served in the present work. The most favorable conditions found for the formation of this product were the use of sodium chloride as electrolyte, and the maintenance of a temperature of 0° during electrolysis. The product tended to turn white on drying, but if washed first with water and then several times with 95% ethanol at 0°, it remained dark gray to black even after it had been warmed to room temperature and allowed to dry in a desiccator.

This substance has marked reducing properties, liberating hydrogen from acid solution and reacting with potassium permanganate solution to yield manganese dioxide. Microscopic examination showed the product to be a mixture of a white and a black substance, which could not readily be separated. Chemical analysis showed the white component to be magnesium hydroxide. The black component did not appear to be metallic magnesium; persistent efforts, however, to identify it positively as a compound containing unipositive magnesium have thus far been unsuccessful.

LAWRENCE, KANSAS

[CONTRIBUTION NO. 893, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Studies of NaCl–KCl Solid Solutions. I. Heats of Formation, Lattice Spacings, Densities, Schottky Defects and Mutual Solubilities[1,2]

BY W. T. BARRETT AND W. E. WALLACE

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Heats of formation, lattice spacings and densities of a series of NaCl–KCl solid solutions homogenized at 630° and quenched to room temperature are presented. Results of a redetermination of the solid state unmixing curve are also given. Data are included showing the number of Schottky defects in this system.

Introduction

Fontell in 1939 made[3] the first application of modern calorimetric techniques to the determination of the heat effects accompanying the formation of an alkali halide solid solution from its component salts. His measurements on the KCl–KBr system were later repeated and refined by Hovi.[4] At present there exist accurate heat of formation data for this and two additional systems, KCl–RbCl[5] and NaCl–NaBr.[6] The existence of this accurate body of thermal data and the obvious relationship to lattice theory has led to several attempts to account for the experimental heats of formation in terms of the lattice energies of the substances involved. Of these the two most recent—Wasastjerna[7] (1948) and Durham and Hawkins[8] (1951)—have been quite successful. Both treatments involved a novel feature. Instead of treating the lattice of the solid solution as uniform throughout, allowances were made for the fluctuations in interionic distances which result from the distribution of ions of unequal size over a common sublattice. Wasastjerna has, in addition, produced evidence suggesting the existence of local order in these solutions and has included in his treatment the effect of order on the calculated heats of formation.

In Wasastjerna's theory the heat of formation is proportional to the quantity $(1/R)(\Delta R/R_0)^2$, where ΔR is the difference in lattice spacing for the components and R_0 is the lattice spacing of the solution. Designating $(10^3/R_0)(\Delta R/R_0)^2$ as δ, his theory indicates that the heat of formation vanishes as δ approaches zero and indeed all deviations from ideal solution behavior disappear when δ is sufficiently small. Examination of Wasastjerna's treatment indicates that the necessary simplifying assumptions become more valid as δ approaches zero so that in effect he has produced a limiting law in δ.[9] For the three systems studied to date δ has been small and has covered only a limited range—7.0, 7.3 and 9.8 for KCl–RbCl, KCl–KBr and NaCl–NaBr, respectively. (δ values are for the equimolal solution.) It is obviously of interest to examine a system having an appreciably larger δ.

For sufficiently large δ's, the solid solutions are so endothermal with respect to their constituent that even at temperatures approaching their melting points continuous solid solubility does not occur. To study the properties of solutions over the entire composition range in a single phase one is limited therefore to systems whose δ values are less than some maximal value. The NaCl–KCl system with $\delta = 18.3$ is a case where δ is nearly maximal for continuous solubility and therefore provides an excellent opportunity for examining Wasastjerna's theory at the upper limit of δ.

This paper contains an account of measurements of (1) heats of formation, (2) lattice spacings, (3) densities, (4) Schottky defects and (5) mutual solid solubility relationships for the NaCl–KCl system. The following paper is devoted to an examination of the experimental data in the light of Wasastjerna's theory, with particular emphasis on the entropy, since this aspect of Wasastjerna's theory has not been subjected to experimental test. If

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(1) From a Thesis submitted by W. T. Barrett to the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, February, 1952.

