90mole-% $SrCl_2$, 55 and 60mole-% respectively. The enthalpy of the phase transition of $RbSrCl_3$ must be so small that it was not detected as kink in the e.m.f. vs. T-curves. There were measured ΔH_R-values for both compounds by solution calorimetry at 25°C (298K). Both are somewhat smaller than the values found electrochemically

Reaction $\underline{0.5RbCl+SrCl_2=Rb_{0.5}SrCl_{2.5}}$

$\bar{E}(mV)=209.5-0.0665T \quad \Delta G_R(kJ/mole)=-10.1+0.0032T$

$(\pm 0.5)(\pm 0.0007)$

$\Delta G_R(298K)=-9.1kJ\cdot mol^{-1}(\pm 0.8). \quad \Delta H_R(calor.)=-8.65kJ\cdot mol^{-1}$

Reaction $\underline{0.5RbCl+Rb_{0.5}SrCl_{2.5}=RbSrCl_3}$

$\bar{E}(mV)=-322.2+0.5116T \quad \Delta G_R(kJ/mole)=15.5-0.0247$

$\Delta G_R=0$ at 629K(356°C) $\quad (\pm 0.5)(\pm 0.0002)$

From both measurements the functions for the reaction $RbCl+SrCl_2=RbSrCl_3$ can be calculated.

$\Delta G_R=(kJ/mole)=5.4-0.00215T$ $\quad$ $\Delta H_R(calor.)=3.61 kJ\cdot mol^{-1}$

The system $RbCl/CaCl_2$

The phase diagram (ref. 9) is shown in fig. 3.

For e.m.f. measurements concerning the formation of $RbCaCl_3$ samples with 60 and 90mole-% $CaCl_2$ were used. Surprisingly, measurements concerning the formation of the other two compounds yielded no constant values; they slowly approached zero. So both compounds must be metastable.

Reaction $RbCl+CaCl_2=RbCaCl_3$

$\bar{E}(mV)=239.1+0.0977T$ $\quad$ $\Delta G_R(kJ/mole)=-23.1-0.0094T$

$\Delta G_R(298K)=-25.9 kJ\cdot mol^{-1}$ $\quad$ $(\pm 0.22)(\pm 0.0003)$

The system $RbCl/MgCl_2$

The phase diagram (fig. 4) was determined in 1974 (ref. 10). There exist two congruently melting compounds, $RbMgCl_3$ and Rb_2MgCl_4, the latter with a phase transition at 415°C. $Rb_3Mg_2Cl_7$ decomposes at 431°C. the incongruently melting Rb_3MgCl_5 is stable at temperatures higher than 361°C.

Reaction $RbCl+MgCl_2=RbMgCl_3$

(samples with 70 and 90mole-% $MgCl_2$)

$\bar{E}=(mV)=280.9+0.064T$

$\Delta G_R(kJ/mole)=-27.1-0.0061T$

$(\pm 1.0)(\pm 0.001)$

$\Delta G_R(298K)=-28.9 kJ\cdot mol^{-1}$

$\Delta H_R(calor.)=-23.15 kJ\cdot mol^{-1}$

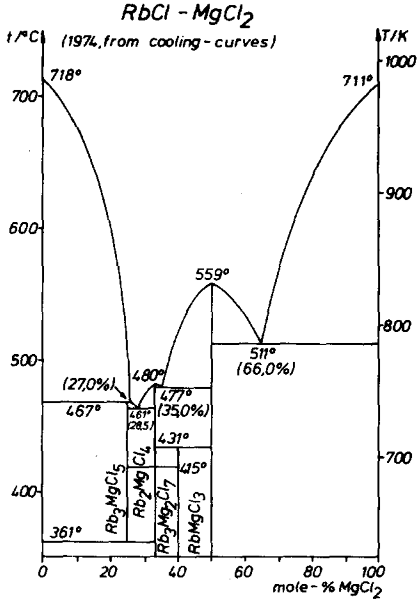

Fig. 4. System $RbCl/MgCl_2$

Reaction $\underline{0.5RbCl+RbMgCl_3=Rb_{1.5}MgCl_{3.5}}$ (sample with 45mol-% $MgCl_2$)

$E(mV)=59.5+0.0182T$ $\Delta G_R(kJ/mole)=-2.9-0.0009T$

$\Delta G_R(298K)=-3,2kJ\cdot mol^{-1}(\pm 0.2)$ $(\pm 0.1)(\pm 0.0001)$

For the reaction $1.5RbCl+MgCl_2=Rb_{1.5}MgCl_{3.5}$ is

$\Delta G_R(kJ/mole)=-30.0-0.0070T$ and $\Delta H_R(calor.)=-24.05kJ\cdot mol^{-1}$

Reaction $\underline{0.5RbCl+R_{1.5}MgCl_{3.5}=Rb_2MgCl_4}$ (sample with 35mol-% $MgCl_2$)

$E(mV)=19.45+0.057T$ $\Delta G_R(kJ/mole)=-0.9-0.0027T$

$\Delta G_R(298K)=-1.7kJ\cdot mol^{-1}(\pm 0.2)$ $(\pm 0.2)(\pm 0.0004)$

For the reaction $2RbCl+MgCl_2=Rb_2MgCl_4$ is

$\Delta G_R(kJ/mole)=-30.9-0.0097T$ and $\Delta H_R(calor.)=-28.00kJ\cdot mol^{-1}$

Reaction $\underline{RbCl+Rb_2MgCl_4=Rb_3MgCl_5}$ (sample with 30mol-% $MgCl_2$)

$E(mv)=-217.8+0.3303T$ $\Delta G_R(kJ/mole)=21.0-0.0319T$

$\Delta G_R=0$ at 659K(386°C) $(\pm 1.0)(\pm 0.001)$

For the reaction $3RbCl+MgCl_2=Rb_3MgCl_5$ is $\Delta G_R(kJ/mole)=-9.9-0.0416T$

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