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

A Study of Some Reactions between Dry Inorganic Salts. II[1]

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In a previous paper[2] results of a study of a series of reactions occurring between certain anhydrous fused salts of alkali halides were presented, the x-ray spectrograph being used to determine the products of the reactions. This series has been extended to include all of the chlorides, bromides and iodides of sodium, potassium, rubidium and cesium. An attempt has been made to relate the direction in which the reaction goes with the melting points, cube edges and sums of the heats of formation of the compounds concerned, very satisfactory correlation being obtained as will be seen from the results tabulated below.

Apparatus and Procedure

The apparatus and method employed were the same as described in the previous paper. The pure salts were intimately mixed and heated to a temperature slightly above the fusion point of the mixture and held in the liquid state for several minutes and then chilled. The resulting mixtures were analyzed by means of the x-ray spectrograph, the finely divided powder being exposed to the Kα rays from a molybdenum target.

The salts of sodium and potassium employed were salts of c. p. or Reagent Quality grade which were fused previous to using. The rubidium salts were prepared by igniting pure rubidium tartrate to carbonate and dissolving the carbonate in the appropriate halogen acid. A similar procedure was employed in preparing the cesium salts, c. p. cesium chloride being used as a starting point and the method of H. L. Wells being followed.[3] The cesium chloride was converted to the nitrate, thence to the oxalate and this, by ignition, to the carbonate, which was then dissolved in hydrobromic or hydriodic acid. The resulting salts were free of nitrates as indicated by the negative test obtained using diphenylamine and sulfuric acid. The pure rubidium and cesium halides were recrystallized from water and dried at a temperature sufficient to remove traces of water or acid. These salts, when analyzed by means of the x-ray spectrograph, proved to give values for their cell constants which agreed in every case, within the experimental error of the method, with the generally accepted values. The unavoidable error appeared to be about ±0.006 Å. depending upon the absolute size of the cube edge being measured.

Results

Several binary mixtures of salts having common ions were examined to determine in which cases solid solutions were formed and the results are shown in Table I. In case a reaction between two anhydrous salts does not go to completion, it is often possible to estimate quite accurately the extent to which the reaction occurs if it is known that one or both of the products of the reaction form a solid solution with one of the reactants. If such solid solutions are known to form it is furthermore possible to say definitely that the reaction has gone to completion if the x-ray patterns correspond to those of the pure products. It has been shown by Vegard[4] and others[5] that the cube edges of many solid solutions are additive, the value of the cube edge depending upon the molecular percentage of the solid solution. This relationship has been called Vegard's Additivity Law and allows the calculation of the mole percentages of the constituents when the cube edges of the components and that of the solid solution are known. It is known that this law does not hold for all types of solid solution, but for the type of solid solution about which this paper is concerned its validity has been quite well established. Moreover, the difference between the cube edges of the components appears to be related roughly to the formation of solid solutions. Havighurst Mack and Blake[5] found that complete miscibility was obtained when the difference between the cube edges of the two components was less than 5% of their mean cube edge. This has been approximately substantiated in this work.

The results of the double decomposition reactions studied are assembled in Table II, which includes the generally accepted values of the cube edges for the reciprocal pairs, their mean values, molecular weights, melting points and sums of heats of formation.

Both sets of reciprocal pairs were fused and examined in cases in which any doubt existed concerning the course of the reaction. In this way it was possible to make certain that the products obtained represented true equilibrium, the products consisting in nearly all cases only of the stable pair since nearly all reactions went to completion in one direction or the other so far as the

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[1] Read at the Cleveland Meeting of the American Chemical Society.

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

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

[4] Vegard, *Z. Physik*, **5**, 17 (1921).

[5] Havighurst, Mack and Blake, This Journal, **47**, 29 (1925).

TABLE I

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

Composition in mole, %	Cube edges in Å.	$\frac{(A_1 - A_2) \times 100^a}{(A_1 + A_2)/2}$	Phase A observed	Phase B observed	Cube edge for a 50% solid soln. (calcd.)	Remarks
50 NaBr	5.940	8.50	6.419	5.971	6.200	Limited miscibility
50 NaI	6.460					
50 KCl	6.280	11.59	7.055	6.280	6.666	Completely immiscible
50 KI	7.052					
50 RbCl	6.570	4.32	6.708	Only one phase	6.715	Completely miscible
50 RbBr	6.860					
50 RbCl	6.570	46.0	6.578	4.109	5.340	Completely immiscible
50 CsCl	4.110					
50 RbBr	6.860	4.32	6.702	Only one phase	6.715	Completely miscible
50 KBr	6.570					
50 CsCl	4.110	4.22	4.202	Only one phase	4.200	Completely miscible
50 CsBr	4.290					
50 RbCl	6.570	4.51	6.418	Only one phase	6.425	Completely miscible
50 KCl	6.280					

[a] Method of Havighurst, Mack and Blake[5] for calculating percentage deviation from the mean cube edge.