(2) This work was assisted by the Atomic Energy Commission and the Office of Naval Research.

(3) N. Fontell, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **10**, No. 6 (1939).

(4) V. Hovi, *Ann. Acad. Sci. Fennicae*, **AI**, No. **55**, (1948).

(5) N. Fontell, V. Hovi and L. Hyvonen, *ibid.*, **IA**, No. **65**, (1949).

(6) M. A. Fineman and W. E. Wallace, THIS JOURNAL, **70**, 4165 (1948).

(7) J. A. Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, [XIV] **3**, 1 (1948); *ibid.*, [XIV] **7**, 1 (1948); *ibid.*, [XV] **3**, 1 (1949). *Cf.* also V. Hovi, *ibid.*, [XV] **12**, 1 (1950).

(8) G. S. Durham and J. A. Hawkins, *J. Chem. Phys.*, **19**, 149 (1951).

(9) This is probably true of Durham and Hawkins' procedure also although it is less obvious in that case.

there exists, as Wasastjerna supposes, local order in alkali halide solid solutions, the entropy of formation should be less than that of random mixing. The solubility relationships were ascertained for use, along with the heats of formation, in estimating the entropies of formation. (Details are given in the following paper.) Determinations of the lattice spacings at various compositions were made because this information was needed to obtain the necessary solubilities. These data are, of course, of interest in themselves in indicating the extent of the departure from Vegard's Rule for a system having a large δ value.

As will be shown later, the entropies of NaCl–KCl solid solutions are surprisingly large; indeed, at some compositions, they exceed the entropy of random mixing. A similar situation was encountered with certain of the solid solutions in the magnesium–cadmium system. There the anomalous entropy was traced to the extra entropy arising from a surprisingly large number of Schottky defects in the crystalline solution. The densities reported in the present paper were for the purpose of establishing (1) the extent of Schottky defects in the NaCl–KCl solid solutions and (2) whether the extra entropy can be accounted for by the observed number of vacant lattice sites.

Experimental

Preparation of the Solid Solutions.—Sodium chloride and potassium chloride were prepared from the Baker and Adamson Reagent Grade salts by recrystallizing twice from water which had a conductivity of 1×10^{-6} ohm^{-1}. The salts were dried by fusing in a platinum dish, cooled and stored in a desiccator.

The purified salts were analyzed gravimetrically for chloride:

Salt	NaCl	KCl
Wt. % Cl found	60.665	47.568
Wt. % Cl calcd.	60.658	47.559

NaCl–KCl solutions are thermodynamically unstable at room temperature. Contact with a very small amount of water at room temperature will cause separation into nearly pure sodium chloride and potassium chloride. The solid solutions were prepared by weighing out the proper amount of the pure salts into a platinum dish, fusing in an electric muffle furnace with occasional stirring for about $^1/_2$ hr. and pouring into another cold platinum dish. The salt cake was then ground and about 6-g. portions placed in 6–8 mm. Vycor glass tubes. The tubes were evacuated with a mechanical vacuum pump, degassed at 150–200°, filled with pure helium to about 300 mm. pressure and then sealed off. The Vycor tubes containing the salts were held from 3 to 8 days at 630° and then quenched by removing from the furnace and immediately immersing in ice-water. All samples were checked for homogeneity by X-ray diffraction. While occasionally the above method failed to give homogeneous samples, the data reported below were taken with homogeneous samples, except, of course, those used to determine solubilities. Certain of the heat of formation samples were heat treated at lower temperatures after the 630° homogenization.

