weighed 0.645 g. corresponding to a 98.7% yield of nitrate. The filtrate was concentrated to about 15 cc. at which point an additional trace of barium and manganese carbonate precipitate was filtered off with washing. The solution was then evaporated to dryness on a watch glass, and the ammonium nitrate product scraped off and weighed; yield 0.527 g. of $NH_4N^{15}O_3$, 99.7% of theory.

Ammonia Oxidation by Orthoplumbate.—It was found that BaO_2, $BaPbO_3$ and $BaMnO_4$ would not effectively oxidize ammonia under the conditions described above. However, Ba_2PbO_4 when used by itself proved to be just as quantitative and had the same kinetic behavior as its mixture with plumbate and manganate. Although Kassner[1] found the presence of barium manganate to be necessary for high temperature ammonia oxidation in which the mixture acts only as a catalyst with the nitrogen oxides not being absorbed, the present research indicates its presence to be unnecessary for low temperature oxidative absorption.

A sample of barium orthoplumbate (20 g., 0.037 mole) was placed in a nickel boat in the heated portion of the apparatus described above. Boats of potassium hydroxide were at either end of the heater to absorb the water formed by the reaction. A mixture of 0.00932 mole of ammonia gas and slightly greater than double this molar amount of oxygen which had previously been prepared in a large steel tank was admitted to a pressure of 890 mm. at room temperature. The heater was turned on and the course of the reaction followed by observing the pressure change as shown by the manometer. The temperature of the heater was kept at 350°. The observed pressures and elapsed times in hours, respectively, were 1165, $^1/_2$; 925, 1; 665, 2; 387, 4; 275, 5; 135, 7; 2, 17.

The product in this case was removed from the absorbent by passing a slow stream of oxygen over the nickel boat containing the barium orthoplumbate, barium plumbate and barium nitrate while the boat was in a silica tube at 750°. The effluent gas was absorbed in a gas washing bottle containing a standardized solution of sodium hydroxide. An excess of standardized acid was added in the presence of hydrogen peroxide to convert nitrite to nitrate and the solution back titrated. This analysis indicated the formation of 0.00931 mole of nitrate, corresponding to a 99.9% yield which confirms the pressure change results.

STANFORD, CALIF.

[CONTRIBUTION NO. 979 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Free Energies and Entropies of Formation of KCl–KBr Solid Solutions at 25°[1,2]

BY W. H. MCCOY AND W. E. WALLACE

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Free energies of formation of KCl–KBr solid solutions at 25° are evaluated from the known solubilities of the pure salts and the solid solutions in water and the recently measured activity coefficients in the saturated aqueous ternary systems. Results are used to obtain entropies of formation of the KCl–KBr solid solutions for comparison with entropies of formation computed from Wasastjerna's theory of alkali halide solid solutions. Calculated and observed entropies are in poor agreement. From the free energy and entropy data one estimates the critical mixing temperature of KCl and KBr in the solid state to be 190 ± 15°K.

Several years ago Wasastjerna presented[3] an elegant statistical thermodynamic treatment of alkali halide solutions which makes possible the calculation of most of their equilibrium properties from a few readily available properties of the component salts. Wasastjerna's procedure consisted essentially in using the well-known treatment of strictly regular solutions after skillfully instituting the modifications necessary to take into account the important long range coulombic contribution. This theory has been conspicuously successful in accounting for the heats of formation of these solutions from their component salts. For example, for KCl–KBr or NaCl–NaBr the computed and observed heats of formation agree within about 10 cal./mole of ion pairs.[3–6] Since the heat of formation represents the difference between the lattice energy of the solid solution and that of the equivalent mixture, each of which is of the order of 175,000 cal., the successful calculation of this difference is truly a remarkable achievement. The theory achieves, in fact, greater quantitative success than might have been anticipated.

In developing his theory, Wasastjerna has postulated the existence of some local order in the alkali halide solid solutions and has evaluated a local order parameter by straightforward methods of statistical mechanics. Hovi has tabulated[7] values of the order parameter σ for KCl-KBr solid solutions at various compositions for a number of temperatures. He finds, for example, that σ for the equimolal solution at 0° is 0.322, which means that there are 32.2% more ClKBr configurations in the solution than one would find if the distribution of the two anions were random. This, of course, means that the configurational contribution to the entropy of formation will be significantly less than for a random distribution. Since the theory neglects non-configurational entropies entirely, it predicts significant negative departures from random mixing entropies.