TABLE II

SHOWING CORRELATION BETWEEN STABLE PAIRS, CUBE EDGES, MOLECULAR WEIGHTS, MELTING POINTS AND HEATS OF FORMATION

Reaction	Reciprocal pairs	Cube edge, Å.				Mol. wts.	M. p., °C.	Sum of hts. of formation
		Phase I	Phase II	Accepted	Average			
1	a NaCl	5.628		5.628		58.45	804	
	KBr		6.555	6.570	6.099	119.01	730	192.39
	b NaBr	5.629		5.94		102.91	755	
	KCl		6.554	6.280	6.11	74.55	772	190.63
2	a NaCl	5.629		5.628		58.45	804	
	RbBr		6.852	6.868	6.248	165.36	682	194.42
	b NaBr	5.632		5.940		102.91	755	
	RbCl		6.856	6.570	6.255	120.90	715	191.30
3	a NaCl	5.628		5.628		58.45	804	
	CsBr		4.282	4.29	4.959	212.73	636	195.83
	b NaBr	5.632		5.94		102.91	755	
	CsCl		4.290	4.110	5.025	168.27	646	192.81
4	a NaCl	5.626		5.628		58.45	804	
	KI		7.052	7.052	6.340	166.03	698	177.12
	b NaI	5.627		6.46		149.93	651	
	KCl		7.050	6.280	6.370	74.55	772	173.76
5	a NaCl			5.628		58.45	804	
	RbI			7.325	6.477	212.37	642	179.13
	b NaI	5.626		6.46		149.93	651	
	RbCl		7.323	6.570	6.515	120.90	715	174.43
6	a NaCl			5.628		58.45	804	
	CsI			4.562	5.095	259.74	621	182.11
	b NaI	5.630		6.46		149.93	651	
	CsCl		4.562	4.110	5.285	168.27	646	175.94
7	a NaBr	7.052		5.94		102.91	755	
	KI		5.937	7.052	6.496	166.03	698	165.09
	b NaI	7.044		6.46		149.93	651	
	KBr		5.946	6.570	6.515	119.01	730	163.49
8	a NaBr			5.94		102.91	755	
	RbI			7.325	6.633	212.37	642	167.10
	b NaI	5.939		6.46		149.93	651	
	RbBr		7.325	6.868	6.664	165.36	682	165.52

TABLE II (*Concluded*)

Reaction	Reciprocal pairs	Cube edge, Å. Phase I	Phase II	Accepted	Average	Mol. wts.	M. p., °C.	Sum of hts. of formation
9	a NaBr			5.94		102.91	755	
	CsI			4.562	5.251	259.74	621	170.08
	b NaI	5.941		6.46		149.93	651	
	CsBr		4.557	4.290	5.375	212.73	636	166.93
11	a KCl	6.286		6.280	5.285	74.55	772	
	CsBr		4.281	4.290		212.73	636	201.77
	b KBr	6.286		6.570	5.340	119.01	730	
	CsCl		4.281	4.110		168.27	646	200.51
12	a KCl			6.280	6.802	74.55	772	
	RbI			7.325		212.37	642	185.07
	b KI	6.286		7.052	6.811	166.03	698	
	RbCl		7.318	6.570		120.90	715	183.73
13	a KCl			6.280		74.55	772	
	CsI			4.562	5.421	259.74	621	188.05
	b KI	6.281		7.052		166.03	698	
	CsCl		4.556	4.110	5.581	168.27	646	185.24
15	a KBr			6.570		119.01	730	
	CsI			4.562	5.566	259.74	621	177.78
	b KI	6.573		7.052		166.03	698	
	CsBr		4.556	4.290	5.671	212.73	636	176.23
17	a RbCl	6.574		6.570		120.90	715	
	CsI		4.563	4.562	5.566	259.74	621	188.72
	b RbI	6.575		7.325		212.37	642	
	CsCl		4.559	4.110	5.717	168.27	646	187.25
18	a RbBr	6.868		6.868		165.36	682	
	CsI		4.559	4.562	5.715	259.74	621	179.81
	b RbI	6.865		7.325		212.37	642	
	CsBr		4.559	4.290	5.807	212.73	636	178.24

limits of the method allowed measurements to be made. In order to make Table II as complete as possible the results for two or three of the reactions reported in the previous paper are included here also.

