[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY SCHOOL OF MEDICINE]

A Study of Some Reactions between Dry Inorganic Salts. V. Reactions below the Fusion Point[1]

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It has been demonstrated[2] that when the sixty reciprocal pairs of the alkali halides were fused and the molten masses quenched the resultant mixtures contained, in almost every case, respectively, the heavy cation united with the heavy anion and the light cation united with the light anion. This pair of salts which has been called the stable pair might, for some purposes, be more conveniently called the pair of balanced mass. In only three cases was any evidence found for incomplete reaction of the reciprocal (unstable) pair when reacting to form the stable pair of balanced mass. When the chlorides, bromides and iodides of sodium, potassium, rubidium and cesium (reactions 1–18 of the series described above) were heated for long periods of time under the fusion point several stable pairs of balanced mass were found to be partially converted to the reciprocal pairs.[3] It was shown in this last paper that some of these reversals resulted in a chemical equilibrium which appeared to follow the mass law. Not much reaction was found to occur in the solid state unless the reaction temperature was within 100° of the fusion temperature.

The purpose of this paper is to report further studies on (1) the relationship between temperature and reaction in the solid state, (2) a study of the remaining 42 reactions of the alkali halide reactions (numbers 19 to 60), and (3) a further study of chemical equilibrium in the solid state.

Apparatus, Materials and Methods.—The salt mixtures were heated in the same furnace and in the same manner as previously described.[3] The X-ray apparatus used for analyzing the mixtures after heating was the one used by Thomas and Wood.[2] The lithium, sodium and potassium salts were Analytical Reagent quality. Rubidium and cesium chlorides, bromides and iodides were C. P. stock supplies from the Maywood Chemical Company. The fluorides of both rubidium and cesium were prepared by dissolving the respective carbonates in hydrofluoric acid. The pure salts were fused and kept over phosphorus pentoxide until needed. The lithium salts were fused in an atmosphere of carbon dioxide.

In order to study further the relationship between the extent of the reaction in the solid state at a given temperature and the melting range it was first necessary to determine the melting ranges for the various salt pairs. This was accomplished by heating the salt pairs in a small wire wound electric furnace and measuring the temperature with a thermocouple which had been calibrated by comparison with the melting points of ten pure chemicals which covered the range of temperatures involved in this investigation. No effort was made to obtain highly accurate results since such were not necessary. Approximately the same results were obtained regardless of whether the reciprocal or stable pair was heated.

Experimental Results

After the melting ranges of the first 18 reactions had been determined several salt pairs which were known to react with each other were heated for thirty-six hour periods at various temperatures. It was found in general that if the reaction temperature was more than 200° under the melting range very little reaction occurred while if the reaction temperature was within 100° of the melting range the extent of the reaction was quite considerable. Results obtained for reaction 4 (NaI–KCl) and reaction 7 (NaI–KBr) showed[3] that reaction in the solid state may be quite rapid if the reaction temperature is only a few degrees under the fusion temperature.

With these general rules in mind the remaining 42 reactions of this series (reactions 19–60 as numbered by Thomas and Wood[2]) were divided into 6 groups and heated for thirty-six hour periods at the various reaction temperatures described in Table I. In this way it was found possible to make most of the reaction temperatures within approximately 100° of the respective melting ranges. The difference was a little more than 100° for a few of the reactions heated at 550°. With the exception of cesium fluoride the accepted cube edges for the various alkali halides, with which the values in Table I are to be compared, have been listed in the above-mentioned papers[2,3] and are not repeated here. The accepted cube edge value for cesium fluoride is 6.008 Å. For convenience the reactions described in Table I have been divided into two groups, *viz.*, reactions 19–42 which include all

(1) This communication is part of a doctoral thesis presented by Harold L. Link to the Faculty of St. Louis University, June, 1939.