As one can compute the entropy of formation of alkali halide solid solutions from theory, it is obviously of interest to measure these quantitites to see if the theory is as effective here as it is in accounting for energies. The first instance in which such a comparison was made was reported in a paper published some months ago from this Laboratory.[8] The system under discussion there was

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(1) From a thesis submitted by W. H. McCoy to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

(2) This work was supported by a grant from the Research Corporation.

(3) J. A. Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **15**, 1 (1949).

(4) N. Fontell, V. Hovi and A. Mikkola, *Ann. Acad. Sci. Fennicae, Math.-Phys.*, AI, No. 54, 1 (1949).

(5) V. Hovi, *Soc. Sci. Fennicae, Commentationes Phys.-Math.*, **15**, 1 (1950).

(6) V. Hovi, *Arkiv Fysik*, **5**, 61 (1952).

(7) V. Hovi, *Soc. Sci. Fennicae, Commentationes Phys.-Math.*, **15**, 1 (1950).

(8) W. T. Barrett and W. E. Wallace, THIS JOURNAL, **76**, 370 (1954).

NaCl–KCl. The measured entropy for that system was found to *exceed* the entropy of random mixing. However, the comparison was not entirely satisfactory for two reasons. First, the entropies were estimated from the phase diagram showing the range of mutual solid solubility of the two salts, a procedure which is undesirable because the errors in the entropies evaluated in this way are probably large and are certainly difficult to assess. Second, as was pointed out earlier,[9] due to the large difference in lattice parameters of the component salts, various approximations in the Wasastjerna treatment are somewhat untrustworthy so that the computed entropies are less satisfactory than might have been desired. The Wasastjerna theory is of such a nature that all the simplifying assumptions become more nearly valid as the lattice parameters of the components approach one another. The a spacings for KCl and KBr differ by only 5% so that this system represents a particularly favorable case from the viewpoint of theory. It is, therefore, of particular interest to evaluate experimentally the entropies of formation of this system. In this paper it will be shown how one can evaluate these entropies and how they compare with values calculated from theory.

Method Employed in Evaluating ΔF_f and ΔS_f.—The entropy of formation (ΔS_f) of a KCl–KBr solid solution is determined by first measuring ΔF_f, its free energy of formation, and combining this with the known heat of formation, ΔH_f, according to the fundamental expression

$$\Delta S_f = \frac{\Delta H_f - \Delta F_f}{T} \tag{1}$$

The free energies of formation, which are also of interest in themselves, may be obtained if one knows the activities of the two salts in the saturated aqueous phases which exist in equilibrium with KCl–KBr solid phases of various compositions. This can be seen from the following series of thermochemical equations

$$\text{KCl(solid)} \longrightarrow \text{KCl(binary aq. soln. at satn.)} \quad \Delta F = 0 \tag{2}$$

$$\text{KCl(binary aq. soln. at satn.)} \longrightarrow \text{KCl(ternary aq. soln. at satn.)} \quad \Delta F = RT \ln \frac{a_1''}{a_1'} \tag{3}$$

$$\text{KCl(ternary aq. soln. at satn.)} \longrightarrow \text{KCl(in solid soln.)} \quad \Delta F = 0 \tag{4}$$

The final state in equation 2 is merely a saturated solution of KCl in water at the temperature under consideration, whereas the final state in equation 3 is water saturated with the solid solution in equation 4. We thus see that

$$(\bar{F} - F^\circ)_{\text{KCl}} = RT \ln \frac{a_1''}{a_1'} \tag{5}$$

where a_1'' = activity of KCl in the saturated ternary system, a_1' is the corresponding quantity for the saturated binary system, and $(\bar{F} - F^\circ)_{\text{KCl}}$ is the difference in partial molal free energy of KCl in solid solution and in the pure state. In a like manner

$$(\bar{F} - F^\circ)_{\text{KBr}} = RT \ln \frac{a_2''}{a_2'} \tag{6}$$

and

$$\Delta F_f = p(\bar{F} - F^\circ)_{\text{KCl}} + q(\bar{F} - F^\circ)_{\text{KBr}} = RT\left[p \ln \frac{a_1''}{a_1'} + q \ln \frac{a_2''}{a_2'}\right] \tag{7}$$

where p and q are mole fractions of KCl and KBr, respectively, in the solid solution. Thus, we see that if we know the activities of KCl and KBr in saturated aqueous solution at 25° and the activities of the salts in the ternary system formed by saturating water with the solid solution of composition p, we may compute the free energy of formation. In each case $a = m\gamma$ so that one needs the molalities and the activity coefficients at saturation. The saturation molalities for KCl–KBr have been measured several times[10–12] and sufficiently reliable data are available. The activity coefficients in the saturated solutions were, however, unavailable. They have recently been obtained using the isopiestic technique[13,14] and employing the procedure suggested by McKay and Perring[15] for treating ternary systems. The details of this aspect of the work and its relevance to the general problem of the behavior of mixed electrolytes in water are presented elsewhere.[16]

