Calculation of the Heats of Formation of Alkali Halide Solid Solutions from Hildebrand's Equation

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TABLE I.

Salt	$K \times 10^5$ at 25°C In ethylene chloride	In ethylidene chloride
o-chloro	ᵃ3.92 ±0.12	0.414 ±0.010
o-methoxy	7.85 ±0.25	1.12 ±0.020
m-methoxy	3.89 ±0.12	0.415 ±0.010

ᵃ Recalculated from data of Ramsey and Colichman by use of method of least squares to establish more precisely the linear relation between the functions involved.

the ions is Coulombic and the ions are considered to be rigid unpolarizable spheres in a continuous medium of uniform dielectric constant equal to the macroscopic dielectric constant of the pure solvent. For a uni-univalent electrolyte, this equation takes the form

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{\epsilon^2}{DkT}\right)^3 Q(b),$$

in which

$$b = \frac{\epsilon^2}{aDkT} \quad \text{and} \quad Q(b) = \int_2^b e^y y^{-4} dy$$

where $y = \epsilon^2/(rDkT)$. Other symbols have their usual meaning.

That deviations from this equation will occur for systems which differ appreciably from the idealized model is expected. An apparent deviation has been reported by Ramsey and Colichman.[2] They found the dissociation constant at 25°C of o-chlorophenyltrimethylammonium perchlorate in ethylene chloride (1,2-dichloroethane) to be approximately tenfold greater than in ethylidene chloride (1,1-dichloroethane). Since the dielectric constants of these solvents at 25°C are approximately equal, 10.23 for ethylene chloride and 10.00[3] for ethylidene chloride, and since there is no apparent reason why the a-values of this salt should be appreciably different in these two very similar solvents, this large difference in K-values seems anomalous. The fact that the product, $\Lambda_0 \eta$, of this salt has the same value within experimental error in these two solvents lends support to the conclusion that its a-values should be substantially the same.

In order to establish with certainty that a large difference in K-values of a given salt in these two solvents exists, the K-value of the ortho-chloro salt in ethylidene chloride and those of the ortho-methoxy and meta-methoxy salts in ethylene chloride have been redetermined. In addition the K-values of the two methoxy salts were determined in ethylidene chloride. Shedlovsky's[4] modification of the Fuoss and Kraus[5] conductance equation was used in obtaining these K-values, given in Table I.

Since the K-values of each of these three salts is very much (from seven to ten times) larger in ethylene chloride than in ethylidene chloride, it seems probable that these differences should be attributable to certain fundamental differences in these two solvents which are not apparent from their macroscopic properties.

On the basis of the reasonable assumption that the a-value of each of the salts is the same in these solvents it follows from the above equation that the large difference in K-values may be due to a difference between the macroscopic dielectric constant of at least one of the solvents and its effective dielectric constant, that is, the dielectric constant which is effective in determining the stability of the associated ion-pair of an electrolyte in that solvent. The conclusion that such a difference does not exist in ethylidene chloride solution is justified by the fact that the molecules of this solvent are known to exist in but one form. However, the results of a number of investigations have established the existence of restricted rotation about the carbon-carbon bond in the molecules of ethylene chloride which consists of three potential minima, 120° apart, in one complete rotation about this bond axis. From a study of the relative intensities of certain Raman lines in the vapor and liquid phases of ethylene chloride, Mizushima et al.,[6] have estimated the equilibrium ratio of the number of molecules in the gauche forms (an angle of 60° between the C—Cl bonds viewed along the C—C bond axis) to the number in the trans-form (180°

between the C—Cl bonds) to be 1.3:1 in liquid ethylene chloride at 25°C. They have also calculated the dipole moment of the gauche forms (one the mirror image of the other) to be 2.55×10^{-18} e.s.u. For comparison the dipole moment of ethylidene chloride molecules, determined by Ghosh et al.,[7] is 2.045×10^{-18} e.s.u.

The existence of these two isomers of ethylene chloride, the polar (the two gauche forms) and the non-polar (trans-) form leads to the conclusion that an ion in ethylene chloride will attract preferentially the gauche molecules and thereby produce an enhancement of the relative population of this form (N_g/N_t) in the near vicinity of the ion above the average in the pure solvent. This long-range ion-dipole interaction would make the effective dielectric constant in ethylene chloride greater than the macroscopic dielectric constant of this solvent and thus cause the measured K-value to be greater than that calculated by the above equation by use of the macroscopic dielectric constant and the correct a-value.

