[Contribution No. 894, Department of Chemistry, University of Pittsburgh]

Studies of NaCl–KCl Solid Solutions. II. Experimental Entropies of Formation and a Comparison of Certain Thermodynamic Properties with Values Calculated from Wasastjerna's Theory[1,2]

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Received July 31, 1953

Experimental entropies of formation of NaCl–KCl solid solutions are obtained from the solid solubility curve and calorimetrically determined heats of formation by reversal of the method of common tangents. These data and the heats of formation are compared with results computed using Wasastjerna's theory assuming (a) a random distribution and (b) a partially ordered solution. The observed heats of formation correspond with (b) but the entropies deviate positively from the ideal entropies of formation, whereas the existence of local order requires a negative deviation. The entropy agrees fairly well with that computed assuming random mixing when the effect of the large number of Schottky defects is included.

Introduction

A few years ago Wasastjerna[3] published a series of significant papers dealing with the statistical thermodynamics of alkali halide solid solutions. Treating them as regular assemblies,[4] with due allowance for the contribution of the non-nearest neighbor interactions in the coulombic term, he was able to evaluate the partition function of the solutions exclusively in terms of properties (density, thermal expansivity and compressibility) of the pure components. This partition function, with some minor improvements by Hovi,[5] has been used to obtain an expression for the heat accompanying the formation of an alkali halide solid solution from its component salts. For KCl–KBr, KCl–RbCl and NaCl–NaBr remarkably good agreement has been found[5,6] between the computed and observed heat effects.

In Wasastjerna's treatment the traditional notion that the species are randomly distributed over the two sub-lattices has been discarded in favor of the idea that a certain amount of local order exists. Some support for this position is provided by Wasastjerna's earlier work[7] dealing with measurements of the intensities of the X-ray diffraction lines of solid solutions. In addition, the heat of formation calculated assuming partial order in the lattice agrees in Wasastjerna's development with experiment better than the value calculated assuming a random distribution. However, Durham and Hawkins have computed[8] heats of formation by a method based on the Born–Mayer theory of ionic lattices under the assumption that the distribution is random and have accounted for the observed data, at least for KCl–KBr, about as well as Wasastjerna. Hence, the existence of partial order does not appear to be completely established.

As pointed out in the preceding paper[9] (hereinafter referred to as I), it is of interest to ascertain the entropies of some of the alkali halide solid solutions because of the intimate relationship between disorder and entropy and the information which such data will provide concerning whether or not the distribution is appreciably non-random. In this paper the solubility relationships and the heats of formation presented in I are used, after making some simplifying assumptions, to obtain what are called "observed" entropies. These are compared with the results expected from Wasastjerna's theory and the ideal value (random mixing). Comparison of the calculated and observed heats of formation are also presented.

The Observed Entropies of Formation

Method Employed.—When curves of free energy *versus* composition at various temperatures are available, the determination of solubility limits is accomplished[10] by the well known "method of common tangents." Entropies in the present case are determined by the reverse of the usual procedure. In principle free energies are determined from the measured solid solubilities and entropies are computed from these with the aid of the known heats of formation. This procedure is clearly an awkward one at best. It was one dictated by necessity. The usual methods for establishing entropies are difficult, to say the least, when applied to NaCl–KCl. Uncertainty about the state of order eliminates an approach based on the Third Law of Thermodynamics. The use of an electrochemical cell is not very feasible in this case so that a procedure based on some equilibrium measurement is the sole remaining practical possibility. These experimental limitations explain in part why there have been no previous determinations of entropies of formation for this type of system.

Relative Partial Molal Heat Contents.—These were needed for the entropy calculations. The partial molal heat contents relative to the pure salts were obtained from the equations

$$\bar{H}_1 - H_1^s = \Delta H - N_2 \frac{d(\Delta H)}{dN_1} \qquad (1)$$

$$\bar{H}_2 - H_2^s = \Delta H - N_1 \frac{d(\Delta H)}{dN_2} \qquad (2)$$

where N_1 and N_2 are mole fractions. The ΔH's from I were plotted on a large scale and ΔH values

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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) J. A. Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, [XIV] No. 3 (1948); [XIV] No. 7 (1948); [XV] No. 3 (1949).

