[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Rates and Mechanism of Phase Changes in Binary Mixtures of Alkali Halides

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Several binary mixtures of alkali halides have been observed to form solid solutions. This change has been detected in several ways. Bruni[1] has observed that the heat of solution of a mixture of sodium chloride–potassium chloride is changed by prolonged heating. Nacken[2] has observed a change in the index of refraction of the same system upon heating. Thomas and Wood[3] and others,[4] using X-ray methods, have observed the formation of solid solutions for several binary mixtures of alkali halides. The X-ray method of investigation leads to the most detailed information regarding the nature of the solid solution, and we have found that interesting facts regarding the mechanism of the change can be obtained.

To the present time very little has been reported regarding the rates of the reactions. Bruni[1] followed the change in heat of solution of sodium chloride–potassium chloride mixtures as a function of time of heating. Link and Wood[5] followed by the X-ray method the extent of the reaction $NaI + KBr = NaBr + KI$ as a function of time of heating. This reaction, while not a formation of a solid solution, is similar in that it results from a migration of ions. They also report[6] that a mixture of potassium chloride–potassium bromide forms a solid solution at 480° in thirty-six hours.

We have used X-ray powder photographs to study the rates of formation of solid solutions of the binary mixtures: KCl–KBr, NaCl–NaBr and NaCl–KCl, at several different temperatures and in the case of the NaCl–KCl system we have also observed qualitatively the rates of decomposition of the solid solution into the two pure components at several temperatures.

The following procedure was used for obtaining data on the rates of formation of the solid solutions: each salt was heated for twenty-four hours at 100°, crushed in a ball mill, sieved and the portion which would go through a sixty mesh but would not go through a one hundred mesh sieve was saved for the experiments. The particle size was accordingly about 0.2 mm. in diameter. This material was then weighed into equimolal binary mixtures. All the mixtures used in these experiments were equimolal. These operations were performed in a sealed room in which the air was continually circulated over trays of calcium chloride by electric fans.

Portions of the mixtures were then heated in porcelain crucibles for varying lengths of time at different temperatures in a resistance furnace, the temperature being measured by a chromel–alumel thermocouple and potentiometer. The temperature was controlled to ±5°. The salt mixtures were not packed in the crucibles, but were poured in. A uniform procedure was followed.

Samples were taken of the heated material and ground in an agate mortar that had been preheated to 80°, loaded into preheated glass tubes which were immediately sealed, and an X-ray powder picture taken in the usual manner. All of these precautions are necessary to exclude moisture from the experiment. The effect of moisture on the rate of solid solution will be discussed later.

A powder photograph of a mechanical mixture of two alkali halides shows all the lines characteristic of both of the two components. A photograph of a solid solution shows a set of lines similar to the set of lines for either pure component. The positions of the lines (and therefore the lattice constant) are intermediate between the positions of the corresponding lines from the two pure components. This is in accordance with Vegard's law[7] which states that the lattice constant of a solid solution varies linearly with the mole fraction of the components. The solid solution photographs show no new lines that require the existence of a superstructure. For instance, in the solid solution KCl–KBr the distribution of the anions is completely random in the anion positions.

KCl–KBr.—The first system to be examined was the system KCl–KBr. A KCl–KBr mixture will not form a solid solution at room temperature if kept free from moisture. We examined samples of a dry mixture over a period of five

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(1) G. Bruni, *Chem. Rev.*, **1**, 345 (1925).

(2) R. Nacken, *Sitz. kgl. preuss. Akad.*, 192 (1918).

(3) E. B. Thomas and L. J. Wood, THIS JOURNAL, **57**, 822 (1935).

(4) B. Broome, *Z. anorg. allgem. Chem.*, **143**, 60 (1925); T. Sasahara, *Sci. Pap. Inst. Phys. Chem. Res.*, **2**, 277 (1925).

(5) H. L. Link and L. J. Wood, THIS JOURNAL, **60**, 2320 (1938).

(6) H. L. Link and L. J. Wood, *ibid.*, **62**, 766 (1940).

(7) L. Vegard, *Z. Physik*, **5**, 17 (1921).

months and found no evidence of reaction. When a sample of the same mixture is exposed to the summer atmospheric humidity or is crystallized from water a solid solution is obtained. The accelerating effect which moisture has on the rate of solid solution makes necessary the technique which was described above. Unless these precautions were taken concordant results could not be obtained.