Rewriting equation 7 in terms of molalities and activity coefficients, we have

$$\Delta F_f = RT\left[p \ln \frac{m''_1 m'' \gamma_1''^2}{m_1'^2 \gamma_1'^2} + q \ln \frac{m''_2 m'' \gamma_2''^2}{m_2'^2 \gamma_2'^2}\right] \tag{8}$$

Here m represents the total molality and m_1 and m_2 give the molalities of KCl and KBr, respectively. As in equation 7 the primes refer to the saturated binary systems and the double primes to the saturated ternary systems. The mean activity coefficient is γ and subscripts 1 and 2 refer to KCl and KBr, respectively.

Numerical Results.—The saturation molalities needed in equation 8 have been determined by Flatt and Burkhardt[11] and by Durham, *et al.*[12] The results of these two investigations are not in exact agreement. The binary solubilities reported by the latter investigators are in good agreement with those recorded in Seidell's compendium[17] and with the results of Isbin and Kobe.[18] From this, one is inclined to favor the results of Durham, *et al.* However, Flatt and Burkhardt's work seems to have been performed with exceptional care. It was decided, therefore, to evaluate free energies and entropies from each set of data.

In Table I we present the activity coefficients and saturation molalities needed for use in equation 8. The first column gives the mole fraction of KBr in the solid phase. The second and third

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

[10] M. Amadori and G. Pampanini, *Atti accad. Lincei*, **21**, I, 667 (1911).

[11] R. Flatt and G. Burkhardt, *Helv. Chim. Acta*, **27**, 1600 (1944).

[12] G. S. Durham, E. J. Rock and J. S. Frayn, This Journal, **75**, 5792 (1953).

[13] D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).

[14] R. A. Robinson and D. A. Sinclair, This Journal, **56**, 1830 (1934).

[15] H. A. C. McKay and J. K. Perring, *Trans. Faraday Soc.*, **49**, 163 (1953).

[16] W. H. McCoy and W. E. Wallace, This Journal, **78**, 1830 (1956).

[17] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Edition, Vol. 1, D. Van Nostrand, Inc., New York, N. Y., 1940, pp. 686, 747.

[18] H. Isbin and K. Kobe, This Journal, **67**, 464 (1945).

columns give the mole fraction of the salt in aqueous solution which is KBr. The fourth and fifth columns give the total molality at saturation. The activity coefficients of KCl and KBr at saturation differ slightly depending on which of the two sets of solubility data are used. This arises because the γ values at saturation are obtained by a short extrapolation of results obtained at concentrations near saturation. Hence, we are extrapolating to slightly different concentrations in the two cases.

TABLE I

CONCENTRATIONS AND ACTIVITY COEFFICIENTS OF AQUEOUS PHASES IN EQUILIBRIUM WITH KCl–KBr SOLID SOLUTIONS

Solid phase	Aqueous phase		$m_{KCl} + m_{KBr}$, Moles/kg. H_2O		γ_{KCl}[c]		γ_{KBr}[c]	
	F–B[a]	D[b]	F–B[a]	D[b]	F–B[a]	D[b]	F–B[a]	D[b]
0.00	0.000	0.000	4.869	4.816	0.588	0.588		
.1	.315	.348	5.460	5.537	.605	.607	0.628	0.629
.2	.450	.460	5.830	5.845	.612	.612	.634	.634
.3	.505	.516	6.003	5.995	.615	.615	.637	.637
.4	.550	.560	6.040	6.095	.617	.617	.639	.639
.5	.586	.594	6.070	6.128	.618	.618	.640	.640
.6	.625	.630	6.120	6.140	.618	.618	.641	.641
.7	.675	.672	6.200	6.142	.620	.619	.642	.641
.8	.745	.735	6.125	6.097	.620	.620	.641	.641
.9	.840	.830	5.945	5.998	.618	.618	.640	.640
1.0	1.000	1.000	5.764	5.736			.636	.638

[a] From data of Flatt and Burkhardt, ref. 11. [b] From data of Durham, *et al.*, ref. 12. [c] From data of McCoy and Wallace, ref. 16.

