with our C_2. Greenwald's constants for oxalic acid and malonic acid are included in the last column of Table VIII together with those which we have calculated from Simms' observations on succinic and azelaic acids. For these calculations we used the method of the present paper. Simms' constants must be reduced slightly to translate them from $\mu = 0.07$ to 0.20. The activity correction is $-\log \gamma_{\mathrm{Ca}^{++}}\gamma_{a^{--}}$. A reduction of log C_2 by 0.1 is entirely reasonable. If that is done, the agreement is good, except for succinic acid.

Money and Davies[9] have determined constants for oxalic acid and a series of cations from the conductivities of the salts (Table VIII). To convert these to $\mu = 0.2$ a reduction of log C_2 by 0.6 – 0.8 is consistent with available data on the activity coefficients of divalent ions. Agreement with our value for oxalic–Mg is then good and the relative behavior of the series of cations is in harmony with our observations on the other acids.

Summary

1. The hydrogen electrode titration curves of a number of mono- and bivalent carboxylic acids have been compared in varying KCl–MCl_2 mixtures of constant ionic strength ($\mu = 0.2$). (M represents Mg, Ca, Sr, Ba or Mg.)

2. The specific effects which have been observed have been reduced to mass action constants for the formation of binary compounds between the cations and the carboxylate anions.

NEW YORK, N. Y. RECEIVED JUNE 8, 1938

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

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

BY HAROLD L. LINK AND LYMAN J. WOOD

Recently all of the possible reactions that might occur between dry alkali halides above the fusion temperature have been studied by Thomas and Wood.[2] Of the possible 60 reactions that might occur between pairs of alkali halides not having a common ion, it was found that 57 of the reactions proceeded (in the fused state) to completion in such a direction that the average cube edge of the stable pair was less than the average cube edge of the reciprocal pair. In these 57 cases, without exception, the larger cation united with the larger anion and the smaller cation with the smaller anion. In each of these 57 cases, also without exception, the sum of the heats of formation of the stable pair was greater than that of the reciprocal pair, *i. e.*, ΔH was minus. In the remaining three cases equilibrium was indicated as represented in the following reactions

$$\mathrm{KBr} + \mathrm{RbCl} \rightleftarrows \mathrm{KCl} + \mathrm{RbBr} \text{ (Reaction 10)}$$
$$\mathrm{KI} + \mathrm{RbBr} \rightleftarrows \mathrm{KBr} + \mathrm{RbI} \text{ (Reaction 14)}$$
$$\mathrm{RbBr} + \mathrm{CsCl} \rightleftarrows \mathrm{RbCl} + \mathrm{CsBr} \text{ (Reaction 16)}$$

The present report concerns studies of reactions that have been made under the fusion point and is limited to double decompositions involving only Na^+, K^+, Rb^+, Cs^+, Cl^-, Br^-, and I^- (see reactions 1–18, Table I). The variation of the speed of reaction with time at a fixed temperature has been studied and also the variation of the speed with temperature for a fixed time. In five cases what appear to be equilibrium mixtures have been obtained and these mixtures have been studied in some detail.

Materials and Experimental Procedure

The salts used were Analytical Reagents with the exception of cesium chloride and bromide, which were prepared from the nitrate according to the method of Wells.[3] The salts were fused and ground to a fine powder and kept in a desiccator until wanted. After heating the various salt pairs at temperatures and for lengths of time indicated in the proper place, all mixtures were examined by the method of X-ray crystal analysis as previously described.[2a]

It is, in general, more difficult to obtain good films from salt mixtures which have been heated under the fusion point rather than above the

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(1) Read at the Rochester meeting of the American Chemical Society, September, 1937. This communication is for the most part from a thesis presented by H. L. Link for the degree of Master of Science.

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

(3) H. L. Wells, *Am. J. Sci.*, [3] **46**, 186 (1893).

fusion point. In many cases the material being examined does not appear to be in the proper crystalline form. The crystals are perhaps too small or are strained and for these and, no doubt, other reasons yield patterns consisting of a limited number of lines that are in many cases difficult to read. In addition to these difficulties, quantitative results from equilibrium studies are difficult to obtain because the formation of solid solutions is not as common as above the fusion point. It is often possible, however, to draw definite conclusions from surprisingly few data.

