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W. E. Wallace

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The Born–Mayer Model for Ionic Solids and the Heats of Formation and Lattice Spacings of Alkali Halide Solid Solutions*

W. E. WALLACE

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania

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Previous attempts to calculate the heats accompanying formation of alkali halide solid solutions from the component salts have met with only limited success. The difficulties may have originated either in the use of Vegard's law to obtain lattice spacings of the solutions or in the general inadequacy of the model employed in computing the energies of the lattices concerned. Since earlier studies were based on the old Born concept of ionic solids, it was of interest to examine the subject again using as a basis the more refined treatment due to Born and Mayer. An expression for the potential energy of a crystalline solution has been developed in terms of the known interaction parameters of the pure constituents and has been used to compute the equilibrium spacings and heats of formation of three chosen systems. The calculated results are compared with experiment. The comparison suggests that further refinement in the model is perhaps necessary before the small changes in lattice spacings and heat contents which accompany solid solution formation can be completely accounted for.

INTRODUCTION

THE ability of certain pairs of the alkali halides to form solid solutions has long been recognized.[1] In some instances, e.g., KCl-KBr,[2] the components are miscible in all proportions at ordinary temperatures. With others, e.g., NaCl-KCl,[3] the components have only a limited solubility in each other and over a portion of the composition range the stable state is a mixture of the two saturated solid solutions. Where direct observation has been possible, it has been noted that the mutual solid solubility of a pair of partially miscible alkali halides increases with temperature, indicating the existence of a heat effect accompanying the formation of a solid solution from its components. For the purpose of the present discussion this heat effect will be referred to as the heat of formation of the solid solution, ΔH_f.

The heat of formation of a solid solution can be readily ascertained if the lattice energies of the pure components and the solid solution are known. Grimm and Herzfeld[4] and, more recently, Tobolsky[5] have applied the Born method for computing lattice energies of ionic crystals to crystalline solutions and have obtained expressions for estimating ΔH_f for alkali halide solid solutions from the observed lattice spacings and assumed interaction potentials of the pure salts. Instead of calculating heats of formation directly Grimm and Herzfeld chose to regard the constant m (appearing in the repulsion potential, B/r^m) as an adjustable parameter to be determined from the calorimetrically observed heats. Values of m ranging between 3 and 8 were required to account for the data. Although these values tended to be smaller than the quantities obtained from compressibilities, the

discrepancies could be attributed to the large uncertainties in the heats of formation determined prior to 1923.

Tobolsky obtained an expression for the heat of formation of an equimolal solid solution containing two moles of ion pairs

$$\Delta H_f \cong 9\delta^2, \qquad (1)$$

where δ is the percentage deviation between the lattice constants a_1 and a_2 of the component salts, and the heat is expressed in calories. Equation (1) was developed under the assumption that the solid solution obeyed Vegard's Law and the energies of the lattices concerned were about 180 kcal. per mole. In comparing the heats computed from Eq. (1) with experiment, Tobolsky observed that the agreement was fairly good considering the approximate nature of the treatment.

Tobolsky's calculated heats were compared with experimental data taken from a compilation by Bruni.[6] Bruni apparently failed to recognize that the early experimenters were not of a uniform practice in reporting heats of formation of an equimolal solid solution, some expressing the heat on the basis of one mole of each component and others on the basis of one mole total. Hence, some of the values reported by Bruni referred

TABLE I. Heats of formation of alkali halide solid solutions.

System	δ	ΔH_f (cal./mole of ion pairs)	
		Calc.-Tobolsky	Observed
KCl-RbCl	4.5	83	203[a]
KBr-KCl	4.8	94	232[a]
NaCl-NaBr	5.5	118	335[b]
KBr-KI	7.1	195	390[c]
NaI-KI	9.1	326	625[d]
NaBr-KBr	10.8	480	700[d]
NaCl-KCl	11.5	594	1050[d]

[a] N. Fontell, Soc. Sci. Fenn. Comm. Phys.-Math., **X**, 12, 1 (1939).
[b] M. A. Fineman and W. E. Wallace, reference 7.
[c] G. Bruni and M. Amadori, Atti ist. Veneto **71**, II, 51 (1911).
[d] N. S. Kurnakov and S. F. Zemczuznj, Zeits. f. anorg. allgem. Chemie **52**, 186 (1907).