The free energies computed from the data in Table I are given in Table II. Column 1 gives the composition of the solution. In succeeding columns we give the free energy of formation calculated from first Durham's and next Flatt and Burkhardt's solubility data, the average of these two free energies, and the free energy of formation calculated from Wasastjerna's theory. Using Wasastjerna's nomenclature

TABLE II

FREE ENERGIES AND HEATS OF FORMATION OF KCl–KBr SOLID SOLUTIONS AT 25°[a]

Mole fraction KBr	$-\Delta F_D$	$-\Delta F_{FB}$	$-\Delta F_{av.}$	$-\Delta F_{calcd.}$	ΔH
0.1	114	126	120	108	70
.2	161	169	165	158	135
.3	186	188	187	168	185
.4	199	216	208	166	215
.5	217	228	223	158	222
.6	212	222	217	164	217
.7	200	193	197	166	196
.8	176	170	173	158	157
.9	125	136	131	128	95

[a] The units are cal. per mole of ion pairs.

$$\Delta F_{calcd.} = Q_{IV} - kT \ln g \qquad (9)$$

where Q_{IV} is the calculated heat of formation, g is Wasastjerna's combinatory number for the system, and k is the Boltzmann constant. The equations which relate Q_{IV} and g to measurable properties of KCl and KBr are rather complex and will not be presented here since they are given in detail elsewhere.[3,5,8,19] The final column in Table II gives the experimental heats of formation of the solutions. These values merit some comment.

Extensive heat of formation data are available for the KCl–KBr solid solutions formed from the melt.[20–22] Only one study has been made of the heats of formation of KCl–KBr solid solutions formed at 25° by crystallization from water.[4] Using the data of Hovi, since these are the most recent data for the heat of formation of solid solutions formed from the melt, one has for the equimolal solution a value of 234 cal./mole of ion pairs Five determinations by Fontell, Hovi and Mikkola of the corresponding quantity for the solid solution formed by crystallization from water at 25° gave a value of 222 cal./mole of ion pairs. The difference is a small but perhaps significant one between the energies of the differently formed solid solutions. Theory indicates that ΔH_f is nearly symmetrical about mole fraction 0.5 and Hovi finds[20] this experimentally for KCl–KBr solutions prepared by fusion. One can, therefore, estimate with little uncertainty ΔH_f for the solutions crystallized from water by means of the value obtained for the equimolal solution and under the assumption that ΔH_f has the same general shape as Hovi's curve for the samples prepared by fusion. It is in this way that one obtains the ΔH_f values listed in the final column of Table II.

Entropies of formation evaluated from equation 1 are shown in Table III where the nomenclature is analogous to that used in Table II. We also have listed ΔS_{ideal}, the entropy of formation if the anionic sites were randomly populated and the system were ideal.

TABLE III

ENTROPIES OF FORMATION OF KCl–KBr SOLID SOLUTIONS AT 25°[a]

Mole frac. KBr	ΔS_D	ΔS_{FB}	$\Delta S_{av.}$	$\Delta S_{calcd.}$	ΔS_{ideal}	ΔS_M
0.1	0.62	0.66	0.64	0.63	0.65	0.96
.2	0.99	1.02	1.01	0.97	0.99	1.38
.3	1.24	1.25	1.25	1.16	1.21	1.48
.4	1.39	1.45	1.42	1.26	1.34	1.60
.5	1.47	1.51	1.49	1.29	1.38	1.59
.6	1.44	1.47	1.46	1.26	1.34	1.34
.7	1.33	1.31	1.32	1.16	1.21	1.21
.8	1.12	1.10	1.11	0.96	0.99	0.99
.9	0.74	0.78	0.76	.58	.65	.65

[a] The units are cal. per degree per mole of ion pairs.

$$\Delta S_{ideal} = -R(p \ln p + q \ln q) \qquad (10)$$

$\Delta S_{calcd.}$ (in column 5) is computed from Wasastjerna's theory using the customary equation

$$\Delta S_f = k \ln g \qquad (11)$$

where g is again the combinatory number. The quantities listed in the final column will be referred to in the next section.

Precision of Measured Free Energies and Entropies of Formation.—Uncertainty in the saturation concentrations introduces roughly ±4 cal. into the ΔF values given in Table II. The γ values at saturation are uncertain by ±0.002

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(19) W. H. McCoy, Ph.D. Thesis, University of Pittsburgh, 1955.

(20) V. Hovi, *Ann. Acad. Sci. Fennicae, Math.-Phys.*, **AI**, No. 55, 1 (1948).

(21) N. Fontell, *Soc. Sci. Fennicae, Commentationes Phys.-Math.*, **X** [6], 1 (1939).

(22) M. M. Popov, *Z. physik. Chem.*, **A147**, 302 (1930); **A167**, 180 (1933).

which introduces another 5 cal. of uncertainty into the reported free energies. They are, therefore, uncertain by about ±10 cal./mole of ion pairs. This means that the entropies are uncertain by about ±0.03 cal./degree mole of ion pairs.