(2) (a) E. B. Thomas with Lyman J. Wood, THIS JOURNAL, **56**, 92 (1934); (b) **57**, 822 (1935); (c) **58**, 1341 (1936).

(3) H. L. Link and Lyman J. Wood, *ibid.*, **60**, 2320 (1938).

TABLE I

SHOWING THE RESULTS OBTAINED BY HEATING VARIOUS SALT PAIRS AT APPROXIMATELY 100° BELOW THE FUSION TEMPERATURE FOR THIRTY-SIX HOURS

No.	Temp., °C.	Stable pair: Initial		a in Å.[a]	After heat treatment: Patterns	Reciprocal pair: Initial		a in Å.[a]	After heat treatment: Patterns
19	550	LiF	NaCl	4.016	5.630 LiF, NaCl	LiCl	NaF	4.014	5.625 LiF(w),[b] NaCl(s), NaF(w)[c]
20	550	LiF	KCl	4.009	6.276 LiF, KCl	LiCl	KF	4.016	6.275 LiF(s), KCl(s)
21	550	LiF	RbCl	*d*	6.572 LiF(w), RbCl	LiCl	RbF		6.570 RbCl(s)
22	550	LiF	CsCl		4.111 CsCl(s)	LiCl	CsF	4.010	4.110 LiF(w), CsCl(s)
23	550	LiF	NaBr	*d*	5.949 LiF(w), NaBr	LiBr	NaF		5.939 NaBr(s)
24	550	LiF	KBr		6.570 KBr	LiBr	KF	4.016	6.590 LiF(w), KBr(s)
25	550	LiF	RbBr		6.858 RbBr	LiBr	RbF		6.862 RbBr
26	550	LiF	CsBr	4.010	4.291 LiF, CsBr	LiBr	CsF		4.290 CsBr(s)
27	450[e]	LiF	NaI	*d*	6.462 LiF(w), NaI(s)	LiI	NaF	*d*	6.467 LiF(w), NaI(s)
28	550	LiF	KI		7.048 KI(s)	LiI	KF		6.525 LiI–KI[f]
29	550	LiF	RbI		7.321 RbI	LiI	RbF		7.319 RbI
30	550	LiF	CsI		4.562 CsI(s)	LiI	CsF		4.559 CsI(s)
31	450[e]	LiCl	NaBr	5.213	5.759 LiCl–LiBr,[f] NaCl–NaBr[f]	LiBr	NaCl	*d*	5.750 LiCl–LiBr,[f] NaCl–NaBr[f]
32	300	LiCl	KBr	*d*	6.567 LiCl(w), KBr(s)	LiBr	KCl	*d*	6.565 LiBr(w), KBr(s)
33	200	LiCl	RbBr		6.857 RbBr(s)	LiBr	RbCl	*d*	*d* LiCl(w), RbBr(w), RbCl(w)[d]
34	200	LiCl	CsBr		4.291 CsBr(s)	LiBr	CsCl		4.266 CsCl–CsBr[f]
35	400	LiCl	NaI	5.127	6.463 LiCl(w), NaI(s), NaCl(s)[g]	LiI	NaCl	6.457	5.628 NaI, NaCl
36	400	LiCl	KI	5.133	7.052 LiCl, KI(s), KCl[h]	LiI	KCl	*d*	6.278 LiI(w), KCl(w), KI(s)[i]
37	300	LiCl	RbI		6.569 RbCl	LiI	RbCl	7.318	6.574 RbI(s), RbCl
38	250	LiCl	CsI	5.140	4.109 LiCl, CsCl(s)	LiI	CsCl		4.561 CsI
39	400	LiBr	NaI	6.432	5.943 NaBr–NaI,[f] NaBr(s)	LiI	NaBr	*d*	5.933 LiI(w), NaBr
40	200	LiBr	KI		7.050 KI	LiI	KBr		6.569 KBr
41	200	LiBr	RbI	*d*	*d* RbI–RbBr[j]	LiI	RbBr	*d*	*d* RbI–RbBr[j]
42	300	LiBr	CsI	*d*	4.290 LiI(w), CsBr	LiI	CsBr		*d* CsI phase
43	550	NaF	KCl	4.623	6.278 NaF, KCl	NaCl	KF	4.620	6.278 NaF(s), KCl(s)
44	550	NaF	RbCl		6.571 RbCl	NaCl	RbF		6.564 RbCl
45	550	NaF	CsCl	4.614	4.109 NaF, CsCl(s)	NaCl	CsF	4.109	5.621 CsCl, NaCl, NaF(w)[d]
46	550	NaF	KBr		6.566 KBr(s)	NaBr	KF	6.569	5.944 KBr, NaBr, NaF(w)[d]
47	550	NaF	RbBr	4.621	6.859 NaF, RbBr	NaBr	RbF		6.863 RbBr(s)
48	550	NaF	CsBr	4.619	4.289 NaF, CsBr	NaBr	CsF		4.279 CsBr
49	550	NaF	KI	4.610	7.054 NaF(w), KI(s)	NaI	KF	7.052	*d* KI(s), NaI(w)
50	550	NaF	RbI		7.322 RbI	NaI	RbF	*d*	7.322 NaF(w), RbI(s)
51	550	NaF	CsI	*d*	4.563 NaF(w), CsI(s)	NaI	CsF		4.563 CsI(s)
52	450	KF	RbCl	*d*	6.568 KF(w), RbCl(s)	KCl	RbF	*d*	6.493 KF(w), KCl–RbCl[k]
53	400	KF	CsCl	5.325	4.111 KF(s), CsCl(s)	KCl	CsF	5.335	4.111 KF, CsCl, KCl[h]
54	450	KF	RbBr		6.855 RbBr(s)	KBr	RbF		6.816 KBr–RbBr[f]
55	450	KF	CsBr	5.334	4.289 KF, CsBr	KBr	CsF	*d*	4.292 KF(w), CsBr(s), KBr[l]
56	450	KF	RbI	*d*	7.320 KF(w), RbI	KI	RbF	*d*	7.318 KF(w), RbI(s)
57	450	KF	CsI		4.562 CsI(s)	KI	CsF	4.562	7.051 CsI(s), KI(w)
58	400	RbF	CsCl	*d*	4.111 RbF(w), CsCl(s)	RbCl	CsF	*d*	4.110 RbF(w), CsCl(s), RbCl[m]
59	400	RbF	CsBr		4.289 CsBr(s)	RbBr	CsF	*d*	4.290 RbF(w), CsBr(s), RbBr(w)[d]
60	400	RbF	CsI		4.561 CsI(s)	RbI	CsF	4.561	*d* CsI(s), RbI