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

[1] W. C. Blasdale, *Equilibria in Saturated Salt Solutions* (Chemical Catalog Company, New York, 1927), p. 88.
[2] W. E. Wallace and M. A. Fineman, Soc. Sci. Fenn. Comm. Phys.-Math. **XIV**, 6, 1 (1948).
[3] R. Nacken, Sitz. kgl. preuss. Akad. Wiss. **192** (1918).
[4] H. G. Grimm and K. F. Herzfeld, *Zeits. f. Physik.* **16**, 77 (1923).
[5] A. V. Tobolsky, J. Chem. Phys. **10**, 187 (1942).

to one mole of ion pairs, whereas others referred to two moles of ion pairs. Expressing all results on a uniform basis (heat effect for a solution containing one mole of ion pairs) and using more recently determined values, where possible, the data presented in Table I are obtained.

TABLE II. van der Waals and repulsion potential constants.

	$C \times 10^{60}$ ergs cm⁶/ion pr.	$\beta_1 \times 10^{12}$ ergs/ion pr.	$\beta_2 \times 10^{12}$
mole fraction NaCl		NaCl-NaBr	
1.00	180	5498	24880
0.75	201	6081	30170
0.50	223	6664	35990
0.25	247	7247	42340
0.00	271	7830	49230
mole fraction KCl		KCl-KBr	
1.00	451	13380	30480
0.75	488	14840	35840
0.50	525	16300	41730
0.25	564	17760	48210
0.00	604	19220	55240
mole fraction KCl		KCl-RbCl	
1.00	451	13380	30480
0.50	570	16590	34360
0.00	692	19790	39060

It has been pointed out elsewhere[7] that attempts to calculate heats of formation from lattice energies impose severe demands upon the model used since ΔH_f appears as the difference in lattice energy of the solid solution and a mechanical mixture of the same total mass and composition. These differences are only 0.6 percent to 0.1 percent of the total energy of the lattice so that the calculated heats are extremely sensitive to imperfections in the model. The treatments offered by Grimm and Herzfeld and by Tobolsky were both based on the earlier Born model where van der Waals forces were neglected and the repulsion potential assumed was of the form B/r^m. Since the van der Waals energies of alkali halide crystals are from ten to twenty times larger than the energy changes associated with solid solution formation, and in view of the approximate nature of the B/r^m repulsion potential, it was of interest to investigate the energetics of crystalline solutions using the more refined treatment of ionic lattices due to Born and Mayer[8] and Mayer.[9] Employing interaction parameters characteristic of the pure compounds, equilibrium spacings of the solid solutions can be determined merely by invoking the minimum potential energy principle. Thereby Tobolsky's assumption of the validity of Vegard's Law[10]

[7] M. A. Fineman and W. E. Wallace, J. Am. Chem. Soc. 70, 4165 (1948).
[8] M. Born and J. E. Mayer, Zeits. f. Physik 75, 1 (1932).
[9] J. E. Mayer, J. Chem. Phys. 1, 270 (1933); 1, 327 (1933).
[10] Grimm and Herzfeld have demonstrated that if the energy of a solid solution is at a minimum, Vegard's Law can be obeyed only if m, the exponent in the repulsion potential, is 2. It is well known that for the salts in Table I m varies between 8 and 10.5. Hence,

for the systems concerned is avoided. In the present paper the equations developed have been used (1) to evaluate the equilibrium spacings of the solid solutions at various compositions and to compare these quantities with experiment and with Vegard's Law and (2) to calculate the heats of formation and compare them with experiment for three chosen binary systems for which reliable data are available.

LATTICE ENERGY OF ALKALI HALIDE SOLID SOLUTIONS

Let us consider a binary solid solution containing four ion species, two cationic components, 1 and 3, and two anionic components, 2 and 4.[11] The lattice energy U is given by

$$-U = \Phi_0 = -\alpha e^2/r_0 - C/r_0^6 - D/r_0^8 + B(r_0) + 1/2 h\nu_0. \quad (2)$$

For the present purpose the $1/r_0^8$ term is assumed to make a negligible contribution to the heats of formation and in the remainder of this paper it has been neglected. Undoubtedly, D/r_0^8 is not negligible compared to the heat of solid solution but it seems unlikely that changes in this term could make an appreciable contribution.

