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A GALVANIC BROMINE CELL FOR MEASURING ΔG-VALUES OF SOLID-STATE REACTIONS IN THE SYSTEMS KBr/MBr_2 (M = Ca, Sr, Ba) *

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ABSTRACT

A galvanic bromine cell of the type

(graphite + Br_2)/KBr/K^+-conducting glass/MBr_2/(graphite + Br_2)

was constructed for measuring the temperature dependence of the electromotive force for reactions of the type $n KBr + MBr_2 = K_nMBr_{2+n}$ (M = Ca, Sr, Ba). It works at temperatures above 300 °C. From a plot of EMF vs. T, the fundamental thermodynamic functions of the reaction were calculated. The phase diagrams of the systems of interest were determined by DTA measurements and X-ray analysis. The compounds $KCaBr_3$ and KSr_2Br_5 are stable at all temperatures; the compounds $K_{2.18}Sr_{0.91}Br_4$ and $K_{2.04}Ba_{0.98}Br_4$ are only stable above those temperatures at which the gain in entropy ($T\Delta S$) compensates for the loss in lattice enthalpy.

INTRODUCTION

In continuation of previous work which used galvanic cells to achieve the relevant thermodynamic functions for solid-state reactions in solid electrolytes, $n AX + MX_2 = A_nMX_{n+2}$ (A = alkaline metal) with X = Cl [1], we now proceed to systems with X = Br. If we consider the formation of $AMBr_3$ from ABr and MBr_2, such cells have the general set-up

(graphite + Br_2)/ABr/A^+-conducting glass/MBr_2(+ $AMBr_3$)/(graphite + Br_2

The EMF (E), measured at temperatures sufficiently high to avoid a breakdown due to high resistivity, is related to the free (Gibbs) enthalpy ΔG^r of the reaction by $\Delta G^r = -nFE$ (n = conducted charge; F = Faraday constant). From the temperature dependence $(\partial \Delta G/\partial T)_p = -\Delta S$ the entropy of reaction ΔS^r can be obtained, and the enthalpy can be calculated from the Gibbs–Helmholtz relation $\Delta G^r = \Delta H^r - T\Delta S^r$.

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

This paper describes a suitable, newly developed bromine cell. Systems of KBr with $CaBr_2$, $SrBr_2$ and $BaBr_2$ were investigated to demonstrate its applicability.

EXPERIMENTAL

Material preparation

The anhydrous alkaline earth bromides were prepared from their hydrates: $CaBr_2 \cdot 6H_2O$ (from $CaCO_3$, Merck, p.A. quality, dissolved in hydrobromic acid), $SrBr_2 \cdot 6H_2O$ (Merck, puriss.), $BaBr_2 \cdot 2H_2O$ (Merck, p.A.). The hexahydrates were first treated in a vacuum desiccator filled with P_4O_{10} for one week and then left for one day in a vacuum oven at 80 °C. The dihydrates formed and $BaBr_2 \cdot 2H_2O$ were heated in a stream of HBr for one day at temperatures increasing in ~ 50 K steps up to melting point and then cooled in an argon atmosphere. The temperature was raised only after water was no longer detected in the exhaust of the reaction tube. Potassium bromide (Merck, p.A.) was dried at 500 °C in a stream of HBr and then melted.

Differential thermal analysis (DTA)

The home-made DTA device was described previously [2]. The samples (~ 0.5 g) were heated to melting point in vacuum-sealed quartz ampoules over a gas flame, homogenized by shaking and solidified by rapid cooling. The solids thus obtained were sufficiently homogeneous for the measurement of heating curves or for annealing experiments. Thermal effects could be detected down to 0.2 J for the usual heating rate of 2 K min^{-1}.

