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EMF-MEASUREMENTS WITH GALVANIC BROMINE CELLS IN THE SYSTEMS RBr/MBr$_2$ (M= Sr, Ba)

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The systems $RbBr/SrBr_2$ and $RbBr/BaBr_2$ were reinvestigated by DTA and X-ray-crystallography. Additionally to the known compounds $RbSrBr_3$, $RbSr_2Br_5$ and $RbBa_2Br_5$, the phases $Rb_{2.23}Sr_{0.885}Br_4$ and $Rb_{2.13}Ba_{0.935}Br_4$ were found, which are structural related to the Th_3P_4- type. By EMF-measurements the thermodynamic functions ΔG, ΔH and ΔS were determined for all compounds.

During the last decade we have measured thermodynamic functions of double chlorides A_nMCl_{n+x} (A=Na,K,Rb; M= M^{2+} and M^{3+}) using a self-developed galvanic chlorine cell for solid electrolytes [1]. 1987 we could present a poster at ESTAC IV in Jena, concerning measurements with an equivalent bromine cell in the systems KBr/MBr_2 (M = Sr,Ba) [2]. In continuation of this work we now present the results for the Rb-compounds in the analogous systems $RbBr/MBr_2$.

The utilized cells have the general set-up

(graphite + Br_2)/RbBr/Rb^+-conducting glass / MBr_2/(graphite + Br_2)

for the formation reaction of the MBr_2-richest compound in the system. The EMF-(E) is related to the free (Gibbs) enthalpy ΔG by $\Delta G = -n \cdot F \cdot E$ (n = transported charge; F = Faraday constant). The temperature dependence of ΔG proved to be linear in the temperature-region, in which the EMF's could be approached in up to 10 h (< 250°C). So linear regression-calculations yielded directly the Gibbs-Helmholtz relation $\Delta G = \Delta H - T \cdot \Delta S$.

Details of the material preparation, the procedure of the measurements (DTA- and X-ray-measurements for checking the phase diagrams $RbBr/SrBr_2$ and $RbBr/BaBr_2$, solution calorimetry for yielding the enthalpies for the reactions $nRbBr + MBr_2 = Rb_nMBr_{n+2}$) and a detailed description of the galvanic cell can be found in [2].

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The system $RbBr/SrBr_2$

According to Riccardi et al [3] two congruently-melting compounds are existing: $RbSr_2Br_5$ and $RbSrBr_3$. By our own investigations this finding must be completed in two points (fig. 1):

1) The compound $RbSrBr_3$ is stable only at temperatures higher than 350°C, indicated by a strong endothermic effect in heating curves. In cooling curves, no effect could be detected; nevertheless $RbSrBr_3$ can't be yielded metastable at ambient temperature by quenching. Additionally, two transitions occur at 472 and 551°C. The thermal effects are small without a hysteresis between cooling and heating curves - these transitions must be displacive.
2) There is existing a third solid phase, $Rb_{2.23}Sr_{0.885}Br_4$, proved by the fact that the formation- and transition-effects for $RbSrBr_3$ are disappearing between 29 and 28 mol-% $SrBr_2$. A solid of this composition displays a new X-ray- pattern which can be derived from the Th_3P_4-type. The compound does not decompose by normal cooling under DTA conditions; after annealing for two days at ~270°C a strong endothermic effect, corresponding to its formation, is found at 290°C in heating curves.

EMF-Measurements

a) The compound $Rb_{0.5}SrBr_{2.5}(RbSr_2Br_5)$

ΔG^r for the reaction $0.5\,RbBr + SrBr_2 = Rb_{0.5}SrBr_{2.5}$ n=0.5

(ΔG^r is identical with ΔG^f, the free enthalpy for the formation from the two binary compounds).

Two samples with 90 and 75 mol-% $SrBr_2$ resp.; temperature range = 530-750 K.