Results

In Table I are listed the results obtained for reactions 1 to 18 at 400° when the heating was continued for thirty-six hours. What previously has been called the stable pair (indicated in Table I by the letter a) was heated in each case and the resulting mixtures were analyzed (by means of the X-ray beam) for evidence of reversal toward the reciprocal pair (indicated in the table by the letter b). As was to be expected from previous work above the fusion point most of the stable pairs showed little or no evidence of any tendency toward reversal. Reactions 3, 5, 8, 9, 11, 14, and 16 showed unmistakable evidence of some reversal. The results obtained from heating the reciprocal pairs are shown in column b. All of the reactions with the exception of 10 and 14 proceeded partially or completely toward the stable pair. Reaction 10 possibly did also since it seems likely that reaction would have preceded the formation of a solid solution. The formation of this solid solution at 400° was not expected since it was known that neither the mixture KBr–KCl nor the mixture RbCl–KCl forms a solid solution at 400°. The cube edge obtained is only 0.001 Å. different from that of either component of the reciprocal pair but the interference diagram obtained can scarcely be the patterns of potassium bromide and rubidium chloride superimposed on each other since in this case interference lines with odd ordered indices would have been obtained such as 111 and 311 and no such lines were obtained. The situation was made even more interesting by reason of the fact that the stable pair, when heated at 400°, produced only patterns of potassium chloride and rubidium bromide. It is, of course, quite possible that a solid solution of compounds that are just being formed may occur more readily than will be the case for a mixture of these same compounds after they have already been formed.

The results in Table I indicate that reactions 3, 5, 8, 9, 11 and 16 should also reach an equilibrium if heated long enough at 400°.

Several of the reactions were examined at higher temperatures. When the reciprocal pair of reaction 14 (KI–RbBr) was heated at 480° for thirty-six hours there was evidence of considerable reaction whereas at 400° no evidence of reaction was found. The lowest fusion temperature of this mixture was found to be about 608°. When the reciprocal pair for reaction 2 was heated at 480° for thirty-six hours the extent of the reaction was found to be 62% as calculated from the resulting solid solution of rubidium

TABLE I

SHOWING THE RESULTS OBTAINED BY HEATING VARIOUS SALT PAIRS AT 400° FOR 36 HOURS

				X-Ray Observations			
			Accepted cube edge	Reciprocal pair—b		Stable pair—a	
Reaction			a[a]	a[a]	Remarks	a[a]	Remarks
1	a.	NaCl	5.628	5.629	Partial reaction	[b]	No reversal
		KBr	6.570	6.561			
	b.	NaBr	5.94	5.947			
		KCl	6.280	6.288			
2	a.	NaCl	5.628	5.628	Partial reaction	5.631	No reversal
		RbBr	6.86	6.868		6.860	
	b.	NaBr	5.94	5.946			
		RbCl	6.570	6.582			
3	a.	NaCl	5.628		Partial reaction	5.628	Partial reversal
		CsBr	4.29			4.265	
	b.	NaBr	5.94	5.971			
		CsCl	4.110	4.182			
4	a.	NaCl	5.628	5.628	Partial reaction	[b]	Little or no reversal
		KI	7.052	7.032			
	b.	NaI	6.46	6.46			
		KCl	6.280				

TABLE I (*Concluded*)

Reaction			Accepted cube edge a[a]	X-Ray Observations Reciprocal pair—b a[a]	Remarks	Stable pair—a a[a]	Remarks
5	a.	NaCl	5.628	5.622	Almost complete reaction	5.626	Partial reversal
		RbI	7.325	7.320		7.327	
	b.	NaI	6.46	[b]			
		RbCl	6.570	[b]		6.575	
6	a.	NaCl	5.628	5.637	Complete reaction	5.628	No reversal
		CsI	4.562	4.564		4.558	
	b.	NaI	6.46				
		CsCl	4.110				
7	a.	NaBr	5.94	5.937	Almost complete reaction	5.937	A very little reversal
		KI	7.052	6.998		6.995	
	b.	NaI	6.46				
		KBr	6.570				
8	a.	NaBr	5.94	[b]	Partial reaction	[b]	Some reversal
		RbI	7.325	[b]		7.257	
	b.	NaI	6.46				
		RbBr	6.86				
9	a.	NaBr	5.94	6.001	Partial reaction	[b]	Some reversal
		CsI	4.562	4.515		4.508	
	b.	NaI	6.46				
		CsBr	4.29				
10	a.	KCl	6.280	6.571	Solid soln. of the four ions	6.281	No reversal
		RbBr	6.86			6.857	
	b.	KBr	6.570				
		RbCl	6.570				
11	a.	KCl	6.280		Partial reaction	[b]	Partial reversal
		CsBr	4.29			4.273	
	b.	KBr	6.570	[b]			
		CsCl	4.110	4.134			
12	a.	KCl	6.280		Partial reaction	[b]	No reversal
		RbI	7.325	7.212		7.315	
	b.	KI	7.052				
		RbCl	6.570	6.570			
13	a.	KCl	6.280	[b]	Complete reaction		Little or no reversal
		CsI	4.562	4.555		4.544	
	b.	KI	7.052				
		CsCl	4.110				
14	a.	KBr	6.570		No reaction	[b]	Partial reversal
		RbI	7.325				
	b.	KI	7.052	7.047			
		RbBr	6.86	6.868		[b]	
15	a.	KBr	6.570	[b]	Partial reaction	[b]	No reversal
		CsI	4.562	4.525		4.560	
	b.	KI	7.052				
		CsBr	4.29				
16	a.	RbCl	6.570		Partial reaction	6.874	Partial reversal
		CsBr	4.29			4.234	
	b.	RbBr	6.86	6.858			
		CsCl	4.110	4.154			
17	a.	RbCl	6.570	[b]	Partial reaction	[b]	Little or no reversal
		CsI	4.562	4.561		4.543	
	b.	RbI	7.325	[b]			
		CsCl	4.110	[b]			
18	a.	RbBr	6.86	[b]	Very little reaction	[b]	Little or no reversal
		CsI	4.562			4.556	
	b.	RbI	7.325				
		CsBr	4.29	4.292			