The first term is the Coulombic potential which of

TABLE III. Lattice spacings of alkali halide solid solutions.

	298°K $r_0 \times 10^8$ cm			0°K $r_0 \times 10^8$ cm		
	Obs.	Calc.-Vegard's Law	Dev.	Calc.-Eq. (8)	Calc.-Vegard's Law	Dev.
			NaCl-NaBr			
Mole Fraction KCl						
1.00	2.8144	—	—	2.790	—	—
0.75	2.8588	2.8560	0.0028	2.837	2.831	0.006
0.50	2.9017	2.8977	0.0040	2.880	2.872	0.008
0.25	2.9411	2.9393	0.0038	2.919	2.913	0.006
0.00	2.9809	—	—	2.954	—	—
			KCl-KBr			
Mole Fraction KCl						
1.00	3.1362	—	—	3.105	—	—
0.75	3.176	3.176	0.000	3.151	3.145	0.006
0.50	3.217	3.216	0.001	3.192	3.184	0.008
0.25	3.257	3.256	0.001	3.229	3.224	0.007
0.00	3.2952	—	—	3.263	—	—
			KCl-RbCl			
Mole Fraction KCl						
1.00	3.1362	—	—	3.105	—	—
0.50	3.216	3.211	0.005	3.185	3.178	0.007
0.00	3.286	—	—	3.251	—	—

at the spacings obtained from Vegard's Law, the solid solutions are not in the equilibrium state. Lattice energies and ΔH_f's such as reported in Table I, column 3, correspond to the "Vegard's law solid solution" and not to the equilibrium state.

[11] In the treatment presented in this section the nomenclature of Born and Mayer is employed with appropriate modifications as necessary.

course is the same for a solution as for a pure material allowing for the altered r_0.

In evaluating C for the solution it has been assumed that the two cationic species and two anionic species are distributed randomly over the cation and anion sites, respectively.[12] Consider the van der Waals interaction of a single ion of species 1 with all other ions.

$$\varphi_1 = S'(N_2c_{12}+N_4c_{14})/r^6 + S''(N_1c_{11}+N_3c_{13})/r^6, \quad (3)$$

where N_1 and N_3 are the fraction of cation sites occupied by cations 1 and 3 respectively, and N_2 and N_4 are corresponding quantities for anion sites. c_{12} refers to the interaction between ions of types 1 and 2, c_{13} between 1 and 3, etc. The simple form of Eq. (3) is an immediate consequence of the assumed random distribution of the several species over the accessible lattice sites. Of the t anions r_t distant from the central ion, N_2t are of species 2 and N_4t are of species 4. The interaction of the central ion with that shell of anions is $(N_2c_{12}+N_4c_{14})t/r_t^6$. Since the various N's are assumed to be independent of position (completely random), summing over all the lattice sites is particularly simple, and Eq. (3) results. To obtain the complete van der Waals potential, one merely needs to find the average energy per ion pair using Eq. (3) and the other three similar expressions for species 2, 3, and 4.

$$C = S'(N_1N_2c_{12}+N_1N_4c_{14}+N_2N_3c_{23}+N_3N_4c_{34})$$
$$+ (S''/2)(N_1{}^2c_{11}+N_2{}^2c_{22}+N_3{}^2c_{33}$$
$$+N_4{}^2c_{44}+2N_1N_3c_{13}+2N_2N_4c_{24}). \quad (4)$$

In evaluating the contribution of the forces of repulsion to the energy of the lattice, $B(r_0)$, Born and Mayer considered the repulsion potential between a pair of ions to be of the form $\alpha e^{-r/\rho}$. Subsequently Huggins and Mayer[13] showed that the behavior of the alkali halides could be accounted for by taking $\rho = 0.345 \times 10^{-8}$ cm and setting $\alpha = bc_{ij}e^{(r_i+r_j)/\rho}$, where r_i and r_j are parameters characteristic of the particular ions and $b = 10^{-12}$ erg/ion pair. When the ions are of opposite charge, $c_{ij} = c_0 = 1.00$; for two cations, $c_{ij} = c_1 = 1.25$, and for two anions, $c_{ij} = c_2 = 0.75$.