[a] Cube edge. [b] w = "weak"; s = "strong." [c] $a = 4.620$. [d] Pattern observed by direct comparison with standard lines. No accurate value for the cube edge could be obtained. [e] Heated for 75 hours. [f] Solid solution. [g] $a = 5.621$. [h] $a = 6.285$. [i] $a = 7.054$. [j] Two solid solutions; one rich in RbI, the other rich in RbBr. [k] $a = 6.281$. [l] $a = 6.578$. [m] $a = 6.578$.

of the reaction mixtures containing lithium salts and reactions 43–60 which do not involve lithium salts. When the stable or balanced pairs of this last group of reactions were heated at the reaction temperatures indicated in Table I, no evidence for any reversal to the reciprocal pair was obtained. On the other hand, when the reciprocal pairs were heated all of them were converted partially or completely to the stable pairs. Evidence for incomplete reaction was obtained for reactions 45, 46, 49, 52, 53, 54, 55, 57, 58, 59 and 60. It was found possible to calculate the extent of the reaction for the reciprocal pairs of reactions 52 and 54 because of the formation of solid solutions. The cube edge of 6.493 Å. reported for reaction 52 corresponds to a solid solution of 26.5 mole per cent. potassium chloride and 73.5 mole per cent. rubidium chloride. The cube edge value of 6.816 Å. reported for reaction 54 corresponds to a solid solution of 15.2 mole per cent. potassium bromide and 84.8 mole per cent. rubidium bromide. The reciprocal pairs of reactions 43, 44, 47, 48, 50, 51 and 56 appeared to go to completion in the direction of the stable pairs. Only in the case of reaction 56 would solid solutions be expected to form if reaction were incomplete.[2,3] The X-ray diffraction patterns obtained corresponded to those of pure rubidium iodide and potassium fluoride and are to be taken as evidence that the reciprocal