(4) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, Cambridge, 1939, p. 245.

(5) V. Hovi, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, [XV] 12 (1950).

(6) V. Hovi, *Arkiv Fysik*, **5**, 6 (1952).

(7) J. A. Wasastjerna, *Acta Soc. Sci. Fennicae*, **3A**, No. 8 (1944).

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

(9) W. T. Barrett and W. E. Wallace, This Journal, **76**, 366 (1954).

(10) See, for example, F. Seitz, "The Modern Theory of Solids," McGraw-Hill Book Co., New York, N. Y., 1940, p. 499.

read at intervals of 0.1 in mole fraction. The slopes were determined using the differentiated form of Lagrange's interpolation formula.[11] The results are shown in Table I. The data are based on heat of formation measurements at 25°. The samples were, however, quenched from 630° and had a configuration characteristic of that temperature, or slightly below. It is assumed in this study that C_p for the solid solution *at constant configuration* is given by the Kopp–Neumann relationship so that the heat of formation *at constant configuration* is independent of temperature. Thus the data in Table I are assumed to be the same as those which would have been obtained had the calorimetry been performed at 630°.

TABLE I

RELATIVE PARTIAL MOLAL HEAT CONTENTS OF NaCl–KCl SOLID SOLUTIONS

Mole fraction NaCl, N_1	$\bar{H}_1 - H_1^s$, cal./mole	$\bar{H}_2 - H_2^s$, cal./mole	Mole fraction NaCl, N_1	$\bar{H}_1 - H_1^s$, cal./mole	$\bar{H}_2 - H_2^s$, cal./mole
0.0	5003	0	0.6	641	1533
.1	3303	80	.7	435	1908
.2	2426	226	.8	310	2288
.3	2031	355	.9	162	3185
.4	1593	600	1.0	0	7217
.5	1167	1033			

Relative Partial Molal Heat Capacities.—To a fairly good approximation these can be taken as zero and the data in Table I can be regarded as temperature independent. A slightly better approximation can be made by taking cognizance of the small temperature coefficient of the partial molal heat contents. In I it was stated that an equimolal solution heat treated at 630° had a heat of formation 13 cal./mole higher than a similar solution heat treated at 500°.[12] Thus ΔC_p averaged over this temperature interval is 0.10 cal./mole °C. In general the thermodynamic properties of a solution relative to the equivalent mixture show a parabolic dependence on mole fraction with a maximum at the equimolal solution and zero values, of course, at mole fraction 0.0 and 1.0. ΔC_p undoubtedly follows this behavior as closely as needed for the present purposes and hence $\Delta C_p = 0.4 N_1 N_2$ from which $\bar{C}_{p_1} - C_{p_1}{}^s = 0.4\ N_2{}^2$ and $\bar{C}_{p_2} - C_{p_2}{}^s = 0.4\ N_1{}^2$. It is assumed that these relations are valid in the range 367 to 630°.

Relative heat capacities computed from the expressions given will certainly be of low accuracy in view of the assumptions made. However, these data are needed merely to correct heat contents and entropies from one temperature to another and such errors as they contain introduce second-order errors into the quantities sought. In fact, the temperature coefficients are so small they could be ignored entirely with little effect on the final entropy results.

The Entropy Calculation.—In the remainder of this paper subscripts 1 and 2 refer to NaCl and KCl, respectively. For two phases, designated by prime and double prime, in equilibrium at temperature T

$$\bar{F}_{i'} = \bar{F}_{i''} = \bar{H}_{i'} - T\bar{S}_{i'} = \bar{H}_{i''} - T\bar{S}_{i''} \qquad (3)$$

where i = 1 or 2. Hence

$$\bar{S}_{i'} - \bar{S}_{i''} = (\bar{H}_{i''} - \bar{H}_{i'})/T \qquad (4)$$

$\bar{S}_{i'} - \bar{S}_{i''}$ ($= \Delta\bar{S}_i$) values were computed from interpolated values of the data in Table I after correcting the appropriate ΔH_i's to the corresponding temperature. The $\Delta\bar{S}_i$'s so obtained each referred to a different temperature. All were then corrected to the common temperature of 630°.