The mechanism of the formation of the KCl–KBr solid solution was studied in the following way. A mixture of KCl–KBr was heated to 500°. Samples of the mixture were removed from the furnace at different times. Powder photographs of samples which have been heated only a few minutes were identical with photographs of the dry unheated mixture. After a few hours of heating, the photographs began to change. The change was: first, the potassium bromide lines shifted toward the positions occupied by the solid solution lines and became more intense; second, the potassium chloride lines remained unshifted but grew weaker. This behavior is accounted for by the following mechanism: the solid solution is formed by the potassium chloride dissolving in the potassium bromide. The lines from the changing phase are somewhat diffuse indicating that the composition is not uniform. However, the phase is usually sufficiently homogeneous to produce X-ray lines which can be measured with a fair degree of accuracy. The fact that the potassium chloride lines disappear before they are shifted appreciably shows that the rate of solution of potassium bromide in potassium chloride is much less than the rate of solution of potassium chloride in potassium bromide. After prolonged heating of the mixtures the photographs become identical with those of solid solutions formed at low temperatures with the help of moisture.

The extent to which solid solution formation has taken place after an intermediate heating period can be estimated from the photographs in two ways. First, the decrease in intensity of the potassium chloride lines with respect to the potassium bromide lines can be used to estimate the extent of the reaction. Second, the shift of the potassium bromide lines toward the final position occupied by the lines for complete solid solution can be used to determine the amount of solid solution formation. The two methods of obtaining the rate of the reaction do not agree closely. Judging from the disappearance of the potassium chloride lines, at 500° the reaction is 50% complete in about twelve hours, but the potassium bromide lines do not shift half way to their final position until about thirty hours of heating.

We have followed the rates of formation of the KCl–KBr solid solution at several temperatures and have given the approximate time required for the potassium bromide lines to shift to their final position in Table I.

TABLE I

TIMES REQUIRED FOR COMPLETE SOLID SOLUTION FORMATION

Temperature, °C.	System		
	KCl–KBr	NaCl–NaBr	NaCl–KCl
700	1 hrs.	1–2 hrs.	Melts
600	12 hrs.	14 hrs.	16 hrs.
500	60 hrs.	72 hrs.	Incomplete at 100 hrs.
400	No appreciable reaction at 100 hrs.		

Link and Wood report[6] that at 480° solid solution is obtained in thirty-six hours. This suggests a faster rate than is indicated by Table I. The difference may be due to smaller particle sizes, tighter packing of the mixture into the furnace, or moisture.

We followed the lattice constant of the potassium bromide as a function of time of heating at each of the temperatures in Table I. These lattice constants are given in Table II. As the

TABLE II

LATTICE CONSTANT OF HEAVY COMPONENT AS A FUNCTION OF TIME OF HEATING FOR SEVERAL TEMPERATURES

KCl–KBr	
Time of heating, hr.	Lattice constant in Å.
700°	
0	6.58
1	6.43
600°	
0	6.58
2	6.52
6	6.48
8	6.47
12	6.43
500°	
0	6.58
12	6.55
24	6.51
36	6.50
48	6.46
60	6.43
400°	
0	6.58
100	6.58

NaCl–NaBr	
Time of heating, hr.	Lattice constant in Å.
700°	
0	5.93
1	Lines smeared
2	5.78
600°	
0	5.93
3	5.91
7	5.88
11	5.82
14	5.78
26	5.78
500°	
0	5.93
12	5.93
24	Lines smeared
36	Lines smeared
48	Lines smeared
60	5.87
72	5.78
400°	
0	5.93
100	5.93

changing potassium bromide phase is not strictly homogeneous, the observed lattice constants should perhaps be called average lattice constants, although the variation in composition is not great.

NaCl–NaBr.—The system NaCl–NaBr is similar to the system KCl–KBr in many respects. The stable condition of an equimolal mixture at room temperature is a solid solution. If a mechanical mixture of the two salts is allowed to become moist, or is crystallized from water, a solid solution results. The mechanism of the formation of the solid solution at high temperatures was studied in the same way as it was studied in the KCl–KBr system. A similar type of mechanism was found. Powder photographs of the dry unheated mixtures show all the powder lines of both components. As the mixture is heated the sodium bromide lines move toward the position occupied by the solid solution lines; the sodium chloride lines remain unshifted and decrease in intensity. The mechanism is therefore diffusion of the sodium chloride into the sodium bromide.

The time required to form a solution as measured by the shift of the sodium bromide lines to their final positions is given for several temperatures in Table I. The lattice constant of the sodium bromide as a function of time is given in Table II for several temperatures.

NaCl–KCl.—The system NaCl–KCl differs considerably from the two above systems. The stable condition for an equimolal mixture at room temperature is not a solid solution. A mixture can become moist and can even be precipitated from water and still no appreciable quantity of one component will dissolve in the other. If a solid solution is prepared at high temperatures (this can be done) then lowered to room temperature it will revert to the mechanical mixture unless it is kept strictly dry.

The time of formation of solid solution as a function of the furnace temperature is given in Table I. Experiments were carried out to determine the rate of unmixing of the solid solution. A solid solution formed at high temperature (above 500°) and left at 450° for one and a half hours is completely decomposed (unmixed). The same is true if the annealing is done at 350 or 270°. Annealing the solid solution for one and a half hours at 210° produces only a slight decomposition. A solid solution can be left at temperatures lower than this without decomposition for at least several days if it is kept dry.