$\overline{EMF}/mV = 194.6 - 0.0178 \cdot T/K$

Range of error ± 3.0 ± 0.007

$\Delta G^r/kJ \cdot mol^{-1} = -9.4 + 0.0009 \cdot T/K$

b) The compound $RbSrBr_3$

ΔG^r for the reaction $0.5\,RbBr + Rb_{0.5}SrBr_{2.5}$ n=0.5

Two samples with 60 and 65 mol-% $SrBr_2$ resp.; temperature range 630-720K

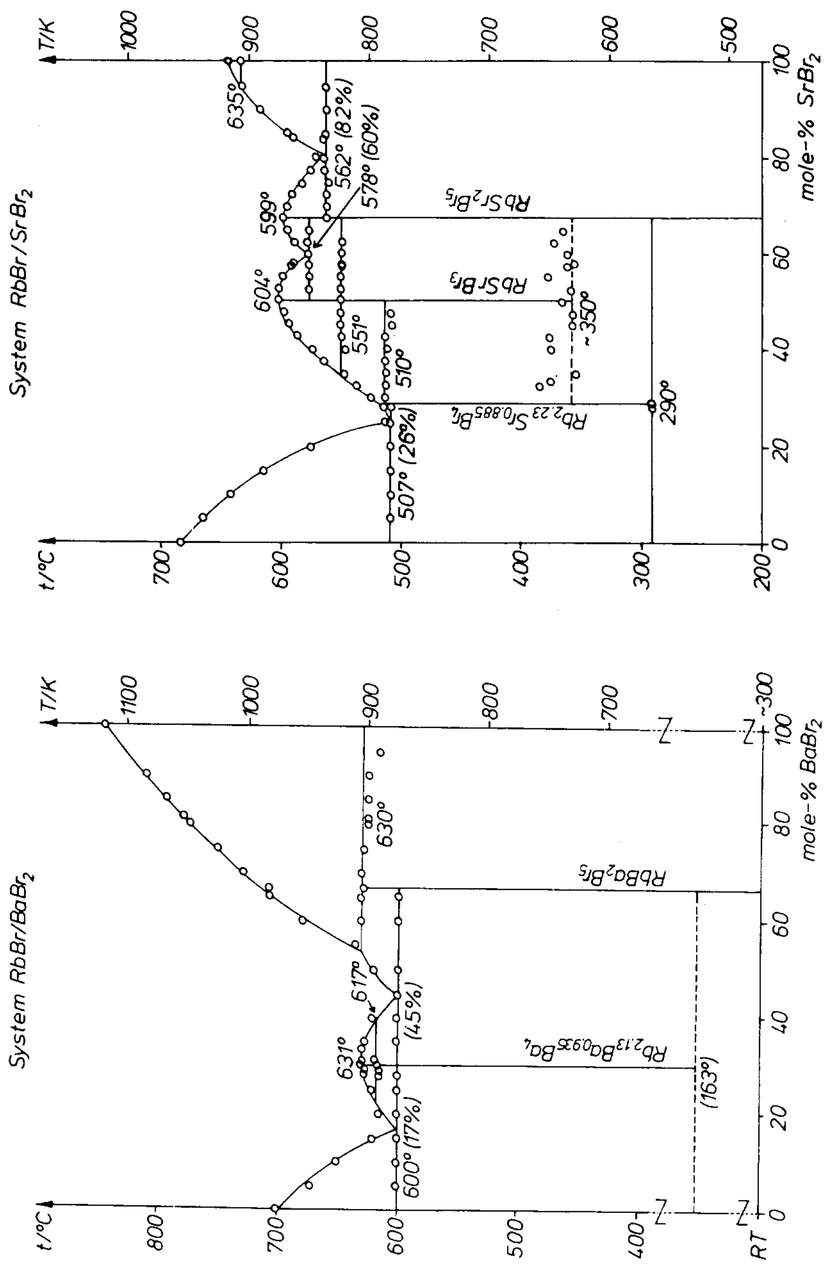

Fig. 1 Phase diagrams of the Systems RbBr/BaBr$_2$ and RbBr/SrBr$_2$
(Temperatures from heating curves; in parenthesis = from EMF-measurements)