At this stage the data consisted in a set of $\Delta\bar{S}_i$'s for various differences in mole fraction. It was necessary to extrapolate $\Delta\bar{S}_1$ to $N_1 = 1$ and $\Delta\bar{S}_2$ to $N_2 = 1$ to obtain $\bar{S}^i - S_i{}^s$. The $\Delta\bar{S}_i$ values were placed on a graph having $-\log N_i$ as the abscissa and $\bar{S}_i - \bar{S}_i{}^s$ as ordinate. The ΔS_i's were fitted together so as to form a smooth curve and zero on the ordinate was established as the intercept on the ordinate axis.

The construction of the curve was aided by the fact that $d\bar{S}_1/d \ln N_1 = d\bar{S}_2/d \ln N_2$, the Gibbs–Duhem–Margules relationship. Furthermore, for ideal solutions the points fall on a straight line with slope $-R$. The curves for NaCl–KCl were in fact almost linear and with slopes differing only slightly from $-R$. $\bar{S}_i - S_i{}^s$ was read from the curve at even intervals and the entropies of formation listed in Table III were computed from the equation

$$\Delta S = N_1(\bar{S}_1 - S_1{}^s) + N_2(\bar{S}_2 - S_2{}^s) \qquad (5)$$

Thermodynamic Quantities from Wasastjerna's Theory

The several equations needed will be given following Wasastjerna's notation with only minor variations.

$$Q = \frac{N_0 c e^2}{R_0} N_1 N_2 \left(\frac{\Delta R}{R_0}\right)^2 \qquad (6)$$

where Q is referred to as the electrostatic contribution to the heat of formation, N_0 is Avogadro's number, c is the Madelung constant, e is the electronic charge, R_0 is the anion–cation distance for the solid solution computed from Vegard's Rule, ΔR is the difference in anion–cation distance for the two pure components.

ΔH_r is the heat of formation if the distribution is random and ΔH_{nr} is the corresponding quantity when there is a degree of local order σ where σ is defined[13] by the relationship that the probability of finding an anion surrounded by unlike cations is $2N_1N_2(1 + \sigma)$. A characteristic quantity θ for each component is defined by

$$\theta_i = \frac{3 + 4T\gamma}{(Kce^2/6R^4) - T\gamma} \qquad (7)$$

where γ and K are the thermal expansivity and compressibility, respectively, and R is the anion–cation distance.

According to the Wasastjerna theory

$$\Delta H_r = Q[(\theta_1 + \theta_2)/8 + {}^1/_2] \qquad (8)$$

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[11] T. R. Running, "Empirical Formulas," John Wiley and Sons, Inc., New York, N. Y., 1917, p. 111.

[12] This in no way conflicts with the earlier statement that the heats of formation measured at 25° apply to 630° as well. The assumed constancy is for constant configuration. Solutions heat treated at different temperatures have different configurations.

[13] This order parameter is identical with that used by H. A. Bethe. *Proc. Roy. Soc.* (*London*), **A150**, 552 (1935).

$$\Delta H_{\mathrm{nr}} = Q\left\{\frac{\theta_1}{8}\left[(1 + \sigma(1 - 4N_2)\right] + \frac{\theta_2}{8}\left[(1 + \sigma(1 - 4N_1)\right] + \frac{\sigma + 1}{2}\right\} \quad (9)$$

$$\Delta S = -R[N_1 \ln N_1 + N_2 \ln N_2] - R[\chi \ln \chi + \lambda \ln \lambda + \mu \ln \mu + \nu \ln \nu] \quad (10)$$

where $\chi = N_1(N_1 - N_2\sigma)$, $\lambda = N_1N_2(1 + \sigma)$, $\mu = N_2N_1(1 + \sigma)$ and $\nu = N_2(N_2 - N_1\sigma)$, the quantities being the probability of finding (in the NaCl–KCl case) Cl^- between Na^+ and Na^+, Na^+ and K^+, K^+ and Na^+ and K^+ and K^+, respectively.