Discussion of Results

The results given in Table III show clearly the failure of Wasastjerna's theory in accounting for the entropies of formation of this system. The entropies instead of deviating negatively from the ideal entropies as would be expected if there were significant departures from a random arrangement actually exceed the entropies of random mixing.

The excess entropy may mean that the change in vibrational entropy is positive and sufficiently large to make an appreciable contribution to the entropy of formation. If so, the configurational entropy could be less than the random mixing entropy in accordance with the notion that there is partial order in the system. This line of reasoning is, however, at variance with one of the basic ideas in Wasastjerna's theory—that the vibrational partition function, and, hence, the vibrational entropy, is independent of configuration. The theory, in effect, is contingent upon there being a zero vibrational contribution to ΔS_f. It seems, therefore, that this theory is incapable of accounting for the entropies of KCl–KBr solid solutions.

It is now of interest to inquire about the origin of the excess entropy in this system. In two other systems which have been investigated in this Laboratory, the entropy was found[8,9,23] to exceed the random mixing entropy, at least for some compositions. In each of these systems there is evidence[24,25] for the existence of an abnormal number of Schottky defects, up to 2% in some cases. The extra entropy in one of the systems, the magnesium–cadmium alloys, corresponds[24] very well with that expected if the observed number of vacancies were randomly distributed through the lattice and part of the entropy excess in the other system, the NaCl–KCl solid solutions, can be accounted for in a like manner.[9] It is, therefore, of interest to see if the entropies in the present case can be accounted for in the same way. Elsewhere it has been shown[26] that the intercomparison of densities and unit cell dimensions indicates a large number of vacant lattice sites in the KCl–KBr solutions. One can compute a maximum value of the entropy of formation $\Delta S_{\max}$ by assuming the anionic vacancies and the chloride and bromide ions to be randomly distributed over the anion sites, and the cationic vacancies, which are postulated to be equal in number to the anionic vacancies, to be randomly distributed over the cationic sites. The results of such a calculation are shown in the last column of Table III. These results are in poor agreement with the observed results.

The next step toward the interpretation of these data would be to separate the total ΔS_f into its vibrational and configurational components. This can be done by low temperature specific heat measurements on the solid solutions so that the measured entropies of formation can be corrected to absolute zero where the vibrational contribution vanishes. Work of this sort is to be undertaken in the hope that once the vibrational term is evaluated, the configurational contribution can be interpreted in terms of Wasastjerna's theory or perhaps some more refined theory.

Critical Mixing Temperature of KCl and KBr in the Solid State.—It is well known that KCl and KBr are miscible in all proportions in the solid state at room temperature. Since the solid solutions are formed endothermally from the components, it is clear that they will become metastable at some low temperature. The critical mixing temperature can be estimated from the free energies of formation at 25° using the thermodynamic relationship

$$\left[\frac{\partial(\Delta F_f/T)}{\partial T}\right]_p = -\frac{\Delta H_f}{T^2} \qquad (12)$$

Mustajoki has shown[27] that the heat capacities of KCl–KBr solid solutions between 50 and 300° are within experimental error of about 1% identical with the sum of the heat capacities of the component salts. Hence, ΔH_f can be regarded as temperature independent and equation 12 may be integrated to give

$$(\Delta F_f)_T = \Delta H_f + \frac{T}{T_1}\left[(\Delta F_f)_{T_1} - \Delta H_f\right] \qquad (13)$$

where T_1 refers to 25°. From this equation a series of ΔF_f curves at various temperatures can be produced As long as the curve is uniformly concave upward, the miscibility is complete. When a re-entrant portion appears so that one can draw a line which is tangent at two points, the stable state is[28] a two phase system. By noting the temperature at which this first becomes possible, the critical mixing temperature is established as 190 ± 15°K.

Pittsburgh, Pennsylvania

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[23] F. A. Trumbore, W. E. Wallace and R. S. Craig, This Journal, **74**, 132 (1952).

[24] D. A. Edwards, W. E. Wallace and R. S. Craig, *ibid.*, **74**, 5256 (1952).

[25] J. M. Singer and W. E. Wallace, *J. Phys. Colloid Chem.*, **52**, 999 (1948).

[26] W. E. Wallace and R. A. Flinn, *Nature*, **172**, 681 (1953).

[27] A. Mustajoki, *Ann. Acad. Sci. Fennicae, Math. Phys.*, **AI**, No. 98, 1 (1951).

[28] L. S. Darken and R. W. Gurry, "Physical Chemistry of Metals," McGraw-Hill Book Co., New York, N. Y., 1953, p. 329.