The sample tubes were opened in a dry-box which had been evacuated and filled with very pure helium. Filling of heat of formation sample bulbs, X-ray tubes and density bulbs was done in the dry-box. Vessels were fitted with temporary stoppers so that they could be removed and sealed off. This dry-box and the procedures involved have been described elsewhere in detail.[10]

The mole fraction of each component of the solid solutions was calculated from the weight of salts used. Weight losses during fusion of the salts were about 0.13 mg. per g. of fused salts indicating that the uncertainty in composition was less than 2 parts per 10,000.

Heats of Formation.—The equipment used was the modified Lange-type twin differential calorimeter described by Fineman and Wallace.[6] The method consisted in bringing the calorimeter to equilibrium with a sealed-off thin wall glass bulb containing about 2 g. of solid solution in one side and a bulb containing a mechanical mixture of the two pure salts of the same mass and composition in the other side. The bulbs were crushed and enough heat added electrically to the mechanical mixture side to return the temperature difference to very nearly zero. This amount of heat was equal to the heat of formation of the amount of solid solution used, subject to small corrections to allow for inequalities in heat capacity of the two sides,[11] temperature difference between the two sides, and differences in masses of solid solution and mechanical mixture. The quantity of sample used varied from about 0.01 to about 0.04 mole, and the measured heat effects ranged from about 3 to about 30 cal.

Lattice Spacings.—The samples for X-ray diffraction were held in sealed, helium filled, Vycor glass tubes[12] with 0.5–0.7 mm. diameter and 0.02–0.04 mm. wall thickness. The samples were ground, passed through a 200-mesh screen and loaded in the Vycor tubes in the dry-box. Patterns were taken using a 114 mm. diameter camera with a 1-mm. pinhole. Nickel filtered copper radiation was employed throughout. The wave lengths used were those recommended by Bragg[13]: $\text{Cu}K\alpha_1$ = 1.54050 Å. and $\text{Cu}K\alpha_2$ = 1.54434 Å. Lattice constants were evaluated from the resolved doublets at Bragg angle ranging from 55 to 85°. Extrapolation to 90° was made by the Bradley and Jay[14] procedure. The observed lattice spacings were corrected from the sample temperature (usually about 35°) to 25° using thermal expansivity[15,16] data for the pure salts and a composition averaged value for the solutions.

Densities.—These were measured by the suspension method. Samples of the solid solutions were pulverized and added to a mixture of carbon tetrachloride and ethylene dibromide. The pure dry liquids were added to the mixture until the solid solution particles were very nearly suspended. A sample of the suspending liquid was then drawn into a pycnometer.[17] A portion of the liquid with the suspended solid solution particles was placed in a sample tube, which was then closed with a ground glass stopper. All of the above operations were done in the helium filled dry-box.[10] The sample tube and pycnometer were removed from the dry-box and placed in a water-bath. Temperature was adjusted until the solid solution particles remained suspended for at least 3 min. The pycnometer volume was read, temperature recorded, the pycnometer weighed and the density calculated. The crystal densities at the measurement temperature (25 to 38°) were corrected to 25° by use of the thermal expansion data.[15,16]

Solubility Relationships.—The solid solubilities were determined by thermostating samples of solid solution at various temperatures, quenching and measuring the lattice constant of each of the two phases present by their X-ray diffraction. The samples of solid solution were originally 0.5 mole fraction NaCl except for the sample annealed at 496°, which was originally 0.6 mole fraction NaCl. The samples, in the Vycor X-ray sample tubes described above, were placed in $^1/_{16}$-in. holes drilled in a copper block which was held in a small electric furnace controlled by a Variac and a Sola constant voltage transformer. A Chromel–Alumel thermocouple (calibrated against a lead melting point stand-

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[10] E. E. Ketchen, F. A. Trumbore, W. E. Wallace and R. S. Craig, *Rev. Sci. Instruments*, **20**, 524 (1949).