An independent method of determining the correct value of the parameter a to be used in the above equation is not in general available. However, the assumption that the a-value of a salt in ethylene chloride is the same as it is in ethylidene chloride provides, in this case, an independently determined a-value to be used for a given salt in ethylene chloride. The a-value found for each of the salts (in the order given in Table I) in ethylidene chloride are 3.50×10^{-8} cm, 3.85×10^{-8} cm and 3.50×10^{-8} cm, respectively. On substitution of the a-value, thus obtained, and the corresponding K-value, determined in ethylene chloride, the effective dielectric constant of ethylene chloride, consistent with these values, is evaluated by successive approximations. The average of the two values of the effective dielectric constant thus obtained is 11.9 ± 0.1. The K-values of these three salts in ethylene chloride calculated by use of 11.9 for D are 3.82×10^{-5}, 8.18×10^{-5}, and 3.82×10^{-5}, respectively. These values are seen to agree within experimental error with those measured.

That the effective dielectric constant of ethylene chloride in the near vicinity of an ion may be as much as 1.7 units greater than its macroscopic dielectric constant (10.23) is indicated by the crude value of 15.5 (calculated) for the dielectric constant of the pure liquid gauche form by Onsager's equation, approximating its density and refractive index to be those of ethylene chloride.

[1] N. Bjerrum, Kgl. Danske Vidensk. Selskab. 7, No. 9 (1926); see also R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. 55, 1019 (1933).
[2] J. B. Ramsey and E. L. Colichman, J. Am. Chem. Soc. 69, 3041 (1947).
[3] Private communication from Arthur E. Martell, Chemical Laboratories, Clark University, Worcester, Massachusetts. Measured at Brown University, Providence, Rhode Island.
[4] T. Shedlovsky, J. Frank. Inst. 225, 739 (1938).
[5] R. M. Fuoss and C. A. Kraus, J. Am. Chem. Soc. 55, 476 (1933); R. M. Fuoss, ibid. 57, 488 (1935).
[6] Mizushima, Morino, Watanabe, Simanouti, and Yamaguchi, J. Chem. Phys. 17, 591 (1949).
[7] Ghosh, Mahauti, and Sen-Gupte, Zeits. f. Physik 54, 711 (1929).

Calculation of the Heats of Formation of Alkali Halide Solid Solutions from Hildebrand's Equation

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HILDEBRAND[1] has derived the expression

$$\Delta H_f = \left(\frac{N_1 V_1 N_2 V_2}{N_1 V_1 + N_2 V_2}\right)\left[\left(\frac{\Delta E_1}{V_1}\right)^{\frac{1}{2}} - \left(\frac{\Delta E_2}{V_2}\right)^{\frac{1}{2}}\right]^2 \quad (1)$$

for the change in heat content on forming one mole of a solution from the pure liquids. ΔE, V, and N are the heat of vaporization, the molar volume and mole fraction, respectively, of the component liquids. In deriving the above equation the important

TABLE I. Heats of sublimation, molar volumes and solubility parameters of alkali halides.

Salt	ΔH_{sub}[a](cal./mole)	V^0(cm³/mole)	δ(cal./cm³)$^{\frac{1}{2}}$
NaCl	182,800	27.02[b]	82.25
NaBr	173,300	32.10[b]	73.48
KCl	164,400	37.52[c]	66.19
KBr	156,200	43.31[c]	60.05
RbCl	160,500	43.22[c]	60.94

[a] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 80.
[b] Nickels, Fineman, and Wallace, J. Phys. and Colloid Chem. **53**, 625 (1949).
[c] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1933).

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

	ΔH_f (cal./mole of ion pairs)			
	Obs.	Calc. (Eq. (1))	Calc.[a] (Wallace)	Calc.[b] (Tobolsky)
NaCl-NaBr				
Mole fraction NaCl				
0.75	257	442	440	
0.50	335	564	540	118
0.25	241	406	380	
KCl-KBr				
Mole fraction KCl				
0.75	186	295	360	
0.50	232	379	450	94
0.25	163	274	300	
RbCl-KCl				
Mole fraction 0.50	203	277	400	83
NaBr-KBr				
Mole fraction 0.50	700	1660		480
NaCl-KCl				
Mole fraction 0.50	1050	2025		594

[a] See reference 2.
[b] See reference 7.

assumptions made are:[1] (1) the intermolecular forces are radially symmetrical, (2) the repulsive forces approach zero very rapidly with distance, (3) the constants of attraction between unlike molecules are the geometric mean between those for the like molecules and (4) thermal agitation maintains complete random mixing of the two components.