The repulsion potential for the solid solution was evaluated by considering only the interaction between a given central ion and the M nearest neighbors and M' next-nearest neighbors

$$B(r_0) = \beta_1 e^{-r_0/\rho} + \beta_2 e^{-ar_0/\rho}, \quad (5)$$

where

$$\beta_1 = bMc_0(N_1N_2e^{(r_1+r_2)/\rho}+N_1N_4e^{(r_1+r_4)/\rho}$$
$$+N_2N_3e^{(r_2+r_3)/\rho}), \quad (6)$$

$$\beta_2 = (bM'/2)[c_1(N_1{}^2e^{2r_1/\rho}+2N_1N_3e^{(r_1+r_2)/\rho}+N_3{}^2e^{2r_3/\rho})$$
$$+c_2(N_2{}^2e^{2r_2/\rho}+2N_2N_4e^{(r_2+r_4)/\rho}+N_4{}^2e^{2r_4/\rho})]. \quad (7)$$

[12] M. Von Laue, Ann. d. Physik 78, 167 (1925). See also reference 7.
[13] M. L. Huggins and J. E. Mayer, J. Chem. Phys. 1, 642 (1933).

In Eqs. (5)–(7) r_0 refers to the equilibrium distance between a given ion and its nearest neighbors, whereas r_1, r_2, etc., are the parameters characteristic of the several ion species; and a is the factor by which the distance from the central ion to the next-nearest neighbors exceeds the distance to the nearest neighbors. Of course, $a = 2^{\frac{1}{2}}$ for the sodium chloride type lattice.

In developing Eqs. (4), (6), and (7) the interactions between a given pair of ions in solution are taken to be identical with those in the pure salt for the same distance of separation. Undoubtedly the numerous param-

TABLE IV. Heats of formation of alkali halide solid solutions.

		ΔH_f (cal./mole of ion pairs)			
	Obs.[a]	Calc.-Eq. (9)	Dev.	Calc.-Eq. (1)	Dev.
NaCl-NaBr					
Mole Fraction NaCl					
0.75	257	440	180		
0.50	335	540	200	118	−117
0.25	241	380	140		
KCl-KBr					
Mole Fraction KCl					
0.75	186	360	170		
0.50	232	450	220	94	−138
0.25	163	300	140		
RbCl-KCl					
Mole Fraction					
0.50	203	400	200	83	−120

[a] For sources of data, see Table I.

eters do vary somewhat with composition, but the effect of this variation on the computed spacings and heats would be difficult to assess.

EQUILIBRIUM SPACINGS AND ΔH_f FOR BINARY SOLUTIONS

Numerical solutions of the expressions derived in the preceding section were carried out for three binary systems: NaCl-NaBr, KCl-KBr, and RbCl-KCl. For the first two systems, reliable data are available over the entire composition range, while for the latter, data are available only for the equimolal solution. The values for C listed in Table II were obtained from Eq. (4) using the van der Waals constants as reported by Mayer[9] and taking $c_{13} = (c_{11}c_{33})^{\frac{1}{2}}$ and $c_{24} = (c_{22}c_{44})^{\frac{1}{2}}$. β_1 and β_2 values also presented in Table II were obtained using $\rho = 0.345 \times 10^{-8}$ cm and the various repulsion parameters as tabulated by Huggins and Mayer.[13]

The equilibrium spacings of the solid solutions can be determined from the relationship developed by Born and Mayer that:

$$r_0\left[\frac{d\Phi(r_0)}{dr}\right] = \frac{3T}{N\beta}\left(\frac{dV}{dT}\right)_P, \quad (8)$$

where β is the compressibility. In the absence of expansion and compressibility data for the systems concerned, the equilibrium spacings could only be evaluated for 0°K.

The quantities given in column 5, Table III were computed from Eq. (8). For the sake of consistency the spacings listed for the five pure compounds were also computed from Eq. (8) instead of resorting directly to experiment. The observed lattice spacings at 25°C have been reported by Nickels, Fineman, and Wallace[14] for NaCl-NaBr solutions, by Oberlies[15] for KCl-KBr solutions, and by Havighurst, Mack, and Blake[16] for RbCl-KCl solutions.