$\overline{\mathrm{EMF}}$/mV = $-204.2+0.3349\cdot T/K$
Range of error ±9.0 ±0.02
ΔG^r/kJ·mol^{-1}= $9.8-0.0162\cdot T/K$
For the reaction $RbBr+SrBr_2=RbSrBr_3$;
ΔG^f/ kJ·mol^{-1}= $0.4-0.0153\cdot T/K$

c) The phase $Rb_{2.52}SrBr_{4.52}(Rb_{2.23}Sr_{0.885}Br_4)$

For this phase two reactions have to be considered: 1) The formation from $RbSr_2Br_5$ in the temperature range ~(550-625)K and 2) The formation from $RbSrBr_3$ at T>625 K. The experiments revealed that the measurements could be carried out down to 540 K, because $RbSrBr_3$ remained metastable.

a) ΔG^r for the reaction $2.02\,RbBr+Rb_{0.5}SrBr_{2.5}= Rb_{2.52}SrBr_{4.52}$ n= 2.02
Two samples with 45 and 60 mol-% $SrBr_2$ resp.; temperature range 530-630 K.
$\overline{\mathrm{EMK}}$/mV = $-47.7+0.0864\cdot T/K$
Range of error ± 5.0 ±0.01
ΔG^r/kJ·mol^{-1}= $9.3-0.0168\cdot T/K$
For $2.52\,RbBr+SrBr_2= Rb_{2.52}SrBr_{4.52}$;
ΔG^f/kJ·mol^{-1}= $-0.1-0.0159\cdot T/K$

b) ΔG^r for the reaction $1.52\,RbBr_2+RbSrBr_3= Rb_{2.52}SrBr_{4.52}$ n=1.52
Sample with 45 mol-% $SrBr_2$; temperature range 530-770 K
EMK/mV = $9.9-0.0042\cdot T/K$
Range of error ±0.5 ± 0.0008
ΔG^r/kJ·mol^{-1}= $-1.45+0.0006\cdot T/K$
For $2.52\,RbBr+SrBr_2= Rb_{2.52}SrBr_{4.52}$;
ΔG^f/kJ·mol^{-1}= $-1.0-0.0147\cdot T/K$
The conformity of the two ΔG^f-equations for the reaction cycles a) and b) is satisfactory.

Solution calorimetry

For the only compound stable at room temperature, $RbSr_2Br_5$, ΔH^f was also determined by solution calorimetry.

Measured solution enthalpies: $\Delta H^{1}_{298}(\frac{1}{2}RbSr_2Br_5) = -49.7 \pm 0.3$ kJ·mol^{-1}
Literature values: $\Delta H^{1}_{298}(RbBr) = 23.0$ kJ·mol^{-1} [7]
$\Delta H^{1}_{298}(SrBr_2) = 70.4$ kJ·mol^{-1} [8]
$\Delta H^{f}_{298}(\frac{1}{2}RbSr_2Br_5) = \{\Delta H^{1}(SrBr_2) + \frac{1}{2}\Delta H^{1}(RbBr)\} - \Delta H^{1}(Rb_{0.5}SrBr_{2.5}) = -9.1$ kJ·mol^{-1}
This value is in good correspondence with the -9.4 kJ · mol^{-1} found with EMF-measurements.

Thermodynamic stabilities and free enthalpies of synproportionation ΔG^S

At ambient temperature only $RbSr_2Br_5$ is stable; thus $\Delta G^r (\equiv \Delta G^f) = \Delta G^s$.
From $\Delta G^r/kJ{\cdot}mol^{-1} = -9.4 + 0.0009{\cdot}T/K$ follows: $\Delta G^s_{298} = -9.1$ kJ·mol^{-1}.
For the phase $Rb_{2.52}SrBr_{4.52}$ beneath 630 K is $\Delta G^r \equiv \Delta G^s$
(Reaction $2.02\ RbBr + Rb_{0.5}SrBr_{2.5} = Rb_{2.52}SrBr_{4.52}$). With $\Delta G^r/kJ{\cdot}mol^{-1} = 9.3 - 0.0168{\cdot}T/K$ follows $\Delta G^r = 0$ at 553 K (280°C). That is the thermodynamic temperature of formation (decomposition).
$RbSrBr_3$ is formed from its neighbour compounds by the synproportionation:

$$0.248\ Rb_{2.52}SrBr_{4.52} + 0.752\ Rb_{0.5}SrBr_{2.5} = RbSrBr_3,$$

With the ΔG^f-values of all three compounds ΔG^s can be calculated:

$$\Delta G^s(RbSrBr_3)/kJ\ \ mol^{-1} = 7.8 - 0.0124\ {\cdot}T/K$$

With $\Delta G^s = 0$ a formation (decomposition) temperature of 629 K (356°C) results.