[a] Cube edge in Å.

[b] Pattern observed by direct comparison with standard lines. No accurate value of the cube edge could be obtained.

TABLE II

SHOWING THE RESULTS OF SOLID SOLUTION STUDIES ON SOME ALKALI HALIDE PAIRS WHEN HEATED FOR THIRTY-SIX HOURS UNDER THE FUSION TEMPERATURE

50 : 50	Cube edge of observed phases						
Mole, %	a	400°	Remarks	480°	Remarks	Fused[a]	Remarks
NaCl	5.628	5.628	No solid solution		Completely soluble	5.811	Limited solubility
NaBr	5.940	5.940		5.789		5.628	
KCl	6.280	6.280	No solid solution		Completely soluble		Completely soluble
KBr	6.570	6.570		6.425		6.423	
KCl	6.280	6.272	No solid solution				Completely soluble
RbCl	6.570	6.562				6.418	
KI	7.052	7.058	No solid solution	One phase	Complete soly. indicated		Completely soluble
RbI	7.325	7.318				7.185	
RbCl	6.570			One phase	Complete soly. indicated	6.708	Completely soluble
RbBr	6.860						
CsCl	4.110		Completely				Completely soluble
CsBr	4.290	4.209	soluble			4.202	
CsBr	4.290	4.294	No solid solution			4.426	Completely soluble
CsI	4.562	[b]					
NaBr	5.940	5.937	Limited soly. of			5.971	Limited solubility
NaI	6.460	6.379	NaBr in NaI			6.419	
RbBr	6.86	[b]	Limited solubility			7.092	Completely soluble
RbI	7.325	[b]					
KBr	6.570	6.599	Limited solubility			6.641	Limited solubility
KI	7.052	6.959				6.962	

[a] Values obtained by Thomas and Wood.[2a,b] [b] No accurate value for the cube edge could be obtained.

bromide and residual rubidium chloride. This solid solution did not form at 400° but there was considerable reaction, perhaps 50% or more as nearly as could be judged by relative intensities of the rubidium bromide and rubidium chloride patterns. The lowest fusion temperature of this mixture was 503°. When the reciprocal pair of reaction one was heated at 500° the reaction appeared to be complete since patterns for pure potassium bromide and sodium chloride were obtained. If there had been any residual sodium bromide or potassium chloride solid solutions would have resulted at this temperature. At 400° the extent of the reaction was much less, four patterns corresponding to the four pure substances being clearly observed. The lowest fusion temperature of this mixture was about 603°. It is not possible to make any quantitative statement concerning the relation between the temperature and the rate of reaction which must depend upon several factors. In general, however, it has been found that if the temperature is much more than 100° below the fusion temperature the rate of reaction is very slow.

In the case of the number one reaction previous calculation of the free energy at 25° has shown that the reaction should proceed spontaneously from reciprocal to stable pair at room temperature. This was tested by subjecting the reciprocal pair, at room temperature, to a pressure of 3500 atmospheres per square inch for ten minutes. The pressure was applied by means of a huge hydraulic press kindly made available by The Reverend Basile J. Luyet of the Department of Biology of St. Louis University. Before mixing the sodium bromide and potassium chloride they were passed through a 200-mesh sieve and dried over sulfuric acid for several days. The reaction was found to proceed from reciprocal to stable pair to the extent of about 50%. This had to be judged from the relative intensities of the patterns for the pure components since solid solutions were not formed.