It will be noticed that in every case the average cube edge of the stable pair is less than the average of the reciprocal pair, *e. g.*, in reaction 1 the average cube edge of the stable pair (NaCl and KBr) is 0.011 Å. less than that for the pair NaBr–KCl, the smaller value representing the lower energy state. Furthermore, it is seen that the two heavier atoms (cation and anion) have combined with each other, as have the lighter two. This relationship holds quite generally throughout the reactions studied. It may be likewise noted that one member of the stable pair invariably has the highest melting point of the four compounds involved. There appears to be some doubt concerning the melting point of potassium iodide, values being reported in the literature from 678 to 773°. The last value is the one reported in the "International Critical Tables" but is certainly in error. It is very easy to show that the melting point of potassium iodide is less than that of potassium bromide, the accepted value for which is 730°. Mellor[6] gives 698° as the most probable value for the melting point of potassium iodide and this figure tentatively has been placed in Table II.

From known solid solubility data reported in our previous paper[2] and from additional data shown in Table I it is possible to say that reactions numbered 1, 2, 3, 7, 8, 9, 11, 12, 15 and 18 (Table II) go to completion. For example, the data for reaction number 2 show that the reaction

$$NaBr + RbCl \longrightarrow RbBr + NaCl$$

goes to completion in the direction indicated. This conclusion is not based on the mere absence of sodium bromide and rubidium chloride patterns. If the reaction did not go to completion, some rubidium chloride would remain which, according to the data shown in Table I, would dissolve in the rubidium bromide and the cube edge of the resulting solid solution would be less than that of pure rubidium bromide. In a similar manner

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[6] J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. II, p. 600.

the cube edge for sodium chloride would be raised by residual sodium bromide. An equimolecular mixture of sodium bromide and rubidium chloride was heated together on the one hand and on the other hand an equimolecular mixture of rubidium bromide and sodium chloride. In each case patterns for pure sodium chloride and rubidium bromide were obtained which results indicate quite clearly that the reaction has gone to completion in the direction indicated. In a similar manner it can be shown that the other reactions whose numbers are listed above go to completion and that the stable pair in each case is the one set opposite the letter (a) in Table II.

In the case of reactions 4, 5, 6, 13 and 17, no solid solutions have been observed, *e. g.*, in the case of equation 4 it is known that sodium chloride does not form a solid solution with either potassium chloride or sodium iodide nor does potassium iodide form a solid solution with sodium iodide. If these reactions did not go to completion, four patterns should be observed instead of only the two that were observed in each case. The mere absence of two patterns is not to be regarded as such satisfactory evidence for a completed reaction as was presented above for the sodium bromide–rubidium chloride reaction. It seems unlikely, however, that even though only a small amount of the reactants might remain, both patterns would be entirely absent. Referring again to reaction 4 it must be admitted that a small amount of potassium chloride might easily be missed in the presence of a large amount of potassium iodide but on the other hand it is not so probable that the entire sodium iodide pattern would fail to appear since the scattering power of the sodium iodide would compare very favorably with that of potassium iodide. At least the first few lines of the sodium iodide pattern might be expected even though the amount of sodium iodide were not very great. A similar argument would apply also to reactions 5, 6, 13 and 17.

Havighurst, Mack and Blake,[5] working with reaction number 4, reported cube edge values close to those for pure sodium chloride and potassium iodide which is in agreement with the values reported in Table II. A. G. Bergman and N. S. Dombrovskaya[7] have investigated the reactions

$$\mathrm{NaCl + KBr \rightleftarrows NaBr + KCl}$$
$$\mathrm{NaBr + KI \rightleftarrows NaI + KBr}$$

The second reaction has been further investigated by Obukhov[8] in which case it is written

$$\mathrm{NaI + KBr \longrightarrow NaBr + KI}$$

In the paper by Bergman and Dombrovskaya four continuous solid solutions and complete reversibility of the reciprocal pair was reported in each case. In the paper by Obukhov if the single arrow be taken to mean that sodium bromide and potassium iodide make up the stable pair the finding is in agreement with the results reported in Table II for reaction number 7.

