Experimental. 2,2-Dibromopropionyl bromide (IV). To 92.5 g (1.0 mole) of boiling propionyl chloride (III) and 1.0 g of red phosphorus, bromine was added over a period of 60 h. The reaction vessel was illuminated with a 500 W bulb. When the bromine colour persisted, nearly 2.0 moles (320 g) having been consumed, the product was distilled. From the distillation 207 g (70 %) of 2,2-dibromopropionyl bromide (IV) was collected, b.p. 70°C at 10 mm Hg. (Found: C 11.84; H 1.00; Br 80.95. Calc. for $C_3H_3Br_3O$: C 12.22; H 1.03; Br 81.32).

1,1-Dichloro-3,3-dibromobutanone-2 (VI). To 21.0 g (0.5 mole) of diazomethane, prepared according to Ref. 9 and dissolved in 1000 ml of dry ether was added 44.3 g (0.15 mole) of 2,2-dibromopropionyl bromide (IV) dissolved in 100 ml of dry ether and kept at 0°C. After 2 h the excess of diazomethane was distilled. Chlorine dissolved in carbon tetrachloride at 0°C was added until nitrogen evolution ceased. The reaction product was washed with water until the washings were almost neutral, the ethereal phase dried with magnesium sulphate and the ether evaporated, the last traces *in vacuo*. The crude product was left at 0°C for a week for crystallization and the crystals collected, 9.0 g (20 %), m.p. 45–50°C. Crystallization from ethanol raised the m.p. to 51–51.5°C. (Found: C 16.09; H 1.41. Calc. for $C_4H_4Br_2Cl_2O$: C 16.08; H 1.35).

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1. Rappe, C. *Acta Chem. Scand.* **20** (1966). *In press.*
2. Rappe, C. *Arkiv Kemi* **21** (1963) 503.
3. Rappe, C. and Kumar, R. *Arkiv Kemi* **23** (1965) 475.
4. Rappe, C. *Arkiv Kemi* **24** (1965) 73.
5. Bachmann, W. E. and Struve, W. S. *Org. Reactions* **1** (1942) 38.
6. Wagner, R. B. and Moore, J. A. *J. Am. Chem. Soc.* **72** (1950) 3655.
7. Rappe, C. and Carlsson, G.-B. *Arkiv Kemi* **24** (1965) 105.
8. King, F. E. and Spensley, P. C. *J. Chem. Soc.* **1952** 2144.
9. Arndt, F. *Org. Syn. II* (1961) 165.

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On the Phase Diagram Barium Chloride — Potassium Chloride

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The phase diagram $BaCl_2-KCl$ has been re-determined with a view to ascertaining the possible presence of complex ions in the liquid mixture. This diagram has a peak at around 33.3 mole% $BaCl_2$, indicating the presence of a congruently melting compound, K_2BaCl_4.

The previously published phase diagrams of this system by Gemsky [1] and Elchardus and Lafitte [2] both exhibit the same general shape as the one obtained from this investigation. But as the latter diagrams are based on relatively few experimental results, the detailed shape of the compound peak is not unambiguously given. As shown by Grjotheim [3] a detailed knowledge of the shape of the peak may provide valuable information as to the nature of the ionic species of the melt.

Compound formation is a general feature of many binary alkali-alkaline earth halide mixtures. A survey of the various bromide mixtures has been given by Kellner.[4] The following compounds have been found to exist in the solid state: $LiSr_2Br_5$, $NaCa_2Br_5$, $KMgBr_3$, K_2MgBr_4, $KCaBr_3$, K_2SrBr_4, KSr_2Br_5, K_2BaBr_4. A correspondingly extensive study of the chloride mixtures has not been carried out, but the existence of the compounds $KCaCl_3$,[5] K_2SrCl_4, KSr_2Cl_5,[6] and K_2BaCl_4 [1,2] is well established.

No investigation of the structure of the binary compounds has been reported in the literature. At present, the structure of K_2BaCl_4 is being investigated by single-crystal X-ray diffraction methods at our Institute.