Solution calorimetry

The apparatus used was a home-made isoperibol calorimeter [3], with a volume of 1.2 l. Samples of 3–6 g thus yielded a virtually ideal solution (dissolution ratio 1 : 3500 mol). From the enthalpies of solution, ΔH^{1}, the enthalpies of formation from KBr and MBr_2, ΔH^{f}, were calculated from

$$\Delta H^{f}_{298} = \left\{ \Delta H^{1}_{298}(MBr_2) + n\Delta H^{1}_{298}(KBr) \right\} - \Delta H^{1}_{298}(K_nMBr_{n+2})$$

Each ΔH^{1} was measured at least three times; KBr was dissolved in a solution of adequate concentration of MBr_2.

X-ray techniques

Powder patterns were made at room temperature with a Philips PW 1050/25 goniometer equipped with a proportional counter and a vacuum

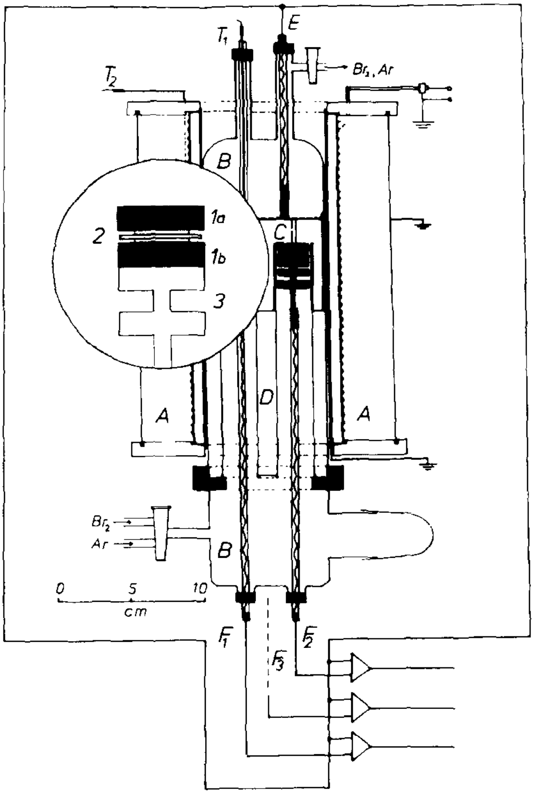


Fig. 1. Cross section of the galvanic cell (for three samples). (A) Non-inductive wound furnace (Kanthal A1 wire, 220 V, 8 A); (B) glass container (Duran-50); (C) graphite block with electrodes and sample disks: (1) graphite electrodes (diameter = 20 mm, h = 4 mm), (2) sample disks (diameter = 13 mm, h = 0.5 mm) separated by a diaphragm, (3) graphite rod with shielding disks; (D) quartz holders; (E) electric contact to the graphite block and electrodes 1a; (F_1), (F_2), (F_3); electric contacts to the electrodes 1b for three samples; (T_1), (T_2) Ni/Cr–Ni thermocouples.

attachment. During exposure (Cu$K\alpha$ radiation) the samples were kept in a helium atmosphere. An Enraf–Nonius 553 Simon–Guinier camera was used for photography at continuously varying temperatures. The samples were encapsulated in quartz tubes of 0.3 mm diameter.

The galvanic cell with bromine electrodes

Figure 1 shows a cross-section of the new EMF cell. Three different substances can be measured at the same temperature. The bromine atmosphere in glass container B, previously filled with argon, was generated by boiling bromine, dried over P_4O_{10}, in a separate vessel. The electrode reactions for the formation of $KCaBr_3$ from KBr and $CaBr_2$ are, for the anode:

$KBr \rightarrow 0.5\ Br_2 + K^+ + e^-$

and for the cathode:

$K^+ + CaBr_2 + 0.5\ Br_2 + e^- \rightarrow KCaBr_3$

The sample sandwich (2) consists of two discs (~ 0.1 g of substance each), one prepared by compressing KBr powder in the absence of moisture, similar to the procedure used in spectroscopy, the second made with a mixture of $CaBr_2$ and $KCaBr_3$ to obtain a reversible cell. These discs are separated by a diaphragm of K-glass, synthesized as described by Østvold [4]. The glass powder was compressed into discs and sintered for 15 h at 1400 K. The electrodes (porous graphite, Fa. Schunk&Ebe, Giessen) were purified by heating in a chlorine stream for 40 h at 1200 K.