Because of the difference in temperature, direct comparison between observed and computed lattice spacings is not possible. It is of some interest, however, to note that the observed deviations from Vegard's Law at 25°C (column 4) agree in sign and rather closely in magnitude with the differences (column 7) between the r_0's calculated from Eq. (8) and the spacings expected (column 6) on the basis of Vegard's Law at 0°K.

The extent of departure from Vegard's Law will, of course, be independent of temperature if the coefficient of thermal expansion of the solid solution is a linear function of composition. The decrease in r_0 between 25°C and 0°K is remarkably constant at about 1 percent for the five salts in Table III. It hardly seems possible that the solutions could have expansions differing substantially from the average for the pure constituents. Allowing for a maximum difference of 10 percent, the deviations in column 4 would be changed by only 0.003 angstrom units in correcting to absolute zero. Hence it appears that the Born-Mayer model is adequate in accounting for the observed spacings, at least for the three systems considered, to within 0.005–0.01 angstrom units or better. Furthermore, it seems that, when viewed from the framework of this model, the reasonably close agreement with the requirement of Vegard's Law is more accidental than fundamental.

ΔH_f is related to the lattice energies of the pure salts and the solid solution as follows:

$$\Delta H_f = U_s - (X_1 U_1 + X_2 U_2), \qquad (9)$$

where X_1 and X_2 are mole fractions of components 1 and 2 present in the solution. To evaluate ΔH_f the equilibrium spacings given in Table III, together with constants from Table II, are inserted into Eq. (2). In calculating ΔH_f, the last term in Eq. (2), the zero point energy, is neglected under the assumption that the change in this quantity is small compared to ΔH_f. The results obtained from Eq. (9) are summarized in Table IV together with results obtained from Eq. (1). Again,

comparison of observed and computed quantities is complicated by the fact that the two refer to different temperatures. If the solid solutions obey the Kopp-Neumann rule (additivity of heat capacities), then ΔH_f is independent of temperature and it is entirely appropriate to compare the ΔH_f's directly without regard to temperature.

Elsewhere attention has been directed[2] to the widespread use of the Kopp-Neumann rule for systems such as listed in Table IV and the dearth of supporting experiments. In what is perhaps the only comprehensive study of the thermal properties of an ionic solid solution, Eastman and Milner[17] observed that a AgCl-AgBr solid solution conformed to the additivity law for heat capacities within 0.1–0.2 percent at temperatures between 100 and 300°K. Below the liquid air range the departure increased somewhat, but down to about 15°K remained less than 1 percent. Eastman and Milner have expressed the opinion that similar behavior would probably be observed with other systems approaching ideal behavior about as closely as the AgCl-AgBr system.[18]

Eastman and Milner's data reveal that ΔH_f for their AgCl-AgBr solution decreases by less than 3 cal./mole between 298 and 0°K. The solid solutions discussed in this paper are probably less ideal than the silver salts, judging from the ΔH_f values (200–300 *versus* 80 cal./mole), but it appears unlikely that a change of more than 20–30 cal./mole would result from correcting the experimental heats of formation to 0°K. If this estimate of the change in ΔH_f with temperature is valid, then the observed heats listed in Table IV are correct for 0°K within about 10 percent and the deviations noted are due primarily to errors in the computed quantities. This suggests that neither the model used in this paper nor the one upon which Eq. (1) is based are adequate in accounting for the small changes in lattice energies which accompany solid solution formation.

When the individual contributions to ΔH_f are examined, it is found that changes in repulsion energy account for approximately two-thirds of the total. Alteration of the Coulombic energy is responsible for most of the remaining heat effect with the van der Waals' forces making a small (2–5 percent) exothermic contribution. Unfortunately it is the energy of repulsion which is least accurately known of the three energy terms involved, so it appears that a better computation of ΔH_f must await a more accurate description of the factors responsible for repulsion in a crystal. In this connection it is of interest to note that the heats of formation of solid solutions may provide a convenient experimental basis for elucidating the detailed characteristics of the repulsion potential since these heat effects can be readily and precisely determined with

[14] Nickels, Fineman, and Wallace, J. Phys. and Colloid Chem. **53**, 625 (1949).
[15] F. Oberlies, Ann. Physik **87**, 238 (1928).
[16] Havighurst, Mack, and Blake, J. Am. Chem. Soc. **47**, 29 (1925).