The system $RbBr/BaBr_2$

According to older investigations two compounds are existing: the incongruently melting $RbBa_2Br_5$ and a congruently melting compound with the composition Rb_2BaBr_4 [3] or $Rb_{2-2x}Ba_{1+x}Br_4$ [4] resp.. Our own DTA- and X-ray-measurements could confirm the existence of $RbBa_2Br_5$, but revealed that the second compound, which has a transition near the melting point, again is a Th_3P_4-related compound with the composition $Rb_{2.13}Ba_{0.935}Br_4$ (fig. 1). With DTA no decomposition could be detected, neither after long annealing at temperatures between 150 and 300°C.

EMF-measurements

a) The compound $Rb_{0.5}BaBr_{2.5}(RbBa_2Br_5)$

ΔG^r for the reaction $0.5\,RbBr + BaBr_2 = Rb_{0.5}BaBr_{2.5}$ n=0.5

Two samples with 75 and 80 mol-% $SrBr_2$ resp.; temperature range 540-680 K

$\overline{EMF}/mV = -2.77 + 0.0640 \cdot T/K$

Range of error ± 1.0 ± 0.002

$\Delta G^r/kJ \cdot mol^{-1} = 0.1 - 0.0031 \cdot T/K$

It is $\Delta G^r \equiv \Delta G^f$ and at ambient temperature $\Delta G^r \equiv \Delta G^s$

From solution calorimetry instead of $\Delta H^1 = 0.1\,kJ \cdot mol^{-1}$ a $\Delta H^r_{298} = 2.9\,kJ \cdot mol^{-1}$ was found. ($\Delta H^1_{298}(BaBr_2) = -23.5\,kJ \cdot mol^{-1}$ [8]; ΔH^1_{298} ($^1/_2\,RbBa_2Br_5$) = $-14.9\,kJ \cdot mol^{-1}$).

b) The compound $Rb_{2.28}BaBr_{4.28}(Rb_{2.13}Ba_{0.935}Br_4)$

ΔG^r for the reaction $1.78\,RbBr + Rb_{0.5}BaBr_{2.5} = Rb_{2.28}BaBr_{4.28}$ n=1.78

Two samples with 40 and 55 mol-% $SrBr_2$ resp.; temperature range 540-740 K

$\overline{EMF}/mV = -29.1 + 0.0666 \cdot T/K$

Range of error: + 2.0 ± 0.002

$\Delta G^r/kJ \cdot mol^{-1} = 5.0 - 0.0114 \cdot T/K$

It is $\Delta G^r \equiv \Delta G^s$; consequently with $\Delta G^r = 0$ the temperature of formation (decomposition) is calculated as 438 K (165°C).

For the reaction $2.28\,RbBr + SrBr = Rb_{2.28}SrBr_{4.28}$;

$\Delta G^f/kJ \cdot mol^{-1} = 5.1 - 0.0145 \cdot T/K$

Crystal structures

According to a private communication of Jessen [4], $RbSr_2Br_5$ is crystallising with the $NH_4Pb_2Cl_5$-structure [5] (R.G. $P2_1/c$) with the monoclinic cell parameters: a=9.431(8)Å; b=8.344(5) Å; c=13,303(6)Å; ß=90.33°; Z=4. The same holds for $RbBa_2Br_5$: monoclinic cell with a=9.758(7)Å; b=8.571(6)Å; c=13.669(1)Å; ß=90,01°; Z=4.