Reaction 7 has been studied at 510° (a few degrees under the fusion temperature) for various lengths of time and the results are shown in Table III.

TABLE III

SHOWING THE RESULTS OBTAINED BY HEATING A 50-50 MOLAR MIXTURE OF NaI AND KBr (REACTION 7) AT 510°

Time of heating, hours	0.5	2.0	15.0	30.0
Extent of reaction	20	35	80	90

Reaction 4 was examined in the same way except that the temperature was 488° (a few degrees under the fusion temperature) instead of 510°. Very similar results were obtained. The extent of the reaction had to be judged in both cases by relative intensities of the patterns since there was only a very small amount of solid solubility.

Equilibrium Studies

The principal interest in the reactions that did not go to completion in either direction centered in the compositions of the reaction mixtures since they were possibly equilibrium mixtures or might become such upon proper treatment. In the case of one of these reactions that does not go to completion in either direction and in case of which no solid solutions are formed (under the given conditions) it is frequently possible to demonstrate, by means of the X-ray analysis, that the four pure components are present (reaction 1, Table I) but the extent of the reaction can only be estimated from the intensities of the various interference lines. On the other hand, if solid solutions are formed, it is sometimes possible to determine the extent of the reaction from the interference patterns.

Because of the formation of suitable solid solutions, reaction 11 has been studied in considerable detail (Table II). It is clear from Table I that the reaction does not go to completion in either direction when either the reciprocal or stable pair is heated at 400° for thirty-six hours. Two interference patterns were obtained in each case, one body centered and the other face centered. From the body centered patterns were calculated cube edge values of 4.134 and 4.273 corresponding to the patterns obtained, respectively, from the reciprocal and stable pairs. These two cube edge values are each intermediate between the cube edge values of cesium chloride and bromide. Since it is known, from Table II, that a 50 mole per cent. mixture of cesium chloride and bromide, when heated at 400°, dissolves completely in each other, forming a solid solution, the intermediate cube edge values are explained very easily. The face centered pattern in each case was quite light by comparison with the body centered pattern which is exactly what would be expected for a mixture of potassium salts and cesium salts. While it was not possible to obtain satisfactory cube edge values in either case, there was no doubt about the nature of the patterns. Several of the lines appeared to indicate values intermediate between potassium chloride and bromide, which would be contrary to the solid solution data of Table II. This situation is not quite comparable to the one described in Table II, however, since in the former case both compounds were heated in the presence of each other, while in this case one of the compounds is formed in the presence of the other.

The solid solution of cesium chloride and bromide gave excellent interference patterns and can be used for calculating the extent of the reaction if it can be shown that all of the cesium chloride and bromide are contained in this solution and that the solution, furthermore, contains none of the potassium chloride nor bromide, *i. e.*, it must be shown that ternary solutions are not present.

TABLE IV

SHOWING CsCl–CsBr SOLID SOLUTION CUBE EDGES RESULTING FROM A STUDY OF REACTION 11

Mole ratio of reacting mix.	Heat treatment		Solid soln. cube edge	Mole ratio of resultant mix. CsCl : CsBr
	T, °C.	Hrs.		
1 KBr:1 CsCl	400	38	4.134	0.87 :0.13
	480	36	4.247	.24 : .76
	480	72	4.253	.211: .789
1 KCl:1 CsBr	400	38	4.273	.09 : .91
	480	36	4.258	.18 : .82
	480	72	4.253	.211: .789
1 KCl:2 CsBr	480	72	4.263	.150: .850
2 KCl:1 CsBr	480	72	4.241	.272: .728

Although the existence of such ternary solutions seemed highly improbable because cesium chloride and bromide are body centered and the cube edges are small and potassium chloride and bromide are face centered and the cube edges are large, the possibility of such ternary solutions was eliminated when the results for reaction 11 were obtained at 480° instead of 400° (Table IV). Considering the last mixture described in Table IV, it is to be seen that the composition of the starting mixture is 2KCl:1CsBr. Because of the larger amount of potassium chloride with respect to cesium bromide it was possible to obtain a satisfactory cube edge of the KCl–KBr solid solution which is known to form at this temperature (Table II). If the CsCl–CsBr solid solution be a binary solution and all of the cesium chloride and bromide in the resultant mixture be contained in this solution, then the two moles of potassium chloride and the one mole of cesium bromide of the original mixture have reacted with each other according to the equation

$$0.272\ \mathrm{KBr} + 0.272\ \mathrm{CsCl} \rightleftharpoons 1.728\ \mathrm{KCl} + 0.728\ \mathrm{CsBr}$$