σ was found by Wasastjerna as usual by maximizing the configurational partition function with respect to σ. The result was

$$\sigma = \frac{1 - 2N_1N_2z - \sqrt{1 - 4N_1N_2z}}{2N_1N_2z} \quad (11)$$

where

$$z = 1 - \exp\left\{\frac{ce^2}{R_0}\left(\frac{\Delta R}{R_0}\right)^2 \frac{[\theta_1(1 - 4N_2) + \theta_2(1 - 4N_1) + 4]}{8kT}\right\} \quad (12)$$

The data used in evaluating the thermodynamic quantities are shown in Table II. The results of calculations are shown in Table III along with the measured values. The assignment of 630° to the calculated results merits some comment. In the calculation of σ only $\Delta H_{\mathrm{r}} - \Delta H_{\mathrm{nr}}$ (not the individual values) enters[14] so that little error is introduced into σ by using values for K, γ and R at room temperature instead of 630°. The calculated entropy depends only on σ and composition so it is for 630°. The calculated heats of formation have a configurational part, *i.e.*, that which depends on σ, characteristic of 630° and all else which refers to room temperature. This corresponds exactly to the situation with the measured heat effects as pointed out in I.

TABLE II

DATA USED TO CALCULATE ΔH AND ΔS FROM WASASTJERNA'S THEORY

	Compressibility (K),[a] Bayres^{-1}	Thermal expansivity(γ) (°C.)$^{-1}$	Lattice constant,[d] Å.	θ
NaCl	4.20×10^{-12}	12.15×10^{-5}[b]	2.8200	7.696
KCl	5.65×10^{-12}	12.45×10^{-5}[c]	3.1458	9.052

[a] From a survey by J. C. Slater, *Proc. Am. Acad. Art Sci.*, **76**, **1** (1945). [b] M. Straumanis, A. Jevins and K. Karlsons, *Z. anorg. allgem. Chem.*, **238**, 175 (1938). [c] A. Eucken and W. Danohl, *Z. Elektrochem.*, 40, 814 (1934). [d] Paper I.

Entropies of Random Mixing When Schottky Defects Are Present

The entropy of formation of NaCl–KCl solid solutions assuming them to be ideal is given in Table III. This is the entropy expected if the Na^+ and K^+ were randomly distributed over the cation sites and if the vibrational contribution to ΔS were zero. It is clear that while the observed heats of formation correspond more closely to ΔH_{nr}, suggesting considerable local order in the lattice, the entropy data are in marked conflict with this notion. The observed departure from ideal is positive whereas a non-random solution has an entropy less than ideal. Hence the data in Table III are inconclusive on the point of the possible existence of order. It should be noted that the observed entropy can exceed the entropy of random mixing even when the configuration is appreciably non-random if there is a large vibrational contribution to ΔS. Thus the large observed ΔS may be due to vibrational effects. This cannot definitely be established without precise heat capacity data for the salts and the solution between absolute zero and 630°.

Another way that a solution may acquire an entropy greater than ideal is by the existence of defects in the lattice. In I it was pointed out that the extent of empty lattice sites in this system is quite large, amounting to a maximum of about 1%. Assuming the anion vacancies are randomly distributed over the anion sites and the cation vacancies, Na^+ and K^+ are similarly distributed over the cation sites, one obtains the following expression for the entropy of random mixing of a lattice containing Schottky defects

$$\Delta S = -\frac{R}{N_1^* + N_2^*}\left[N_1^* \ln N_1^* + N_2^* \ln N_2^* + 2N_{\mathrm{v}} \ln N_{\mathrm{v}} + (1 - N_{\mathrm{v}}) \ln (1 - N_{\mathrm{v}})\right] \quad (13)$$

where N_1^* and N_2^* represent the mole fraction of Na^+ and K^+ on the cation sites, respectively, and N_{v} is the mole fraction of vacant anion or cation sites. ΔS in equation 13 refers to the entropy of a solution containing one mole of ion pairs, which in this case involves a total of $2N_0(1 + N_{\mathrm{v}})$ lattice sites. The entropies calculated from equation 13 are also shown in Table III.