To avoid electric noise a shielded, non-inductive-wound furnace (A) is used with the control-thermocouple T_2. Temperature is measured in the block with a shielded thermocouple T_1 protected from the bromine atmosphere by quartz. After changing the temperature of the furnace within 20 min, the temperature difference between the samples and the block is less than 1 °C. The temperature difference between the electrodes is less than 0.5 °C, thus additional thermal power is avoided.

The electric connections to the voltage follower (Intersil-ICL 7650, $R_i > 10^{12}\ \Omega$) consist of short graphite rods and coal-fibre with a very low thermal conductivity. EMF and temperature are recorded by a four-channel strip-chart recorder. The apparatus was checked with a $(C + Br_2)/KBr/(C + Br_2)$ cell and with a $(C + Br_2)/KBr/K^+$-conducting diaphragm/$KBr/(C + Br_2)$ cell. In both cases the EMF must be zero and independent of temperature.

Before starting the actual measurement, the sample sandwich was heated in the bromine atmosphere to the starting temperature. This temperature was maintained until the EMF remained constant for 4 h. (This time varied between 3 and 9 h, and was sometimes more than 20 h.) The reversibility of the cell was checked by successively passing an electric charge of ~ 1 mC in both directions. Then the EMF must return to its original value within ~ 20 min. In this way the d.c. resistivity of the cell could also be determined ($\approx 10^8\ \Omega$ at 475 K, $\approx 10^7\ \Omega$ at 525 K, $\approx 10^6\ \Omega$ at 575 K and $\approx 10^4\ \Omega$ at 775 K).

The temperature programme was now started. The temperature was changed in pre-selected steps (20–30 K) every 3–4 h on heating and every 4–6 h on cooling. Electrochemical equilibrium was effectively reached after a maximum of 1.5 h on heating and after a maximum of 4 h on cooling. Generally two up-and-down cycles were measured.

The upper temperature limit was given by the onset of melting, i.e. the temperature of the lowest melting eutectic. The lower limit was given by the temperature at which the curve of EMF against temperature began to deviate from linearity. This temperature was found to be 300 ± 20 °C.

RESULTS

Phase diagrams and the structures of the compounds

The system KBr/$CaBr_2$ was reinvestigated some years ago [5]. One congruently melting compound exists, $KCaBr_3$(m.p. 639 ° C). The room-temperature modification with a $TlPbI_3$ type of structure changes to a high-temperature modification ($GdFeO_3$ type) in the range 250–290 ° C.

According to literature data, two compounds exist in the system KBr/$SrBr_2$: the congruently melting KSr_2Br_5 [6–9] and a second compound, K_2SrBr_4 [6,8,9] or K_4SrBr_6 [7]. Our own investigations yielded the system given in Fig. 2a:

(a) The incongruently melting compound near 30 mol% $SrBr_2$ has the exact composition $K_{2.18}Sr_{0.91}Br_4$. This is demonstrated by the appearance of the eutectic at 527 ° C and the phase transition of KSr_2Br_5 at 511 ° C in the range 29.4–33.3 mol% $SrBr_2$. This compound belongs to a group of phases with non-integer stoichiometry. The first example (detected in 1983) was