Equation (1) should apply not only to liquid solutions but solid solutions which fulfill the above conditions. There are now available in the literature[2] reliable data on the heats of formation of solid solutions of alkali halides as well as computed values from the older Born[3] and the newer Born-Mayer[4] model for ionic solids. It is of interest to calculate the ΔH_f of these same systems by Eq. (1) for comparison with experimental and computed values.

In the present model of ionic solids assumptions 1 and 2 above are made. However, in the case of solid solutions of ionic substances the assumptions concerning the constants of attraction cannot be rigorously justified but may be approximated by the geometric mean. As for the fourth assumption, it has often been assumed[5] that in ionic solid solutions in which the components are sufficiently alike, there is a random distribution of the particles over the lattice sites. This assumption has been verified by Eastman and Milner[6] for one case—a AgCl-AgBr solid solution.

To apply Eq. (1) to solid solutions of ionic substances, the various terms now refer to the pure component ionic solids. The ΔE term is no longer the heat of vaporization, but the heat of sublimation of the pure salt to an infinitely dilute gas of the ions. The values of ΔE and V as well as the solubility parameters $[\delta = (\Delta E/V)^{\frac{1}{2}}]$ for the alkali halides to be considered are listed in Table I.

Table II contains the experimental heats of formation for several solid solutions of alkali halides and the computed values from Eq. (1), as well as those computed by Wallace[2] and by Tobolsky.[7] The values obtained using the simple Hildebrand equation, although larger than the observed values, are of the same order of magnitude. It is of further interest to note that the computed values from Eq. (1) agree with experiment as well as those calculated from the more refined but tedious methods of Wallace and of Tobolsky.

[1] J. H. Hildebrand, *Solubility of Non-Electrolytes* (Rheinhold Publishing Corporation, New York, 1936).
[2] W. E. Wallace, J. Chem. Phys. **17**, 1095 (1949).
[3] *Handbuch der Physik*, XXIV/2, 623 (1933).
[4] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).
[5] M. A. Fineman and W. E. Wallace, J. Am. Chem. Soc. **70**, 4165 (1948).
[6] E. D. Eastman and R. T. Milner, J. Chem. Phys. **1**, 444 (1933).
[7] A. V. Tobolsky, J. Chem. Phys. **10**, 187 (1942).

Passivation of Metals*

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THE passivation of some metals by films of substances such as O_2 and the stability of these films in a corroding medium might be explained on the basis of the band theory of metals and surface thermodynamics.

It can be shown from the band theory of metals[1] that the consideration of a real crystal as a finite lattice leads to the existence of surface states. Shockley[2] has shown that the surface states occur near the overlapping bands of all metals. These surface states can be looked upon as residual valences of the metal. Saturated molecules such as N_2 and CO_2 are polarized by the surface of the metal and are held by van der Waals forces (physical adsorption). The heats of adsorption of these substances are relatively low and can be estimated by several theoretical[3] methods and directly measured.

Stronger interaction with the surface states is possible with molecules which have unpaired electrons such as O_2 and NO. (O_2, $^3\Sigma$ in the ground state is paramagnetic; NO has an odd number of electrons, is paramagnetic and behaves under many circumstances as a free radical.) Molecules of this type can be considered as having residual valences. The residual valences of the metal can be saturated by the residual valences of these molecules leading to much stronger bonds between the metal and O_2 and NO than is obtained between N_2 and CO_2. This increased bonding strength leads to the passivation† of certain metals by O_2 and NO films, whereas the films of saturated molecules such as N_2 and CO_2 are ineffective.

In general, it would be expected that the strongest bonding (due to these residual valences) would be exerted by the transition metals (due to contributions of the d-orbitals), hence metal alloys such as stainless steel are effectively passivated by O_2 and NO.

The behavior of passive films immersed in corroding media is readily explained by the thermodynamics of surface equilibria:

If γ_{so}†† is the interfacial tension between the metal and the passivating film, γ_{sc} the interfacial tension between the metal and the corroding medium and γ_{oc} the interfacial tension between the film and the corroding medium, then the following inequalities can be written:

If
$$\gamma_{sc} \geqslant \gamma_{so} + \gamma_{oc}, \tag{1}$$

then the passivating film is stable in presence of the corroding medium and the film is protective because the corroding medium has no tendency to wet the metal surface.

If
$$\gamma_{so} \geqslant \gamma_{sc} + \gamma_{oc}, \tag{2}$$

then the passivating film is unstable or metastable in the presence