[11] This correction requires a value for the heat of solution of the mechanical mixture which is correct to 5 to 10%. As the total molality was rather low (about 0.02 *m*), the heat of solution could be obtained by assuming the heat content of each pure salt to be independent of the NaCl–KCl ratio at constant total molality. Thus, a sufficiently precise heat of solution of the mixture could be computed from the integral heats of NaCl and KCl in water at 0.02 *m*, taken to be 975 and 4165 cal./mole, respectively.

[12] Vycor is considerably more transparent to X-rays than Pyrex and therefore is much superior as a sample holder.

[13] W. L. Bragg, *J. Sci. Instruments*, **24**, 27 (1947).

[14] A. J. Bradley and H. Jay, *Proc. Phys. Soc.*, **44**, 573 (1932).

[15] M. Straumanis, A. Ievins and K. Karlsons, *Z. anorg. allgem. Chem.*, **238**, 175 (1938).

[16] A. Eucken and W. Danohl, *Z. Elektrochem.*, 40, 814 (1934).

[17] W. Lipkin, J. Davison, W. Harvey and S. Kurtz, *Anal. Chem.*, **16**, 55 (1944).

ard certified by the National Bureau of Standards) was inserted into one of the holes in the copper block. At the end of the thermostating period the sample tubes were allowed to drop directly from the furnace into cold water. By analyzing the X-ray diffraction pattern, two a_0 values from each film were obtained. A large scale plot of a_0 *versus* composition had been previously prepared by X-ray diffraction measurements on a series of homogeneous samples and the compositions of the two saturated solutions were read from this plot.

Results of Measurements

Heats of Formation of the Solid Solutions.—The limited mutual solid solubilities of NaCl and KCl at temperatures below 500° and earlier calorimetry involving this system indicated that the solid solutions are formed endothermally from their components. The present results confirm that the solutions are formed with an absorption of heat. The measured values are shown in Table I. It is to be noted that these results pertain to a solution which was formed at 630° (the homogenization temperature) and quenched to room temperature, The calorimetry was performed at 25°. Thus, while the vibrational energies of the solutions were characteristic of 25°, their configuration was the frozen-in equilibrium configuration for a temperature of 630°, or slightly below.

The heat of formation of the equimolal solution is in good agreement with the early value obtained by Zhemchuzhnuii and Rambach,[18] 1050 cal./mole, and the more recent value of Popov, *et al.*,[19] 1058 ± 10 cal./mole.

The effect of quenching temperature on the heat of formation was measured by an adaptation of the method employed to obtain the data in Table I. The differential calorimeter was used with one side containing a sample of an equimolal solid solution heat treated at 630° and the other side containing a sample identical in all respects except that it was heat treated at 500°. In two such measurements the sample quenched from 630° was found to have the larger heat of formation to the extent of 11 and 15 cal./mole. From these data one calculates ΔC_p between 500 and 630° to be 0.10 cal./°C. mole, a value which corresponds, possibly fortuitously, with an average value of 0.07 cal./°C. mole obtained by Popov, *et al.*,[20] from direct specific heat measurements on NaCl–KCl solutions between 20 and 600°.

Table I

Heats of Formation of NaCl–KCl Solid Solutions Measured at 25°

Mole fraction of NaCl	No. of experiments	Heats of formation, cal./mole
0.100	4	402 ± 2
.300	4	858 ± 2
.500	6	1046 ± 6
.700	5	877 ± 2
.900	4	464 ± 3

The heats of formation of KCl–KBr, NaCl–NaBr and KCl–RbCl were quite satisfactorily represented[4–6] by an equation of the form $\Delta H = aN + bN^2 + cN^3$, where N is the mole fraction. The data in Table I cannot be represented by the same type of equation. Several attempts were made to develop a three-constant equation of different form for the KCl–NaCl data. These were all without success.

Lattice Spacings.—As the two pure salts and the several solid solutions all crystallize in the NaCl-type structure, there is only one lattice parameter for each composition. The data are given in Table II. Again it is to be noted that while the measurements are for 25° the frozen-in configuration is characteristic of about 630°. The values in Table II are uncertain to ±0.0005 Å. arising principally from a variation of ±2° in the sample temperature during the time of exposure. Also included in Table II are the values expected from Vegard's additivity rule[21] and differences between those and the observed values.

