ration had little effect on the solubility values, whereas the presence of very small amounts of water after the preparation was complete caused an increase in the apparent solubility.

6. The effect of light during the preparation was studied and the conclusion reached that bromine reacted to a certain extent with recently distilled ethyl ether in the presence of light giving rise to side reactions and impurities.

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[Contribution from the Chemical Laboratory of St. Louis University]

A Study of Some Reactions between Dry Inorganic Salts. III*

By E. B. Thomas with Lyman J. Wood

In two previous papers[1,2] the authors have reported results obtained from a study of a few of the possible reactions occurring between the dry alkali halides in the fused state. The remaining 42 of the 60 possible reactions have now been studied and some of the previously reported reactions have been studied in greater detail. Also 12 new salt pairs having a common ion have been examined in order to determine in which cases solid solutions can be formed. These solid solubility relationships as well as the course of the reactions mentioned above have been determined by the method of x-ray crystal analysis.

The general plan of the work was very similar to that followed in the previous work. The material to be examined was melted and held in the molten condition for a short time, after which it was quenched and quickly placed in a desiccator to avoid the possible absorption of water. The mixture was then ground to a fine powder (approximately 200-mesh) and placed in a small, thin-walled glass tube of 0.6–0.7 mm. inside diameter, in which container it was exposed to the x-ray beam. The molybdenum K_α doublet, filtered through zirconia, was used for all exposures, the scattered rays being photographed according to the well-known powder method of Debye, Scherrer and Hull.

Those mixtures which showed a tendency to absorb water were handled in a "Dry Box" to which rubber sleeves were attached, or were ground in a mortar on a hot-plate from which the small tubes were filled. The chloride, bromide and iodide of lithium and the fluorides of rubidium and cesium were found to be extremely hygroscopic, and the fluoride of potassium moderately so.

Results

In order to supplement the table of miscibilities previously published,[2] all the binary mixtures of salts having a common ion, in which the percentage deviation from the mean cube edge is less than 10, have been examined in order to determine in which cases solid solutions are formed. The results obtained are shown in Table I. As is to be seen, no solid solutions have been observed in any case in which the per cent. deviation from the mean cube edge is greater than 8.20.

In Table II are assembled the results for the 42 new reactions not reported in the previous papers. These results were found to be in excellent agreement with the former findings. In each case the reaction goes to completion in such a direction that the average cube edge of the stable pair is less than that of the reciprocal pair. In each case the stable pair has the cation of smaller atomic weight united with the anion of smaller atomic weight, and the cation of larger atomic weight united with the anion of larger atomic weight. In each case the sum of the heats of formation of the stable pair is greater than that of the reciprocal pair. With the exception of the lithium salts one member of the stable pair always has the highest melting point of the four compounds involved.

It should be mentioned that the value for the cube edge of sodium bromide used in this paper is a little larger than the previously used value of 5.940 Å. which is listed by Wyckoff[3] as the favored value. A survey of the literature showed that Davey[4] reported a value of 5.936 Å. for the cube edge of sodium bromide, that Wyckoff[5] reported a value of 5.95 Å., while Ewald's "Structurbericht" lists the value of 5.962 Å. A very careful com-

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(*) Read at the Kansas City Meeting of the American Chemical Society.

[1] E. B. Thomas and Lyman J. Wood, This Journal, **56**, 92 (1934).

[2] E. B. Thomas with Lyman J. Wood, *ibid.*, **57**, 822 (1935).

[3] Wyckoff, "The Structure of Crystals," Second edition, The Chemical Catalog Co., New York, 1931.

[4] W. P. Davey, *Phys. Rev.*, **21**, 143 (1923).

[5] R. W. G. Wyckoff, *J. Wash. Acad. Sci.*, **11**, 429 (1921).