TABLE II

RESULTS OF SOLID SOLUBILITY STUDIES OF KCl–KBr AND CsCl–CsBr

Composition, mole %		Temp., °C.	Time, hr.	Cube edge, Å. Obsd.	Theory	Remarks
KCl 50	KBr 50	400	36	6.280		Immiscible
				6.570		
KCl 50	KBr 50	480	36	6.425	6.425	Miscible
KCl 33	KBr 33	400	72	6.347		23%KBr–77%KCl
	CsCl 33			4.241		25%CsCl–75%CsBr
CsCl 50	CsBr 50	360	36	4.200[a]	4.200	Miscible
CsCl 50	CsBr 50	400	36	4.209	4.200	Miscible
CsCl 25	CsBr 75	400	84	4.243	4.245	Miscible
CsCl 75	CsBr 25	400	84	4.156	4.155	Miscible

[a] Result taken from F. Meyer, B.S. Thesis, St. Louis University, June, 1938.

pair has been completely converted to the stable pair. In the other cases the same conclusion is based on the absence of any diffraction patterns corresponding to the reciprocal pairs.

The 24 reactions numbered 19–42 are of considerable interest since all of the reaction mixtures contain lithium salts. In the studies above the fusion point it was found that the stable pair always contained the highest melting compound in the case of each reaction except the reaction mixtures containing lithium salts. In the case of the lithium reactions, only the stable pairs of reactions 21, 22, 25, 26, 29 and 30 contained the highest melting compounds. Referring to Table I it will be seen that no evidence was obtained for any reversal of the stable pairs of reactions 19–30. In six of these reactions the stable pair contains the highest melting compound and in six the reciprocal pair. The only common factor that has been discovered is that each stable pair contains lithium fluoride.

The reciprocal pairs of the other twelve reactions (31–42) all contain the highest melting compound and the stable pairs of most of the reactions showed some reversal to the reciprocal pair when heated at the temperatures indicated in Table I. No evidence of any reversal of stable pairs for reactions 32, 33, 34 and 40 was observed.

Reaction No. 11.—In a previous study[3] of reaction number 11 at 480° (under the fusion temperature) it was found that when either the reciprocal or stable pair was heated an equilibrium was formed as represented by the equation

$$CsCl + KBr \rightleftarrows CsBr + KCl$$

and that when the composition of the reacting mixture was changed the equilibrium shifted in accordance with the demands of the mass law. Further studies of this reaction have been made at 440, 400 and 360°. The observations, though not yet fully completed, indicate that the reaction proceeds to equilibrium at each temperature and that the composition of the equilibrium mixture changes with the composition of the reaction mixture in accordance with the demands of the mass law. Efforts to calculate ΔH for reaction 11 by means of van't Hoff's reaction isochor after the manner of Tubandt and Reinhold[4] when working with the solid reactions occurring between the pairs Ag_2S–CuI and Ag_2S–Cu_2Se gave values for ΔH of the correct sign but several times as large as was to be expected from the best available experimental values. A detailed description of these and other similar studies is being made the subject of a future report.