Discussion

Each of the three mixtures of alkali halides for which we have studied solid solution formation contains a common ion. In the first mixture discussed it was K^+. In the second and third mixtures the common ions were Na^+ and Cl^-, respectively. The formation of solid solution takes place through a diffusion of ions. Each component of a mixture might be expected to dissolve in the other. However, the X-ray data show in the case of all three mixtures that the rates of solution of the two components are by no means equal. For instance, it was found that potassium chloride dissolved in potassium bromide much faster than potassium bromide dissolved in potassium chloride; or K^+ and Cl^- ions diffuse into the potassium bromide crystal much faster than K^+ and Br^- ions diffuse into the potassium chloride crystal. As there is only one positive ion the difference in behavior must be due to the difference in size of the two negative ions and the difference in lattice constants of the two crystals. The chloride ion is smaller than the bromide ion[8] and the lattice constant[9] of potassium bromide is greater than that for potassium chloride, therefore, one might expect that chloride ions could diffuse into potassium bromide more easily than bromide ions could diffuse into potassium chloride. In the second mixture sodium chloride was observed to dissolve in sodium bromide, presumably for the same reason. In the third mixture the solid solution was formed by the sodium chloride dissolving in the potassium chloride. The mechanism of formation of solid solution in all three cases is a dissolving of the substance having the smaller ion and smaller lattice constant in the substance having the larger ion and larger lattice constant.

The data in Table II show how the rate of formation of solid solution changes with temperature for the KCl–KBr system and the NaCl–NaBr system. The reactions are very rapid at 700° while at 400° no appreciable reaction occurs in one hundred hours. If the above-mentioned precautions for the exclusion of water are not taken, erroneously fast rates are obtained. It has been observed[5] that a NaCl–NaBr mixture forms a solid solution if held thirty-six hours at 480°. But it has also been reported (ref. 5, Table II) that the

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[8] L. Pauling, "Nature of the Chemical Bond," p. 9, Cornell University Press, Ithaca, N. Y., 1939.

[9] R. W. G. Wyckoff, "Structure of Crystals," Chemical Catalog Co., New York, N. Y., 1931.

reaction does not go to completion when the mixture is fused. The difference in behavior very likely was due to cooling the melt rapidly. The melting point is not congruent, and there is some separation of the components on freezing. Time is required at a temperature not far below the melting point if equilibrium (see Table I) is to be reached.

The data are not complete for the NaCl–KCl system because photographs taken during the reaction were too fuzzy to give accurate lattice constants. The variation in composition of the changing phase seems to be greater in this case than in the other two cases. After sixteen hours at 600°, the reaction was complete and the lines were sharp. At 500°, the rate is too slow to be measured and at 700°, the mixture is melted. Several procedures have been given for preparing a solid solution of NaCl–KCl. The reason for the difficulty in the preparation is that it is unstable at room temperature in contradistinction to the other two solid solutions. Some observers have reported the non-existence of this solid solution. Quenching the melt does not give a complete solid solution, presumably because the freezing point is not congruent and there is some separation of the two salts on freezing. However, if the quenched melt is annealed at 600° for one hour, a complete solid solution is obtained. This is more rapid than is indicated in Table I. The difference in behavior is probably due to particle size. It might be expected that quick freezing and decomposition of any solid solution formed at a high temperature might lead to small particles of salt, and that this finely divided material would then come to equilibrium at the high temperature in less time than is required by the coarser mixtures. The quickest method for preparing a solid solution is to melt the mixture and then freeze the melt at 600°. This is not a practical method, however, because it is difficult to cool the large solid mass rapidly enough to prevent decomposition just below the transition temperature (480°). The best method for preparing such a solid solution seems to be the following: melt the mixture then quench it. Powder the quenched melt in a ball mill or mortar and pestle. Anneal this material (without melting) at 600° for one hour. Remove a small sample of the powder from the hot furnace with a brass spoon. Grind (not too vigorously) with a warmed (80°) mortar and pestle and load into a dry sample tube. This method has the important advantage of taking the solid solution from 600°, where it is stable, down to a few degrees above room temperature in a few seconds.

The most important precaution which must be taken in doing this work is the elimination of water vapor. Summer atmospheric humidity is particularly dangerous. In the presence of damp air KCl–KBr or NaCl–NaBr mixtures form solid solutions spontaneously and independently of the heat treatment. NaCl–KCl mixtures in the presence of moisture revert to the mechanical mixture whatever its original condition.

Summary

Using X-ray powder photographs as a method of analysis we have observed the rates and mechanisms of the formation of solid solutions in equimolal mixtures of KCl–KBr, NaCl–NaBr and NaCl–KCl at several temperatures. In the case of the NaCl–KCl system we have also observed qualitatively the rates of decomposition of the solid solution. Methods for preparing a complete solid solution of NaCl–KCl are discussed.

PRINCETON, N. J. RECEIVED MAY 13, 1941