In Table III the cube edge and heats of formation data are summarized. In each case the sum of the cube edges of the stable pair is less than that of the reciprocal pair and the sum of the heats of formation is greater. By means of the crystal lattice constant, the repulsive exponent in the Born potential expression and the proper Madelung constant Sherman[9] has calculated the crystal energies U_0 of the alkali halides. To these values of U_0 have been added the pv products to obtain the changes in heat content U. The differences in the sums of these U values for the stable pairs and the reciprocal pairs are listed also in Table III. The sum of the U values for the stable pair is greater in each case.

It is generally recognized that heats of formation are not in general to be used for predicting the direction in which a chemical reaction will go

TABLE III

SHOWING CORRELATION BETWEEN STABLE PAIRS, CUBE EDGES, MOLECULAR WEIGHTS, MELTING POINTS AND HEATS OF FORMATION

Reaction	Stable pairs	*Diff.* in av. cube edge of stable and reciprocal pairs, Å.	Diff. in hts. of formation of stable and reciprocal pairs, kg. cal.	*Diff.* in *U* values as calculated by Sherman,[9] kg. cal.
1	NaCl–KBr	−0.011	+1.76	+2.1
2	NaCl–RbBr	− .007	+3.12	+2.3
3	NaCl–CsBr	− .066	+3.02	+3.3
4	NaCl–KI	− .030	+3.36	+4.2
5	NaCl–RbI	− .038	+4.70	+4.9
6	NaCl–CsI	− .190	+6.17	+6.8
7	NaBr–KI	− .019	+1.60	+2.1
8	NaBr–RbI	− .031	+1.58	+2.6
9	NaBr–CsI	− .124	+3.15	+3.5
11	KCl–CsBr	− .055	+1.26	+1.2
12	KCl–RbI	− .009	+1.34	+0.7
13	KCl–CsI	− .160	+2.81	+2.6
15	KBr–CsI	− .105	+1.55	+1.4
17	RbCl–CsI	− .151	+1.47	+1.9
18	RbBr–CsI	− .092	+1.57	+0.9

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(7) Bergman and Dombrovskaya, *J. Gen. Chem.* (U. S. S. R.), **3**, 729 (1933).

(8) Obukhov, *ibid.*, **3**, 787 (1933).

(9) Jack Sherman, *Chemical Reviews*, **11**, 146 (1932).

but that the decrease in free energy can be used with confidence. Because of missing specific heat data and latent heats of fusion it is not at present possible to calculate the decrease in free energy for any of the reactions listed in Table II. It is believed, however, that the decrease in free energy would not in most cases be greatly different from the differences in heats of formation listed in Table III since the slopes of the specific heat curves would be expected to be quite similar to each other. Furthermore, since the temperature of fusion will in all cases be several hundred degrees absolute, the latent heat of fusion would probably not be an important factor in any case.

The point is well illustrated by use of the reaction

$$\mathrm{KF} + \mathrm{NaCl} \longrightarrow \mathrm{KCl} + \mathrm{NaF}$$

in which case the data have been found available for calculating the decrease in free energy according to the well-known equation

$$\Delta F = \Delta H - T\Delta S$$

The entropy was obtained by means of the equation

$$S_{\mathrm{T}} = \frac{L_f}{T_f} + \int_0^T C_p \frac{\mathrm{d}T}{T}$$

where S_{T} is entropy at temperature T, L_f is molecular heat of fusion, and T_f is fusion temperature in degrees absolute. The integral of C_p $\mathrm{d}T/T$ was obtained by graphical integration of the specific heat curves according to the method of Lewis and Randall. The value obtained for $T\Delta S$ was -0.38 Kg. cal./g. mole, from which the change in free energy was calculated according to the equation

$$\Delta F = -8.33 - (-0.38) = -7.95 \text{ kg. cal./g. mole}$$

The large negative value for ΔF indicates that the reaction should tend to go as indicated in the above equation; this conclusion is in agreement with the x-ray results for this reaction reported in our previous paper,[2] which showed that this reaction goes to completion. It is to be noted that the entropy change obtained is small by comparison with ΔH. It is to be expected that the entropy changes for all of the reactions shown in Table II will be small and furthermore Table III shows that in only one or two cases does there appear to be a possibility that the sign of ΔF might be changed by applying the entropy correction.

An effort to make an accurate correlation between the diminution in cube edge and the difference in the heats of formation was not successful although it would not be surprising to find that the free energy changes (when they become available) are definitely related to the cube edge diminutions.