TABLE I

SHOWING RESULTS OF X-RAY ANALYSIS OF BINARY MIXTURES HAVING A COMMON ION

Comp. in mol, %	Cube edges, Å.	[a]	Phase A	Phase B	Cube edge 50% solid soln., calcd.	Remarks
50LiCl	5.140	9.10	5.149		5.384	Completely immiscible
50NaCl	5.628			5.628		
50LiBr	5.489	8.20	5.489		5.724	Completely immiscible
50NaBr	5.959			5.948		
50LiI	6.000	7.41	6.049		6.231	Limited miscibility
50NaI	6.462			6.415		
50NaI	6.462	8.74	6.462		6.757	Completely immiscible
50KI	7.052			7.048		
50KF	5.328	5.51	5.469	Only one phase	5.479	Completely miscible
50RbF	5.630					
50KI	7.052	3.80	7.185	Only one phase	7.188	Completely miscible
50RbI	7.325					
50LiCl	5.140	6.57	5.310	Only one phase	5.315	Completely miscible
50LiBr	5.489					
50LiBr	5.489	8.90	5.491		5.745	Completely immiscible
50LiI	6.000			5.999		
50KBr	6.570	7.07	6.962		6.811	Limited miscibility
50KI	7.052			6.641		
50RbBr	6.868	6.45	7.092	Only one phase	7.091	Completely miscible
50RbI	7.325					
50CsBr	4.290	6.15	4.425	Only one phase	4.426	Completely miscible
50CsI	4.562					

[a] $(A_1 - A_2) \times 100/0.5(A_1 + A_2)$.

parison of sodium bromide with sodium chloride in our laboratory gave a value very near to 5.951 Å. Because of the greater density of the sodium bromide this value must be smaller than the value that would have been obtained by mixing the sodium chloride directly with the sodium bromide, which of course could not be done since the two salts are known to form solid solutions with each other. Some electrolytic copper was filed to a fine powder and mixed directly with the sodium bromide. Using a value of 3.605 Å. for the cube edge of copper, a value of 5.959 Å. was obtained for the cube edge of sodium bromide. This latter value has been substituted for the previously used value of 5.940 Å.

For reactions 31, 32, 33, 34, 39, 40, 41, 42, 52, 54 and 56, two interference patterns were obtained in each case which corresponded, respectively, to the pure components of the stable pair. In each of these cases it is known that at least one solid solution is formed between one of the components of the stable pair and one of the components of the reciprocal pair. It may be concluded that all of these reactions go to completion, since if such were not the case interference patterns corresponding to solid solutions would have been obtained, rather than the patterns corresponding to the pure components of the stable pair. In this way quite small amounts of unchanged components of reciprocal pairs could have been detected since very small changes in cube edges are easily measured.

The fact that reaction mixtures 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 43, 44, 45, 46, 47, 48, 49, 50 and 51 gave no evidence of becoming moist after fusion, despite the fact that at least one member of the reciprocal pair is definitely hygroscopic, may be regarded as an indication that reaction has proceeded to completion, although such evidence is not nearly as conclusive as that presented above.

No solid solutions are formed between the compounds involved in reactions 35, 36, 37, 38, 53, 55, 57, 58, 59 and 60. However, had reaction not gone to completion in these cases, four patterns should have been obtained instead of only the two which were observed. Although the mere absence of two patterns is not to be regarded as such satisfactory evidence for completeness of reaction as that described in the foregoing cases, it is very unlikely that both patterns (for the reciprocal pair) would be missed if present in even small quantities, since the scattering power of one member of the reactant pair compares favorably in each of these cases with that of one of the members of the stable pair.