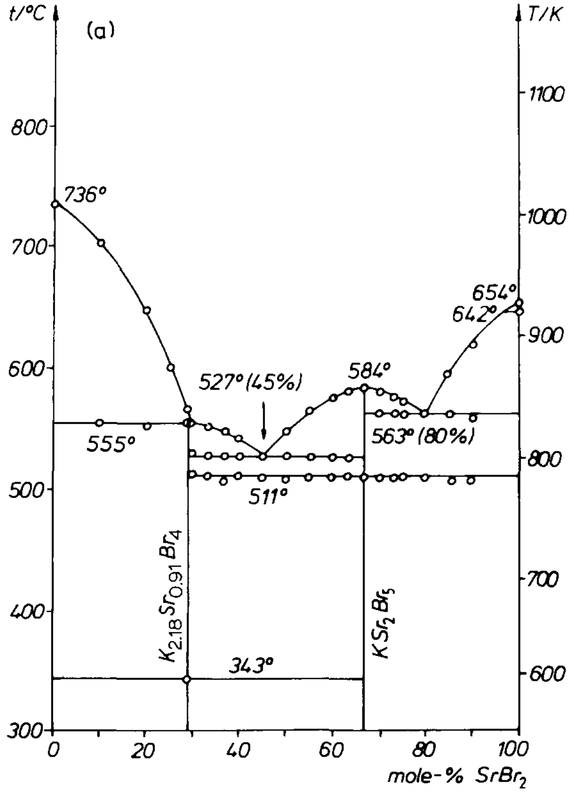


Fig. 2. Phase diagrams for the systems KBr/$SrBr_2$ and KBr/$BaBr_2$ (from DTA heating curves).

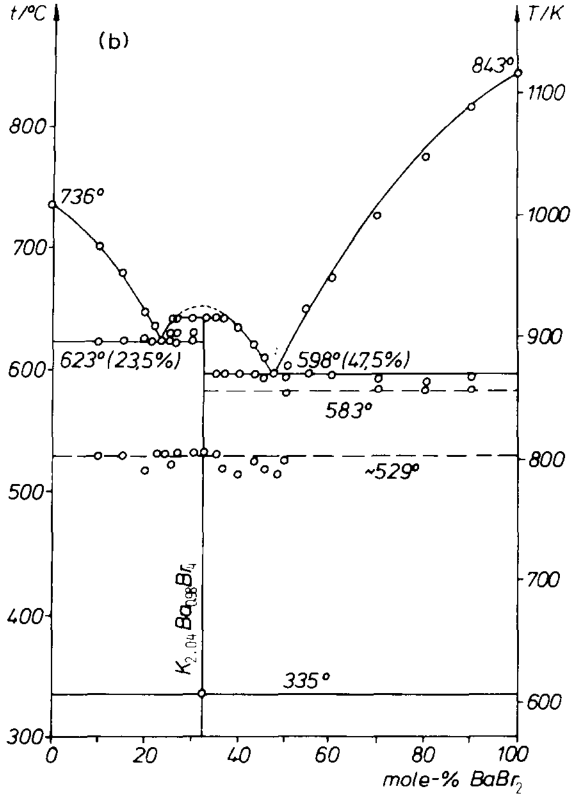


Fig. 2 (continued).

$K_{2.08}Ba_{0.96}Cl_4$. These phases seem to be related to the cubic structure of Th_3P_4 (the three Th-sites are occupied by K_2Ba) where 0.04 Ba^{2+} are displaced by 0.08 K^+. The surplus of cations (2.04 instead of 2.00) enforces a symmetry lower than cubic, which we had only found below the melting point of $K_{2.08}Ba_{0.96}Cl_4$ from dynamic high-temperature Guinier patterns. As in the case of the Ba compound, the strongest reflections of the Sr compound can be indexed as pseudo-cubic. According to EMF measurements, $K_{2.18}Sr_{0.91}Br_4$ is only stable at elevated temperatures ($\geq 296\,°C$). After annealing for 8 weeks at 260 °C, it had begun to decompose and gave an endothermic DTA effect at 343 °C in a heating experiment.

(b) The compound KSr_2Br_5 (m.p. 571 °C) exhibits a phase transition at 511 °C. The low-temperature modification crystallizes with the monoclinic $NH_4Pb_2Cl_5$ structure [10,11]: $a = 9.323$ Å; $b = 8.297$ Å; $c = 13.286$ Å; $\beta = 90.047°$, space group $P2_1/c$; 4 formula units per cell. The X-ray photograph of the high-temperature modification is similar, but shows fewer reflections.