Table IV shows data for three reactions that appear to require special comment. In the case of reaction number 10

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

it is to be noted that the cube edges of potassium bromide and rubidium chloride are equal to each other, *viz.*, 6.570 Å., and that the average cube edge of potassium chloride and rubidium bromide differs from this figure by less than the experimental error. If potassium bromide and rubidium chloride were the end-products of the reaction, their respective interference lines would fall one on top of the other since their cube edges are equal. However, since no interference lines with odd indices were observed and since both potassium

TABLE IV

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Reaction	Reciprocal pairs	Cube edge, Å.				Mol. wts.	M. p., °C.	Sum of hts. of formation
		Phase I	Phase II	Accepted	Average			
10	a KCl	6.575		6.280		74.55	772	
	RbBr		Only one phase	6.868	6.574	165.36	682	200.36
	b KBr	6.574		6.570		119.01	730	
	RbCl			6.570	6.570	120.90	715	199.00
14	a KBr	7.166		6.570		119.01	730	
	RbI		6.722	7.325	6.947	212.37	642	174.80
	b KI	7.164		7.052		166.03	698	
	RbBr		6.710	6.868	6.960	165.36	682	174.82
16	a RbCl	6.684		6.570	5.430	120.90	715	
	CsBr		4.228	4.290		212.73	636	202.44
	b RbBr	6.686		6.868	5.489	165.36	682	
	CsCl		4.232	4.110		168.27	646	202.54

bromide and rubidium chloride would produce such lines, it would be necessary to assume a homogeneous solid solution of the four kinds of ions. It would be necessary to assume the same homogeneous solid solution if it were supposed that the reaction went to completion in the direction of potassium chloride and rubidium bromide, since the two single patterns could be easily distinguished from each other. If it were assumed that the reaction did not go to completion in either direction two different patterns would be expected, each containing interference lines with odd indices. It would again be necessary to assume a homogeneous solid solution of the four kinds of ions.

The possibility that the single observed pattern is due to a compound was apparently eliminated by the results obtained from a mixture of two moles of potassium chloride and one of rubidium bromide. No lines with odd indices were observed. If a solid solution of the four ions be assumed, the cube edge would be expected to be the sum of two-thirds of 6.28 Å. and one-third of 6.868 Å. or 6.475 Å. The observed cube edge was found to be 6.476 Å. The situation is made even more interesting since it is known that solid solutions, stable at room temperature, are formed by the mixtures KBr–KCl; KBr–RbBr; RbCl–KCl and RbCl–RbBr (Table I).

Reactions 14 and 16 appear not to have gone to completion. Two patterns are obtained in both cases which do not correspond to any of the pure compounds. The same results were obtained regardless of which reciprocal pair was used as a starting point. The patterns for reaction 14 gave cube edges of 7.165 and 6.716 Å. The patterns for reaction 16 gave cube edges of 6.685 Å. (61.4 mole per cent. of rubidium chloride and 38.6 mole per cent. of rubidium bromide) and 4.230 Å. (66.6 mole per cent. of cesium bromide and 33.4 mole per cent. of cesium chloride). While the agreement between the percentage figures is not as good as could be desired, the authors do not believe that this lack of agreement is due to faulty observation. Measurements for the individual lines of the various patterns could be checked most satisfactorily but the cube edge values calculated from these lines were in much worse agreement with each other than was the case for the reactions of Table II. The authors are inclined to regard the explanation given as tentative. Probably the most interesting point to be noticed is that while these two reactions are the only two which appear definitely not to go to completion, there is no appreciable difference in the sums of the heats of formation in either case. Careful annealing carried out in both cases had little or no effect on the results.

Summary

The eighteen possible double decomposition reactions involving the chlorides, bromides and iodides of sodium, potassium, rubidium and cesium have been investigated by means of the x-ray spectrograph and the following conclusions appear to be justified:

1. Fifteen of the eighteen reactions have been found to go to completion in the direction of diminution of mean cube edge.
2. For each of these fifteen reactions the algebraic sum of the heats of formation was always a positive quantity.
3. One member of the stable pair has invariably been found to possess the highest melting point of the four compounds involved.
4. Stable pairs have been found in every case to consist of compounds in which the heavier atoms (cation and anion) have united with each other, the lighter atoms likewise uniting with each other.
5. In the case of one reaction in which the average cube edge on the two sides of the equation was the same the x-ray analysis could be best explained by assuming a homogeneous solid solution of the four ions involved.
6. In the case of two reactions for which the algebraic sums of the heats of formation were very nearly zero the reactions did not go to completion in either direction under the conditions of the experiment.

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