TABLE III

HEATS AND ENTROPIES OF FORMATION OF NaCl–KCl SOLID SOLUTIONS

Mole fraction NaCl (N_1)		0.1	0.3	0.5	0.7	0.9
		Observed quantities				
ΔH, cal./mole		402	858	1046	877	464
ΔS, e.u./mole at 630°		0.63	1.45	1.66	1.47	0.70
		Calcd. quantities (630°)				
σ		0.082	0.290	0.474	0.345	0.103
ΔH_{r}, cal./mole		477	1185	1505	1351	620
ΔH_{mr}, cal./mole		457	992	1067	1040	574
ΔS, e.u./mole	Eq. 10	0.64	1.12	1.14	1.07	0.63
	Ideal	.65	1.21	1.38	1.21	.65
	Eq. 13	.68	1.34	1.57	1.45	.69

Discussion of Results

In I it was pointed out that the various approximations involved in Wasastjerna's treatment of alkali halide solid solutions become more valid as the differences in lattice constants of the components diminishes. Thus for KCl–RbCl and KCl–KBr, whose components have nearly equal lattice constants, the computed and observed heats of formation agree almost exactly. With NaCl–NaBr the individual lattice constants differ more and there is slightly poorer agreement between measured and calculated heats. The NaCl–KCl solid solutions involve the greatest differences in lattice constants and theory is least successful in accounting for the observed heat effects. Yet even in this case the discrepancies would ordinarily be considered slight.

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(14) Equation 11 is obtained from Γ, the configurational partition function, which involves only $\Delta H_{\mathrm{r}} - \Delta H_{\mathrm{nr}}$, $\Gamma = (N_1^{N_1}N_2^{N_2}/\chi^{\chi}\lambda^{\lambda}\mu^{\mu}\nu^{\nu})^{N_0} \exp{(\Delta H_{\mathrm{r}} - \Delta H_{\mathrm{nr}})/RT}$.

In fact, it might be said that if this were the first comparison of theory and experiment, agreement would be considered very satisfactory.

As for the entropy results, they do not confirm the notion that local order exists in these solutions. From Table III it is apparent that the best accounting for the entropies is in terms of a random distribution, including the observed number of Schottky defects. It should be realized, however, that the awkward way of evaluating the entropies of formation makes it difficult to assess their reliability so that conclusions based upon them must be viewed with caution. This is especially true since the vibrational contribution, which may be appreciable, is unknown. Wasastjerna follows the usual practice of factoring the partition function into vibrational and configuration parts, which assumes the vibrational modes to be independent of configuration and implies that the vibrational specific heat of the solution and the equivalent mixture are identical and ΔS(vib.) is zero. To explain the discrepancy of the observed and calculated entropy as vibrational in origin means that one of the basic theoretical tenets is in need of revision (which is undoubtedly true) and leaves questions of the internal consistency of Wasastjerna's theory to be answered.

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[Contribution from the Department of Chemistry of the University of Texas]

Mechanism of the Reduction of Potassium Tetracyanonickelate(II) and Potassium Hexacyanocobaltate(III) with Potassium in Liquid Ammonia[1]

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Received August 12, 1953

Uncertainties remaining from earlier work on the reduction of potassium tetracyanonickelate(II) with potassium in liquid ammonia at −33.5° have been clarified by means of potentiometric titrations. Two one-electron steps are involved when the salt is in excess, and one two-electron reaction when potassium is in excess. Potassium tetracyanocobaltate(I) has been shown to be an intermediate in the reduction of potassium hexacyanocobaltate(III) to potassium tetracyanocobaltate(0).