In the present investigation the phase diagram $BaCl_2-KCl$ has been determined by thermal analysis, the results of which is given in Table 1. The phase diagram is depicted in Figs. 1, 2, and 3. Fig. 1 also gives the agreement of the present results with earlier data. The compound K_2BaCl_4 has a congruent melting point of 661 ± 0.5°C, and the eutectics at 658 and 648 (± 0.2°C) contain 25.9 and 42.9 mole % $BaCl_2$, respectively. The high tem-

Table 1. The system $BaCl_2-KCl$. Temperature obtained by thermal analysis.

Comp. mole% $BaCl_2$	Liquidus curve °C	Solidus curve eutectic temp.°C
0	771.5	
5.0	753.0	
10.0	734.4	658.0
20.0	685.7	658.0
22.5	672.5	657.7
24.9	660.7	657.8
25.9	658.1	
26.7	659.3	
27.5	660.2	658.1
28.2	660.4	
29.1	660.8	
30.0	660.9	(658.3)
30.5	661.7	
30.9	661.5	
31.4	661.3	(657.9)
31.7	660.7	
32.0	661.5	(657.9)
32.5	661.0	(658.2)
33.0	661.1	
33.3	661.1	
33.5	660.5	645.4
34.3	660.4	
34.5	659.9	645.9
35.0	659.6	646.3
35.5	659.5	647.3
36.0	658.1	
36.5	658.1	647.1
37.5	656.8	646.9
38.5	655.4	
40.0	652.8	647.3
41.0	650.7	
42.5		647.4
45.0	665.0	647.9
50.0	708.6	648.0
60.0	771.7	648.0
70.0	819.5	648.0
80.0	875.2	648.0
90.0	906.0	648.0
92.5	914.2	
94.0	919.8	
96.0	930.0	924.0 [a]
97.0	938.2	924.0 [a]
98.0	946.1	924.0 [a]
100.0	961.0	

(Numbers): Uncertain, possibly solidus line temp.
[a] phase transition temperature.

perature modification of $BaCl_2$ (transition point 924°C) appears to be cubic.

As can be seen from Fig. 2, the maximum of the peak is not positioned at exactly 33.3 mole % $BaCl_2$ but somewhat displaced

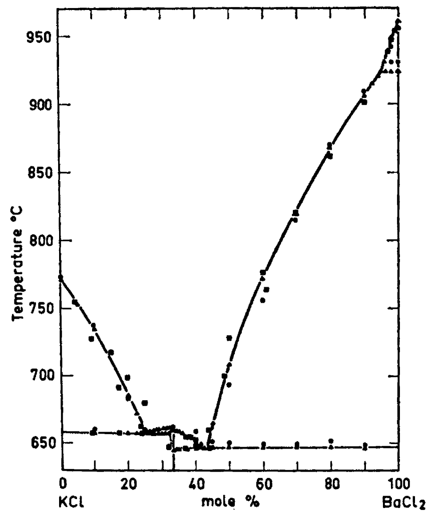

Fig. 1. The phase diagram $BaCl_2-KCl$. ▲, the present work; ●, Gemsky [1]; ■, Elchardus and Lafitte.[2]

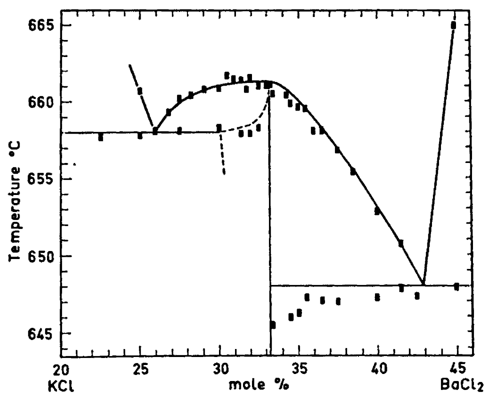

Fig. 2. The phase diagram $BaCl_2-KCl$ from the present work. The compound peak.

towards a composition with less $BaCl_2$. Within the experimental error, the top of the peak between 30 and 33.3 mole% may be considered as being horizontal. This may indicate either a more or less complete dissociation of the compound on melting, or the existence of solid solubility in the system, or both.