$RbSrBr_3$ has three high-temperature modifications analogous to $RbCaBr_3$ [6]: it crystallizes from the melt with the cubic perovskite-structure, then a tetragonallydistorted perovskite structure follows and finally the orthorhombic $GdFeO_3$-type results. All dates were calculated from Simon-Guinier-photos.

H-$RbSrBr_3$: 604-551°C cubic: Pm3m a= 5.921Å; Z=1
M-$RbSrBr_3$: 551-472°C tetragonal; P4/mbm a= 8.309Å; c= 5.919Å; Z=2
D-$RbSrBr_3$: 472-356°C orthorhombic; Pnma a= 8.328Å; b= 11.766Å; c= 8.223Å;Z=4

The structure of the third phase could not yet be solved. however. the pattern is similar to those of other phases $A_{2+2x}M_{1-x}X_4$, we previovsly have found with X=Cl for M= Sr,Ba,Pb [6] and with X=Br for A=K and M= Sr,Ba [2]. The structures of these phases are related to the Th_3P_4-type, according to Bärninghausen they are crystallising with incommensurable cells.

Table 1 Energy proportions ($kJ \cdot mol^{-1}$) for the formation of ternary bromides from ABr_2 and the right neighbour-compound at 298 K.

	ΔG^r(298 K)	=	ΔH^r	-	($T \cdot \Delta S$)
1/2 $RbSr_2Br_5$	-9.1	=	-9.4		+03
1/2 KSr_2Br_5	-6.9	=	-6.9		±0
$RbSrBr_3$	+5.1	=	+9.9		-4.8
$KSrBr_3$		non existent			
$Rb_{2.23}Sr_{0.885}Br_4$	+4.3	=	+9.3		-5.0
$K_{2.18}Sr_{0.91}Br_4$	+5.4	=	+11.2		-5.8
1/2 $RbBa_2Br_5$	-0.8	=	+0.1		-0.9
1/2 KBa_2Br_5		non existent			
$Rb_{2.13}Ba_{0.935}Br_4$	+1.6	=	+5.0		-3.4
$K_{2.04}Ba_{0.98}Br_4$	+4.9	=	+10.6		-5.7

Discussion

As previously shown [2], there is a strong analogy between the features of double chlorides and bromides K_nMX_{n+2} (M=Sr,Ba). A certain similartiy also exist between K- and Rb-double bromides of the two alkaline earth metals; as the energy-values, compiled in table 1, demonstrate. However with potassium a 1:1-compound of strontium and a 1:2 of barium does not exist.

Thus, the same conclusions about thermodynamic stabilities can be drawn, as it was done with the potassium compunds.

Furthermore, a close awalogy between double chlorides and bromides Rb_nMBr_{n+2} (M=Br,Ba) exist (compare table 1 of this paper with table 2 in [2].

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Zusammenfassung - Die Systeme $RbBr/SrBr_2$ und $RbBr/BaBr_2$ wurden mittels DTA und Röntgenaufnahmen an Kristallpulvern neu untersucht. Zusätzlich zu den schon bekannten Verbindungen $RbSrBr_3$, $RbSr_2Br_5$ und $RbBa_2Br_5$ wurden die Phasen $Rb_{2,23}Sr_{0,885}Br_4$ und $Rb_{2,13}Ba_{0,935}Br_4$, die sich strukturell vom Th_3P_4-Typ ableiten lassen, neu gefunden. Für alle Verbindungen wurden durch EMK-Messungen in galvanischen Feststoffzellen die thermodynamischen Funktionen ΔG, ΔH und ΔS bestimmt.

Резюме- Методом ДТА и рентгеновской кристалографии вновь были исследованы системы $RbBr/SrBr_2$ и $RbBr/BaBr_2$. В дополнение к ранее известным соединениям $RbSrBr_3$, $RbSr_2Br_5$ и $RbBa_2Br_5$, были найдены фазы $Rb_{2,23}Sr_{0,885}Br_4$ и $Rb_{2,13}Ba_{0,935}Br_4$, которые структурно связаны с соединением типа Th_3P_4. С помощью эдс измерений для всех соединений были определены термодинамические функции ΔG, ΔH и ΔS.