Table II

Lattice Spacing of NaCl–KCl Solid Solutions Measured at 25°

Mole fraction NaCl	Lattice spacing, Å. Obsd.	Vegard's rule	Deviation × 10^4
0.0000	6.2916	....	...
.1002	6.2354	6.2264	90
.2997	6.1185	6.0963	222
.3835	6.0654	6.0417	237
.4999	5.9913	5.9658	255
.5037	5.9883	5.9634	249
.5981	5.9256	5.9019	237
.6990	5.8571	5.8361	210
.8243	5.7705	5.7565	160
.9003	5.7156	5.7050	106
1.0000	5.6400	....	...

Densities.—The observed densities corrected to 25° are presented in Table III along with the corresponding quantities computed from the unit cell dimensions given in Table II. The latter are uncertain in all cases by ±0.03%, reflecting the constant uncertainty of 0.01% in the lattice spacings. Assuming that (1) the fraction of interstitial ions (Frenkel defects) is negligible and (2) the vacancies are equally numerous on the anionic and cationic sites, the data in columns 2 and 3 may be employed to compute the percentage Schottky defects listed in column 4.

Table III

Densities of NaCl–KCl Solutions

Mole fraction NaCl	Density, g./cm.^{3} at 25° Obsd.	Calcd. (lattice sp.)	Schottky defects, %
0.0000	1.9880 ± 0.0001	1.9881	0.00
.1002	1.9964 ± .0002	1.9982	.09
.2997	2.0117 ± .0009	2.0217	.49
.4999	2.0368 ± .0008	2.0538	.82
.6990	2.0683 ± .0003	2.0922	1.14
.9003	2.1321 ± .0009	2.1365	0.20

An interesting aspect of the density measurements was that the densities appeared to vary systematically with particle size, increasing with decreasing size. The data in column 2 of Table III refer to "large" particles, $^1/_2$ to 2 mm. in linear di-

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(18) S. Zhemchuzhnuii and J. Rambach, *Z. anorg. Chem.*, **65**, 403 (1910).

(19) M. M. Popov, S. M. Skuratoff and M. M. Strel'tsova, *J. Gen. Chem.* (*Russ.*), **10**, 2023 (1940).

(20) M. M. Popov, S. M. Skuratoff and I. N. Nikanowa, *ibid.*, **10**, 2017 (1940).

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

mensions. With pure KCl the "very fine" particles, which appeared only as a cloudiness in the liquid, were more dense than the large particles by 0.0012 g./cm.^{3}. Even larger differences were noted for some of the solutions. The equimolal solution showed the maximum difference, 0.017 g./cm.^{3} or 0.8%. In some cases, including pure KCl, the density of the fine particles exceeded that calculated from the X-ray data.

The source of these differences has not been established. Perhaps in pure KCl the effect of the surface forces is sufficient to account for the large density of the fine particles. The much greater differences between the large and fine particle densities for the solutions suggest that some other factor must be involved. One possibility is that when the large particles are broken up to produce the very fine particles, fracture occurs in planes possessing a considerable number of Schottky defects. In this way the fraction of Schottky defects in the fine particles would be reduced and the density increased.

Mutual Solid Solubilities.—Earlier it was indicated that entropies of the solid solutions were to be estimated using the solid solubility data at various temperatures. Sufficient data were available in the "International Critical Tables"[22] for carrying out the desired calculations. However, as the original work was rather old, it seemed desirable to verify a few solubilities before using them for calculating entropies. Immediately, substantial differences were found between the measured solubilities and the data given in the "International Critical Tables," whereupon the entire solid solubility curve was redetermined. The results of this redetermination are shown in Table IV and in Fig. 1.