(c) $SrBr_2$ reveals a phase transition at 642 °C, the enthalpy of which is comparable with the enthalpy of melting (at 654 °C).

TABLE 1

Solution enthalpies and derived enthalpy values (kJ mol^{-1})

	ΔH^1	ΔH^f	ΔH^s
$KBaBr_3$	−66.5	−15.1	–
$K_{0.5}SrBr_{2.5}$	−55.1	−5.1	−6.4
$K_{2.18}Sr_{0.91}Br_4$	−25.6	+6.0	+11.1
$K_{2.04}Ba_{0.98}Br_4$	+7.5	+11.1	–

In the system $KBr/BaBr_2$ only one compound exists, formerly described as K_2BaBr_4 [6,7]. Our own findings again yielded a non-integer stoichiometry: $K_{2.04}Ba_{0.98}Br_4$. At ~ 530 °C a very sluggish phase transition begins. The melting behaviour is complicated (Fig. 2b): at 639 °C two non-miscible liquids may be formed. The meaning of the double-effect at 623/628 °C is not clear.

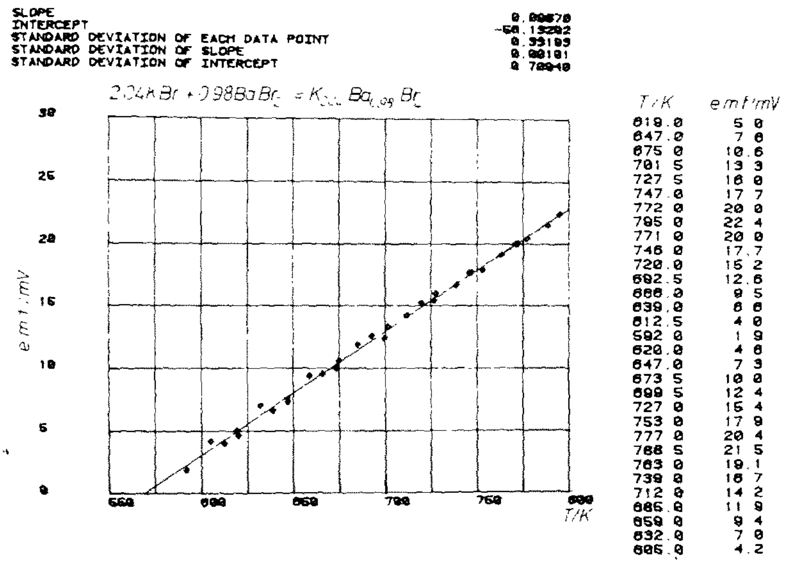
Like the analogous Sr compound, $K_{2.04}Ba_{0.98}Br_4$ is stable only above 282 °C, as revealed by EMF measurements. After annealing for 2 months at 260 °C an exothermic effect was found at 335 °C. Small effects at 583 °C found in the range 50–90 mol% $BaBr_2$ are assumed to originate in a phase transition of $BaBr_2$, which could be seen for $BaBr_2$ from a high-temperature X-ray photograph. However, $BaBr_2$ itself showed no thermal effect. We found a similar behaviour for $CaBr_2$ [5] and explained it as a mineralizing effect of the ($KBr + BaBr_2$) matrix, which strongly enhances the transition velocity.

Solution calorimetry

The mean value for the solution enthalpy of KBr in the various MBr_2 solutions was found to be $\Delta H^1 = +20.4 \pm 0.3$ kJ mol^{-1}. The values for $SrBr_2$ (-70.4 kJ mol^{-1}) and $BaBr_2$ (-23.5 kJ mol^{-1}) were taken from the literature [12]. Our measurements for $CaBr_2$ yielded $\Delta H^1 = -66.5 \pm 0.6$ kJ mol^{-1}. Table 1 gives the measured ΔH^1 values for the ternary compounds together with their enthalpies of formation from KBr and $MBr_2(\Delta H^f)$. The enthalpies of synproportionation, ΔH^s, represent the formation of $K_{0.5}SrBr_{2.5}$ from "K_2SrBr_4" + $SrBr_2$ and of "K_2SrBr_4" from KBr + $K_{0.5}SrBr_{2.5}$, respectively.