Eastes and Burgess[2] reported that addition of potassium to potassium tetracyanonickelate(II) in liquid ammonia at −33.5° resulted in reduction to potassium tetracyanonickelate(I) but they were unable to reduce the latter to potassium tetracyanonickelate(0) upon addition of excess potassium. Burbage and Fernelius,[3] however, demonstrated both of these one-electron reductions in liquid ammonia at 0° but their efforts to effect both of these reactions at −33.5° were successful in some cases but not in others. More recently, the reduction of another cyanide complex to a product in which the central metal atom is apparently in the zero oxidation state has been reported by Hieber and Bartenstein[4] who have demonstrated the reduction of potassium hexacyanocobaltate(III) to potassium tetracyanocobaltate(0). Particularly in view of the fact that Hume and Kolthoff[5] have provided evidence in support of the view that the reduction of the $[Ni(CN)_4]^=$ ion in aqueous media does not involve a one-electron step, it seemed worthwhile to attempt to bring another kind of evidence to bear upon the mechanism of these interesting reduction reactions. Accordingly, these reactions have been studied by means of potentiometric titration techniques developed in these laboratories[6]; the results of these experiments are described below.

Experimental

Materials.—Potassium tetracyanonickelate(II) was prepared by the method of Fernelius and Burbage.[7] *Anal.* Calcd. for $K_2Ni(CN)_4$: Ni, 24.4. Found: Ni, 24.1. In preliminary experiments, it was found that this salt is soluble in liquid ammonia at its boiling point to the extent of approximately 45 g./100 ml. of solution.

Potassium hexacyanocobaltate(III) was prepared as described by Bigelow.[8] *Anal.* Calcd. for $K_3Co(CN)_6$: Co, 17.7. Found: Co, 17.4. The solubility of this salt was found to be <0.2 g./100 ml. of solution.

Potassium samples were purified and prepared for use in the manner described previously.[6]

Potentiometric Titrations.[6]—In a typical experiment, a solution of 0.1068 g. of potassium tetracyanonickelate(II) in 40 ml. of liquid ammonia was titrated with 0.0821 *N* potassium solution. An orange-red precipitate began to form upon the first addition of potassium and the first significant change in potential was observed after addition of 5.6 ml. of potassium solution as compared with 5.4 ml. calculated on the assumption of a one-electron change. During addition of the next 3.0 ml. of potassium solution, the potential increased as shown in Fig. 1, the rate of reaction of the added potassium decreased progressively, and the color of the precipitate became increasingly intense. This titration was not carried to the tetracyanonickelate(0) stage owing to the extreme slowness with which equilibrium was reestablished after about 8.5 ml. of titrant had been added.

In a related case, 0.0659 g. of potassium dissolved in 40 ml. of liquid ammonia was titrated with 0.1401 *N* potassium tetracyanonickelate(II) solution. A brown precipitate formed immediately. As is evident from the data of Fig. 2, the end-point corresponding to the change in potential that occurred upon addition of 12.0 ml. of the cyanonickelate(II) solution is in agreement with the value of 12.0 ml. calculated on the basis of a two-electron change.

In a manner analogous to the first of the two runs described above, 0.0427 g. of potassium hexacyanocobaltate(III) and 0.168 g. of potassium iodide (as a supporting electrolyte) dissolved in 50 ml. of liquid ammonia was titrated with 0.0397 *N* potassium solution (Fig. 3). Upon addition

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[1] This work was supported in part by the Office of Naval Research, Contract N6onr-26610.

[2] J. W. Eastes and W. M. Burgess, This Journal, **64**, 1187 (1942).

[3] J. J. Burbage and W. C. Fernelius, *ibid.*, **65**, 1484 (1943).

[4] W. Hieber and C. Bartenstein, *Naturwissenschaften*, **13**, 300 (1952).

[5] D. N. Hume and I. M. Kolthoff, This Journal, **72**, 4423 (1950).

[6] G. W. Watt and J. B. Otto, Jr., *J. Electrochem. Soc.*, **98**, 1 (1951).

[7] W. C. Fernelius and J. J. Burbage, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 227.

[8] J. H. Bigelow, *ibid.*, p. 225.