[17] E. D. Eastman and R. T. Milner, J. Chem. Phys. **1**, 444 (1933).
[18] This opinion is shared by the present author.

calorimeters currently available and since the repulsion energies may comprise a substantial part of the observed heat of formation.

In summary, it may be said that it appears that the best existing model for ionic solids, the Born-Mayer model, does not serve as an adequate basis to account completely for the small changes in lattice spacing and energy associated with the formation of alkali halide solid solutions. In particular, a better representation of the repulsion potential is needed. It seems that experimental and theoretical studies of the energy changes accompanying solid solution might open an attractive avenue for investigating the detailed characteristics of the forces at work in ionic crystals.

Rotation-Vibration Spectra of Diatomic and Simple Polyatomic Molecules with Long Absorbing Paths. II. The Spectrum of Carbon Monoxide below 1.2μ

G. HERZBERG
National Research Council, Ottawa, Canada

AND

K. NARAHARI RAO
Yerkes Observatory of the University of Chicago, Williams Bay, Wisconsin
(Received March 30, 1949)

The third overtone of CO at 1.19μ has been photographed under high dispersion. From this band precise values for the rotational constants of the CO molecule are derived. They agree excellently with the values obtained from the ultraviolet spectra but are considered to be much more accurate. The equilibrium internuclear distance of CO in the ground state is $r_e = 1.1281_9 \times 10^{-8}$ cm. An attempt to obtain also the fourth overtone failed even with path lengths of 3000 m atmos. The second overtone was observed under low resolution with a path length of 30 m.

1. INTRODUCTION

ROTATION-VIBRATION spectra in the photographic infra-red have thus far been observed almost exclusively for molecules containing hydrogen. For these molecules moderate path lengths (between 4 and 100 m) have proved to be sufficient to obtain strong absorption bands below 1.2μ. Much greater path lengths are required for molecules not containing hydrogen, partly because the vibrational frequencies are lower and therefore only higher overtones fall in the photographic region, and partly because the mechanical and electrical anharmonicities which determine the intensities of overtone bands are smaller. With the long optical paths described in paper I of this series[1] it becomes possible to study these spectra with the high resolution of a 21 foot grating. Up to now this has been done for CO, CO_2 and N_2O. The present paper describes the results for CO.

2. APPARATUS; DESCRIPTION OF SPECTRA

The large absorption tube described in I was filled with CO to a pressure of 1 atmos. The gas was obtained from the Matheson Company and is specified by them to be 92 percent pure. It was used without further purification.

Attempts were made to obtain both the 4−0 and 5−0 bands. However in spite of the use of up to 136 traversals corresponding to 3000 m atmos no trace of the 5−0 band was found. To be sure this band is expected in a region (9564A) where strong overlapping by H_2O lines occurs and where therefore a weak band is more difficult to observe. The 4−0 band was obtained with path lengths of 500 to 1000 m atmos.[2] Figure 1 shows one of the spectra obtained.

The lines of the CO band were measured against third order Fe lines. The averages of six measurements of each of three plates were used for the evaluation. In this way any constant shift relative to the comparison spectrum arising for example from slight temperature or pressure changes during the long exposures should be substantially eliminated. For the conversion to vacuum the index of refraction of air from Barrell and Sears[3] as recommended by Birge[4] was used. The wave numbers of unblended and not too weak lines are believed to be accurate to within less than 0.01 cm^{-1} relative to one another and within 0.03 cm^{-1} on an absolute scale.

Compared to similar CO_2 bands the intensity of the 4−0 band appears surprisingly low. However, a similar

[1] H. J. Bernstein and G. Herzberg, J. Chem. Phys. **16**, 30 (1949).

[2] A larger path cannot be used here because of the low sensitivity of the *I–Z* plates at 11900A.

[3] H. Barrell and J. E. Sears, Phil. Trans. Roy. Soc. (London) **238**, 1 (1939).

[4] R. T. Birge, Phys. Rev. **60**, 771 (1941).