In Table II are to be found the results of solid solution studies made necessary by the investigation of reaction 11 described above. Table III shows in detail the X-ray diffraction data for a CsCl–CsBr solid solution formed at 360°. Other

TABLE III

SHOWING THE INTERPLANAR DISTANCES OF THE 50–50 CsCl–CsBr SOLID SOLUTION FORMED AT 360°

Line no.	I	*hkl*	*d* Obsd.	*d* Calcd.	*a* Obsd.	*a* Calcd.
1	2	100	4.23	4.200		
2	10	110	2.96	2.970		
3	1	111	2.41	2.425		
4	5	200	2.09	2.100		
5	3	210	1.873	1.878		
6	9	211	1.714	1.715	4.198	4.200
7	6	220	1.484	1.485	4.198	4.200
8	1	300 or 221	1.400	1.400	4.200	4.200
9	7	310	1.329	1.328	4.203	4.200
10	1	311	1.266	1.266	4.199	4.200
11	v w	222	1.203	1.213		
12	v w	320	1.162	1.165		
13	7	321	1.123	1.122	4.202	4.200
14	w	322	1.014	1.019		
15	1	330	0.990	0.990	4.200	4.200
				Av.	4.200	4.200

(4) Tubandt and Reinhold, *Z. physik. Chem.*, **140A**, 291 (1929).

similar data are summarized in Table II. Particular attention should be called to the results obtained from heating an equimolar mixture of potassium chloride, potassium bromide and cesium chloride (Table II). When potassium chloride and potassium bromide are heated together at 400° no solid solution results. However, when cesium chloride is heated with potassium chloride and potassium bromide at 400°, a solid solution of potassium chloride and potassium bromide results. The cube edge obtained for this solid solution indicates that only the potassium chloride formed by the interaction of the cesium chloride and potassium bromide dissolves in the residual potassium bromide. The cesium bromide in the CsCl–CsBr solid solution is less than when an equimolar mixture of cesium chloride and potassium bromide is heated and very nearly the same as when 2 moles of potassium chloride and 1 mole of cesium bromide are heated together (Table IV). Within the limits of experimental error, the extent of the reaction is, in each case, in agreement with the demands of the mass law.

TABLE IV

EQUILIBRIUM MIXTURES OF REACTION 11 AT 400°

Before heating	100		100				100
	CsCl	+	KBr	⇄	CsBr	+	KCl
After heating	25		25		75		175
Before heating					100		200
	CsCl	+	KBr	⇄	CsBr	+	KCl
After heating	25		25		75		175
Before heating	100		100				
	CsCl	+	KBr	⇄	CsBr	+	KCl
After heating	19		19		81		81

Summary

Reactions occurring between the alkali halides in the solid state have been studied. Salt pairs corresponding to all sixty of the possible reactions have been heated for long periods of time below the fusion point and the resulting mixtures analyzed by the method of X-ray crystal analysis. The reaction mixtures of the forty-two reactions included in this report contained lithium salts or fluorides or both, the remaining eighteen reactions having been previously reported.[3]

1. Twelve of the reaction mixtures contained both lithium salts and fluorides. The highest melting component was contained in the stable pair in six cases and in the reciprocal pair in six cases. In each case lithium fluoride was a member of the stable pair. No evidence was found for the reversal of any of the stable pairs to the corresponding reciprocal pairs.

2. Twelve of the reaction mixtures contained lithium salts but no fluorides. The highest melting component was contained in the reciprocal pair in each case. Eight of these stable pairs showed some tendency toward reversal to the reciprocal pair and four did not.

3. Eighteen of the reaction mixtures contained fluorides but no lithium salts. The highest melting component was contained in the stable pair in each case and no evidence was obtained for the reversal of any of the stable pairs to the reciprocal.

4. Evidence for partial or complete conversion of the reciprocal to the stable pair was obtained for forty of the forty-two reactions.

5. It was found that in general there was very little reaction in the solid state if the reaction temperature was more than 200° below the melting range and that there was likely to be considerable reaction if the reaction temperature was within 100° of the melting range.

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