The heat of melting of K_2BaCl_4 was calorimetrically determined to 16.0 ± 0.7 kcal/mole. From this value, and applying

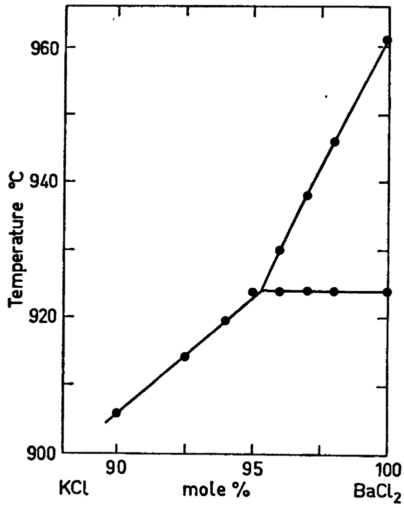

Fig. 3. The phase diagram $BaCl_2-KCl$. Phase transition of $BaCl_2(s)$.

the method of Brynestad,[7] an attempt was made to calculate the degree of dissociation of molten K_2BaCl_4 from the shape of the peak. This proved unsuccessful, as it was impossible to make the same model fit both branches of the peak. Now this method is only applicable if there is no solid solubility in the system, or if the activities in the solid solution are known.

Preliminary X-ray Guinier powder diagrams of the K_2BaCl_4 compound and a solid mixture with 30 mole% $BaCl_2$ exhibited both the same general diffraction pattern. There was, however, a slight displacement of some principal diffraction lines for the latter mixture. The d-values

Table 2. The system $BaCl_2-KCl$. Principal diffraction lines from Guinier X-ray diagrams.

Comp. mole% $BaCl_2$	d_{hkl} Å	$I/I°$
33.3	3.80	70
	2.97	100
	2.93	100
	2.53	80
30.0	3.81	70
	2.97	100
	2.91	100
	2.54	80

are given in Table 2. The conclusion is reached that in the system $BaCl_2-KCl$ there is a region of solid solubility around 30−33 mole% $BaCl_2$, as indicated by the dotted line in Fig. 2.

The investigation of the system $BaCl_2-KCl$ is presently being continued. With a detailed knowledge of the structure of the compound K_2BaCl_4 it will be possible to gain information also on the structure of the melt. The problem will be pursued by X-ray methods, and also by conductometric measurements on the compound in the solid state.

EXPERIMENTAL

Materials. The chemicals used in the measurements were commercially available reagent grade barium chloride and potassium chloride (*Pro analysi*, Merck A.G., Darmstadt, Germany). The chemicals were dried under vacuum at 450°C overnight before each measurement; and were weighed into a graphite crucible to a total of about 125 g for each run.

Apparatus and method. The liquidus and solidus data reported were obtained from cooling curves taken by ordinary thermal analysis. The apparatus and technique used for thermal analysis have been described elsewhere.[3] The preliminary X-ray investigations were carried out with a Nonius type Guinier camera using Cu$K\alpha$ radiation ($\lambda(K\alpha_1)$ = 1.5405 Å). The heat of melting was determined in a modified Oelsen type calorimeter [8] rebuilt for high temperature purposes.

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1. Gemsky, H. *J. Chem. Soc.* **106** (1913) 51.
2. Elchardus, E. and Lafitte, P. *Bull. Soc. Chim. France* **51** (1932) 1572.
3. Grjotheim, K. *Contribution to the Theory of Aluminium Electrolysis, Kgl. Norske Videnskab. Selskabs, Skrifter* **1956** No. 5.
4. Kellner, G. *Z. anorg. Chem.* **99** (1917) 165.
5. Ugai, Yu. A. *Dokl. Akad. Nauk SSSR* **70** (1950) 653.
6. Schmalzried, H. *Z. physik. Chem. (Frankfurt)* **33** (1962) 129.
7. Brynestad, J. *Z. physik. Chem. (Frankfurt)* **30** (1961) 123.
8. Bjørge, B. and Førland, T. *Internal report*, Institute of Inorganic Chemistry, NTH, Trondheim 1958.

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