and the cube edge of the KCl–KBr solid solution should be

$$\frac{0.272}{2}\,6.57 + \frac{1.728}{2}\,6.28 = 6.320\ \text{Å}.$$

whereas the value obtained from the inter-

TABLE V

SHOWING THE EXTENT OF REACTION 11 OCCURRING FROM EACH SIDE AT 400 and 480°

Temp., °C.	Time, hrs.	Case	Mole ratio of reacting mixture	Composition of resulting mixture
400	38	A	1 CsCl:1 KBr	$0.87\ \mathrm{CsCl} + 0.87\ \mathrm{KBr} \longrightarrow 0.13\ \mathrm{CsBr} + 0.13\ \mathrm{KCl}$
400	38	B	1 CsBr:1 KCl	$.91\ \mathrm{CsBr} + .91\ \mathrm{KCl} \longrightarrow .09\ \mathrm{CsCl} + .09\ \mathrm{KBr}$
480	36	C	1 CsCl:1 KBr	$.24\ \mathrm{CsCl} + .24\ \mathrm{KBr} \longrightarrow .76\ \mathrm{CsBr} + .76\ \mathrm{KCl}$
480	36	D	1 CsBr:1 KCl	$.82\ \mathrm{CsBr} + .82\ \mathrm{KCl} \longrightarrow .18\ \mathrm{CsCl} + .18\ \mathrm{KBr}$
480	72	E	1 CsBr:1 KCl	$.789\ \mathrm{CsBr} + .789\ \mathrm{KCl} \rightleftarrows .211\ \mathrm{CsCl} + .211\ \mathrm{KBr}$
480	72	F	1 CsCl:1 KBr	$.211\ \mathrm{CsCl} + .211\ \mathrm{KBr} \rightleftarrows .789\ \mathrm{CsBr} + .789\ \mathrm{KCl}$
480	72	G	2 CsBr:1 KCl	$.300\ \mathrm{CsCl} + .300\ \mathrm{KBr} \rightleftarrows 1.700\ \mathrm{CsBr} + .700\ \mathrm{KCl}$
480	72	H	1 CsBr:2 KCl	$.272\ \mathrm{CsCl} + .272\ \mathrm{KBr} \rightleftarrows 0.728\ \mathrm{CsBr} + 1.728\ \mathrm{KCl}$

ference pattern was 6.322 Å. The very excellent agreement between the values indicates clearly that at 480° two binary solid solutions are formed which together contain all of the mixture. In view of this excellent agreement the authors have used only the CsCl–CsBr solid solution for calculating the resultant mixtures for this reaction, the results of which are shown in Table V.

The cube edges of the CsCl–CsBr solid solutions obtained for reaction 11 are shown in Table IV and the extent of the reaction for each direction is shown in Table V. It is clear that at 480° equilibrium is approached quite closely in thirty-six hours. By drawing a composition–temperature diagram from the data in Table IV it was estimated that the composition of the equilibrium mixture at 490° should be KBr 21%, CsCl 21%, KCl 79%, CsBr 79%. A reheating of a mixture of potassium chloride and cesium bromide (stable pair) in a 1:1 mole ratio at 480° for seventy-two hours produced a CsCl–CsBr solid solution having a cube edge of 4.253 Å. (av. of two closely agreeing results) and the reciprocal pair heated in the same way produced likewise a cube edge of 4.253 Å. (cases E and F, Table V). That equilibrium has been reached can scarcely be doubted.

Cases G and H of Table V are very interesting. The shift in the reaction is in the direction that would be expected from mass action considerations. Furthermore, the amount of the shift is in almost exact quantitative agreement with what might be expected. In case G the shift to the left is just slightly too much and in case H the shift is just slightly too little. Reactions 3 and 16 are now being investigated in an effort to determine whether or not a similar effect can be discovered in these cases also.

Summary

1. Eighteen double decomposition reactions occurring between the sodium, potassium, rubidium and cesium halides (chloride, bromide, iodide) were investigated between 400 and 500° (below the fusion point) and the resultant mixtures examined by the method of X-ray crystal analysis.

2. When the reciprocal pairs (large cation–small anion and small cation–large anion combinations) were heated at 400° for thirty-six hours, reaction proceeded to some extent toward the stable pairs in 16 of the 18 cases.

3. When the stable pairs were heated at 400° for thirty-six hours, reaction proceeded to some extent toward the reciprocal pair in 7 cases.

4. One reaction was subjected to a pressure of 3500 atmospheres per square inch for ten minutes and it was found to proceed partially toward the stable pair.

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RECEIVED OCTOBER 11, 1937