TABLE II

RESULTS OF DOUBLE DECOMPOSITIONS

Reaction	Stable pairs	Accepted cube edge, Å.	Observed cube edges, Å. Phase I	Phase II	Change in mean cube edge	Diff. in sums of hts. of formation
19	LiF	4.014	4.015		−0.059	
	NaCl	5.628		5.627		+10.18
20	LiF	4.014	4.014		− .087	
	KCl	6.280		6.281		+18.32
21	LiF	4.014	4.010		− .093	
	RbCl	6.570		6.571		+19.79
22	LiF	4.014	4.012		−1.512	
	CsCl	4.110		4.111		+22.53
23	LiF	4.014	4.018		−0.068	
	NaBr	5.959		5.943		+11.85
24	LiF	4.014	4.011		− .117	
	KBr	6.570		6.573		+21.74
25	LiF	4.014	4.014		− .118	
	RbBr	6.868		6.860		+24.56
26	LiF	4.014	4.016		−1.596	
	CsBr	4.290		4.292		+27.31
27	LiF	4.014	4.018		−0.072	
	NaI	6.462		6.461		+13.71
28	LiF	4.014	4.005		− .131	
	KI	7.052		7.052		+25.20
29	LiF	4.014	4.012		− .146	
	RbI	7.325		7.325		+18.01
30	LiF	4.014	4.018		−1.716	
	CsI	4.562		4.562		+32.33
31	LiCl	5.140	5.137		−0.009	
	NaBr	5.959		5.943		+ 1.67
32	LiCl	5.140	5.142		− .035	
	KBr	6.570		6.565		+ 3.42
33	LiCl	5.140	5.148		− .025	
	RbBr	6.868		6.860		+ 4.78
34	LiCl	5.140	5.138		− .084	
	CsBr	4.290		4.290		+ 4.68
35	LiCl	5.140	5.144		− .013	
	NaI	6.462		6.460		+ 3.33
36	LiCl	5.140	5.138		− .044	
	KI	7.052		7.050		+ 6.88
37	LiCl	5.140	5.136		− .553	
	RbI	7.325		7.320		+ 8.23
38	LiCl	5.140	5.140		− .204	
	CsI	4.562		4.562		+ 9.70
39	LiBr	5.489	5.486		− .004	
	NaI	6.462		6.456		+ 1.86
40	LiBr	5.489	5.488		− .014	
	KI	7.052		7.047		+ 3.47
41	LiBr	5.489	5.496		− .027	
	RbI	7.325		7.315		+ 3.47
42	LiBr	5.489	5.492		− .119	
	CsI	4.562		4.560		+ 5.02
43	NaF	4.620	4.618		− .028	
	KCl	6.280		6.268		+ 8.13
44	NaF	4.620	4.621		− .034	
	RbCl	6.570		6.565		+ 9.60
45	NaF	4.620	4.616		−1.453	
	CsCl	4.110		4.112		+12.45
46	NaF	4.620	4.621		−0.048	
	KBr	6.570		6.567		+ 9.89
47	NaF	4.620	4.620		−0.050	
	RbBr	6.868		6.858		+12.72
48	NaF	4.620	4.619		−1.528	
	CsBr	4.290		4.289		+15.46
49	NaF	4.620	4.626		−0.059	
	KI	7.052		7.048		+11.50
50	NaF	4.620	4.615		−0.073	
	RbI	7.325		7.317		+14.30
51	NaF	4.620	4.622		−1.644	
	CsI	4.562		4.562		+18.62
52	KF	5.328	5.330		−0.006	
	RbCl	6.570		6.561		+ 1.46
53	KF	5.328	5.330		−1.425	
	CsCl	4.110		4.111		+ 4.31
54	KF	5.328	5.331		−0.002	
	RbBr	6.868		6.859		+ 2.82
55	KF	5.328	5.322		−1.480	
	CsBr	4.290		4.289		+ 5.57
56	KF	5.328	5.331		−0.015	
	RbI	7.325		7.322		+ 2.80
57	KF	5.328	5.334		−1.585	
	CsI	4.562		4.561		+ 7.12
58	RbF	5.630	5.629		−1.419	
	CsCl	4.110		4.110		+ 2.85
59	RbF	5.630	5.630		−1.476	
	CsBr	4.290		4.288		+ 2.75
60	RbF	5.630	5.632		−1.570	
	CsI	4.562		4.560		+ 4.32

Of the eighteen reactions previously reported[2] three reactions (Nos. 10, 14 and 16) were found not to go to completion in the direction of the minimum average cube edge as did the other 15 reactions and as the 42 additional reactions, which have now been studied, have been found to go. Reaction No. 10

$$\mathrm{RbBr} + \mathrm{KCl} \rightleftarrows \mathrm{KBr} + \mathrm{RbCl}$$

has not been further investigated since the data and discussion previously given appeared to be adequate. In the case of reaction No. 14

$$\mathrm{KBr} + \mathrm{RbI} \rightleftarrows \mathrm{KI} + \mathrm{RbBr}$$

the interference lines were found to correspond to two phases of which the cube edge of phase I was 6.710 Å. and the cube edge of phase II was 7.165 Å. It has been found possible to calculate the composition of the equilibrium mixture by assuming that 6.710 Å. is the cubic edge of a binary solid solution of potassium bromide and rubidium bromide and 7.165 Å. is the cube edge of a ternary solid solution of potassium iodide, rubidium iodide and rubidium bromide. The calculations were carried out by solving the simultaneous equations

$$6.570\,\frac{x}{1-y} + 6.868\,\frac{1-x-y}{1-y} = 6.710$$

$$7.325\,\frac{x}{1+y} + 7.052\,\frac{1-x}{1+y} + 6.868\,\frac{y}{1+y} = 7.165$$

where x is the moles of potassium bromide in the binary solid solution and y is the moles of rubidium bromide in the ternary solid solution and the numbers 6.570, 6.868, 7.325 and 7.052 are the respective cube edges of potassium bromide, rubidium bromide, rubidium iodide and potassium iodide.