TABLE IV

MUTUAL SOLID SOLUBILITIES OF NaCl AND KCl

Time, days	Thermostat temp., °C.	Composition of phases Mole fraction NaCl	
25	367	0.170	0.956
31	367	.170	.956
24	422	.291	.904
35	422	.288	.904
11	462	.388	.861
19	462	.388	.862
8	496	.564	.708

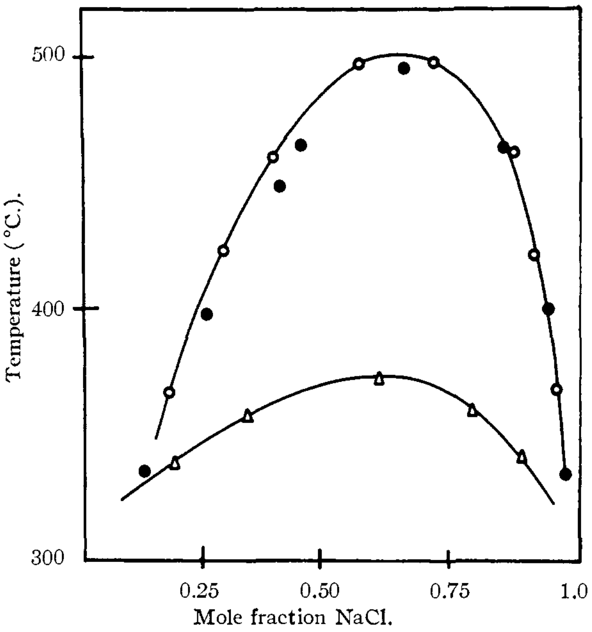

Fig. 1.—Solid solubilities of NaCl–KCl: ○, this work; ●, Nacken; Δ, "International Critical Tables."

The measured solubilities in Table IV were obtained in all cases by starting with the homogenous solid solutions. It is perhaps in order to indicate why no attempts were made to approach equilibrium from the direction of a mixture. Nacken measured[23] these same solubilities using a procedure which seems in all respects sound. In his work equilibrium was approached from both directions and it was found that precipitation was complete well within 8 days at all temperatures above 335°. This observation was corroborated by Matsen and Beach[24] who found complete phase segregation in 1.5 hr. for temperatures extending down to 270°. The long times in the thermostat, the constancy of the solubilities over periods of 7 to 10 days and the sharpness of the diffraction lines left little doubt that the system was in equilibrium.

Solid solubilities obtained by Nacken and in the present study are shown in Fig. 1 along with results given in the "International Critical Tables." The reason why the latter set of data diverge so sharply from the first two is fairly clear. The ICT results appear to be based on several investigations including Nacken's, each being given equal weight. All investigators except Nacken located the phase boundary by conventional thermal analysis (*i. e.*, cooling curves), which, due to the sluggishness of the phase segregation reaction, leads to too low a temperature. Nacken's procedure was essentially the same as that employed in this paper, except that the method of analysis was based on refractive index measurements. Nacken's uncertainty in temperature was stated to be ±10° and in mole fraction appears to be about ±0.01 whereas the corresponding quantities in this study are ±2° and ±0.002. In all cases the difference between Nacken's and the present results is within the limit of combined errors. Nacken's critical conditions are 495° and 65 mole % NaCl whereas in this study they were found to be 502° and 64 mole % NaCl.

The asymmetry of Fig. 1 follows the familiar pattern, namely, that at a given temperature it is more difficult to replace a small ion in the lattice with a large one than to do the reverse. This same feature is evident in the heats of formation where the energy rises more rapidly on the NaCl end.

PITTSBURGH, PA.

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[22] "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 68.

[23] R. Nacken, *Sitzber. preuss. Akad. Wiss., Physik.-math. Klasse*, 192 (1918).

[24] F. A. Matsen and J. Y. Beach, THIS JOURNAL, **63**, 3470 (1941).