Electromotive force measurements

This section gives the results of the temperature-dependent EMF measurements. For each reaction, two or more samples were used. The measured values for each sample were subjected to a linear regression analysis. An example is given in Fig. 3. The differences between them, together with the standard deviations, were taken for the assessment of the real range of error.



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SLOPE                                          0.09870
INTERCEPT                                    -58.13202
STANDARD DEVIATION OF EACH DATA POINT          0.33193
STANDARD DEVIATION OF SLOPE                    0.00101
STANDARD DEVIATION OF INTERCEPT                0.70040
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 T/K     emf/mV
619.0     5.0
647.0     7.0
675.0    10.6
701.5    13.3
727.5    16.0
747.0    17.7
772.0    20.0
795.0    22.4
771.0    20.0
746.0    17.7
720.0    15.2
692.5    12.6
666.0     9.5
639.0     6.6
612.5     4.0
592.0     1.9
620.0     4.6
647.0     7.3
673.5    10.0
699.5    12.4
727.0    15.4
753.0    17.9
777.0    20.4
788.5    21.5
763.0    19.1
739.0    16.7
712.0    14.2
686.0    11.9
659.0     9.4
632.0     7.0
606.0     4.2
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Fig. 3. Computer plot of EMF vs. T for the reaction 2.04 KBr + 0.98 $BaBr_2$ = $K_{2.04}Ba_{0.98}Br_4$.

The mean of the regression lines was used to calculate $\Delta G^r = \Delta H^r - T\Delta S^r$ with temperature-independent enthalpies and entropies for the reaction KBr + nearest-neighbour compound of interest. For the system $KBr/SrBr_2$, with more than one compound, the thermodynamic functions ΔG^f, ΔH^f, ΔS^f for the formation reactions from KBr and $SrBr_2$ were also calculated. *Reaction:*

$KBr + CaBr_2 = KCaBr_3$ (60 and 90 mol% $CaBr_2$)

$\overline{EMF}/mV = 142.1 + 0.0201T/K$

$\Delta G^r/kJ\ mol^{-1} = -13.7 - 0.0019T/K$ $\quad \Delta G^r(298\ K) = -14.3 \pm 0.6\ kJ\ mol^{-1}$

$\Delta H^r = -13.7 \pm 0.4\ kJ\ mol^{-1}$ $\quad \Delta S^r = 1.9 \pm 0.5\ J\ K^{-1}\ mol^{-1}$

Reaction:

$0.5\ KBr + SrBr_2 = K_{0.5}SrBr_{2.5}$ (75, 80, 85, 95 mol% $SrBr_2$)

$\overline{EMF}/mV = 142.30 - 0.0011T/K$

$\Delta G^r/kJ\ mol^{-1} = -6.9$ $\quad \Delta G^r(298\ K) = -6.9 \pm 0.5\ kJ\ mol^{-1}$

$\Delta H^r = -6.9 \pm 0.4\ kJ\ mol^{-1}$ $\quad \Delta S^r = 0.0 \pm 0.4\ J\ K^{-1}\ mol^{-1}$

Reaction:

$1.725\ KBr + 0.91\ K_{0.5}SrBr_{2.5} = K_{2.18}Sr_{0.91}Br_4$ (45, 50, 65 mol% $SrBr_2$)

$\overline{EMF}/mV = -67.1 + 0.1176T/K$

$\Delta G^r/kJ\ mol^{-1} = 11.2 - 0.0197T/K$ $\quad \Delta G^r = 0$ at 569 K (296 °C)

$\Delta H^r = +11.2 \pm 0.3\ kJ\ mol^{-1}$ $\quad \Delta S^r = 19.6 \pm 0.6\ J\ K^{-1}\ mol^{-1}$

Reaction:

$2.18\ \mathrm{KBr} + 0.91\ \mathrm{SrBr_2} = \mathrm{K_{2.18}Sr_{0.91}Br_4}$

$\Delta G^{\mathrm{f}}/\mathrm{kJ\ mol^{-1}} = 4.9 - 0.0197T/\mathrm{K}$

Synproportionation:

$0.23\ \mathrm{K_{2.18}Sr_{0.91}Br_4} + 0.79\ \mathrm{SrBr_2} = \mathrm{K_{0.5}SrBr_{2.5}}$

$\Delta G^{\mathrm{s}}/\mathrm{kJ\ mol^{-1}} = -8.0 + 0.0045T/\mathrm{K}$ ($\Delta G^{\mathrm{s}} = 0$ at ~ 1800 K)

Reaction:

$2.04\ \mathrm{KBr} + 0.98\ \mathrm{BaBr_2} = \mathrm{K_{2.04}Ba_{0.98}Br_4}$ (40, 70, 90 mol% $\mathrm{BaBr_2}$)

$\overline{\mathrm{EMF}}/\mathrm{mV} = -53.8 + 0.0970T/\mathrm{K}$

$\Delta G^{\mathrm{r}}/\mathrm{kJ\ mol^{-1}} = 10.6 - 0.0191T/\mathrm{K}$ $\quad \Delta G^{\mathrm{r}} = 0$ at 555 K (282°C)

$\Delta H^{\mathrm{r}} = +10.6 \pm 0.4\ \mathrm{kJ\ mol^{-1}}$ $\quad \Delta S^{\mathrm{r}} = 19.1 \pm 0.4\ \mathrm{J\ K^{-1}\ mol^{-1}}$

DISCUSSION

A bromine cell may also be applied to the investigation of ternary halides of the type $\mathrm{K}_n\mathrm{MBr}_{n+2}$, as recently proved for ternary chlorides and a chlorine cell [13]. The ternary bromides investigated also have stability criteria as found for the corresponding ternary chlorides. $\mathrm{KCaBr_3}$ (distorted perovskite structure) is stabilized mainly by a gain in lattice enthalpy, ΔH^{r} (Table 2), as found for $\mathrm{KCaCl_3}$ and other perovskites [14]. The same holds for $\mathrm{KSr_2Br_5}$ and $\mathrm{KSr_2Cl_5}$ [15]. All these compounds consist of connected polyhedra, like KBr and the $\mathrm{MX_2}$ compounds. Thus, the degree of order is

TABLE 2

Energy proportions (kJ mol^{-1}) for the formation of ternary halides from KX and the nearest-neighbour compound at 298 K

	ΔG^{r}(298 K)	=	ΔH^{r}	−	$(T\Delta S^{\mathrm{r}})$
$\mathrm{KCaBr_3}$	−14.3		−13.7		−0.6
$\mathrm{KCaCl_3}$	−15.3		−12.4		−2.9
$1/2(\mathrm{KSr_2Br_5})$	−6.9		−6.9		±0
$1/2(\mathrm{KSr_2Cl_5})$	−5.1		−5.1		±0
$\mathrm{K_{2.18}Sr_{0.91}Br_4}$	+5.4		+11.2		−5.8
$\mathrm{K_{2.10}Sr_{0.95}Cl_4}$	+5.4		+10.4		−5.0
$\mathrm{K_{2.04}Ba_{0.98}Br_4}$	+4.9		+10.6		−5.7
$\mathrm{K_{2.08}Ba_{0.96}Cl_4}$	+7.4		+13.2		−5.8

not significantly changed, and the entropy change is only small or zero. The other two compounds $K_{2.18}Sr_{0.91}Br_4$ and $K_{2.04}Ba_{0.98}Br_4$, as well as their chloride analogues [15], probably crystallize in a strongly distorted Th_3P_4 structure with a surplus of cations. These phases are formed from their adjacent compounds by a considerable gain in entropy; the $(T\Delta S)$ term thus compensates for the loss in lattice enthalpy at sufficiently high temperatures. Again there is a close analogy between the ternary bromides and chlorides.

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