The results of the calculations are shown in Table III. The hypothesis upon which these calculations rest was tested in the laboratory by preparing and melting a mixture having the composition of 47.48 mol % potassium iodide, 45.80 mol % rubidium iodide and 6.72 mol % rubidium bromide. Upon analyzing this mixture the interference pattern indicated the presence of only one

TABLE III

SHOWING THE RESULTS AND CALCULATIONS FOR THE REACTION $KBr + RbI \longrightarrow KI + RbBr$ (REACTION NO. 14)

	Cube edge, Å.	Calculated molecular ratio	Composition in mol, %
Phase I	6.710	0.491:0.437 = KBr:RbBr	KBr 51.00 RbBr 49.00
Phase II	7.165	0.509:0.491:0.072 = KI:RbI:RbBr	KI 47.48 RbI 45.80 RbBr 6.72
Ternary mix having comp. of Phase II	7.172		

component having a cube edge of 7.172 Å., which is to be compared with the value 7.165 Å. which has been assumed to be the cube edge for a ternary solid solution of potassium iodide, rubidium iodide and rubidium bromide (Table III). The composition calculated for the equilibrium mixture is represented by the equation

$$0.491\ KBr + 0.491\ RbI \rightleftarrows 0.509\ KI + 0.509\ RbBr$$

It is quite interesting to note that the equilibrium mixture is very close to an equimolecular mixture of the four kinds of molecules and that there is only 0.02 kcal./mole difference in the sums of the heats of formation of the two reciprocal pairs.

The equilibrium mixture for reaction 16 was previously reported as being approximately

$$0.64\ RbCl + 0.64\ CsBr \rightleftarrows 0.36\ RbBr + 0.36\ CsCl$$

although the agreement between the equilibrium composition when calculated from phase I and when calculated from phase II was not very close. The average cube edge of phase I and phase II is smaller than the average cube edge of the pair RbBr–CsCl and greater than that of the pair RbCl–CsBr indicating that the reaction should probably go to completion in the direction of RbCl–CsBr. Several new laboratory determinations have been made but thus far the results obtained do not deviate from the values previously reported.

At the present time reactions occurring between the dry alkali halides below the fusion point are being studied. The free energy change has been calculated for one such reaction, *viz.*

$$NaBr + KCl \longrightarrow KBr + NaCl$$

and has been found to be

$$\Delta F = \Delta H - T\Delta S = -1.93 \text{ kcal./mole at } 25°$$

This calculation is in agreement with the x-ray evidence previously reported[2] for the reaction occurring between sodium bromide and potassium chloride below the fusion point.

The reaction

$$TlCl + KI \longrightarrow TlI + KCl$$

has been examined by Chernomordik,[6] using thermal methods and has been found to be irreversible in the direction indicated. The average cube edge of the pair TlCl–KI is 5.446 Å. and that of the pair TlI–KCl is 5.239 Å. Furthermore, the large cation is united with the large anion and the small cation with the small anion. This fact as well as the decrease in average cube edge is in agreement with the generalizations described above for 57 of the 60 reactions studied.

Summary

Reactions occurring between the dry halides of lithium, sodium, potassium, rubidium and cesium in the fused state have been studied.

1. Of the 60 possible reactions, 57 have been found to go completely in such a direction that the average cube edge of the stable pair is less than that of the reciprocal pair.

2. In each of these 57 cases the sum of the heats of formation of the stable pair is greater than the sum of the heats of formation of the reciprocal pair.

3. In each case the stable pair has the cation of larger atomic weight united with the anion of larger atomic weight, and the cation of smaller atomic weight united with the anion of smaller atomic weight.

4. In the case of the other three reactions in which there is either no difference in the average cube edge or no difference in the sum of the heats of formation of the stable and reciprocal pairs, equilibrium has been found to be established. In two of the three cases the equilibrium mixture was composed of very nearly equimolecular quantities of the four kinds of molecules involved in the reaction.

ST. LOUIS, MISSOURI RECEIVED APRIL 21, 1936

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(6) Chernomordik, *J. Gen. Chem.* (U. S. S. R.), **4**, 456–465 (1934).