THE DISSOCIATION ENERGIES OF GASEOUS ALKALI HALIDES

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I. INTRODUCTION

It has been generally assumed that a classical electrostatic model should be adequate for the calculation of dissociation energies of the gaseous alkali halides. An accurate comparison of the theoretical predictions of such a simple model with the experimental results has been difficult until recently because of lack of information concerning the gaseous equations of state, which are needed to correct for gaseous imperfections, and because of lack of sufficient data to apply the third law of thermodynamics to the available vapor-pressure data to obtain reliable heats of vaporization. In recent years a great deal of attention has been directed to the polymerization of vapors of alkali halides, a manifestation of the gaseous imperfection, and sufficient data are now available to correct data for the alkali halide vapors to the hypothetical perfect-gas standard state. Also, low-temperature heat-capacity measurements for the solids, microwave determinations of internuclear distances, and infrared observations of vibrational frequencies now allow accurate calculations of entropies and free-energy functions for most of the alkali halides.

II. HEATS OF VAPORIZATION

The initial experimental observations are measurements of the vapor pressures of either the solid or the liquid phases. A variety of different methods of determining vapor pressures has been applied, and the rather serious discrepancies between different methods of measurement pose a difficulty in evaluating the data. Each method usually has its characteristic sources of error, and a very careful detailed consideration of all the experimental methods and of the exact procedures used is necessary to evaluate the available data adequately.

With reliable values of P_{eq}, the equilibrium vapor pressure, as a function of temperature and values of f/P, the ratio of fugacity to pressure at equilibrium conditions, the treatment of the data is quite straightforward. The third-law treatment of the vapor-pressure data to obtain ΔH°_{298}, the enthalpy of sublimation at 298.15°K. for the reaction MX(s) = MX(g), is illustrated by the equation

$$\frac{\Delta H^\circ_{298}}{T} = -\Delta\left(\frac{F^\circ - H^\circ_{298}}{T}\right) - R \ln\left(\frac{f}{P}\right) - R \ln P_{eq} \quad (1)$$

The function $\Delta[(F^\circ - H^\circ_{298})/T]$ is the difference between the standard free-energy functions of the gas and of the condensed phase as obtained from spectroscopic data and from heat-capacity and heat-of-transition data extending to very low temperatures. When all the data are accurate, each vapor-pressure value, whether in the solid or in the liquid range, should yield the same value of ΔH°_{298}.

When static vapor-pressure measurements are available, P_{eq} is obtained directly. In many instances, kinetic methods such as the transpiration method, in which an inert gas is saturated by the salt vapor, or the Knudsen method, which involves the rate of vaporization through an orifice into an evacuated space, are used. The evaluation of these measurements requires knowledge of the average molecular weight, and the data are most directly evaluated by treating the vapor as a mixture of monomer and polymeric species. From such data, one can obtain directly the fugacity of the monomer, and the last two terms of equation 1 are replaced by $-R \ln f_{eq}$, where f_{eq} is given by the equilibrium partial pressure of monomer obtained by representing the gas imperfection in terms of polymeric species.

For both the static and the kinetic methods, different investigations yield a range of values of P_{eq}. The value of f/P required for treatment of static vapor-pressure data depends upon the value of P_{eq} chosen.

In a parallel manner, the proportion of monomer to dimer chosen for evaluation of kinetic data depends upon the total vapor pressure. Thus the correction for gas imperfection or for polymerization cannot be made independently of the value of the total vapor pressure.

The treatment of the experimental data was carried out in the following sequence. All available data were carefully examined with respect to possibility of error and general degree of reliability to arrive at a first approximation to the most acceptable equilibrium vapor-pressure curve for each alkali halide. The comparison of the vapor-pressure measurements for liquid and solid can be tested much more precisely after one has applied the third law of thermodynamics. This was first done for both static and kinetic measurements without correcting for gas imperfection. The original equilibrium vapor-pressure measurements were substituted into the following equation, which may be compared with equation 1.

$$\frac{\Delta H^*_{298}}{T} = -\Delta \left(\frac{F^\circ - H^\circ_{298}}{T}\right) - R \ln P_{eq} \qquad (2)$$

As this calculation does not correct for gaseous imperfections, the resultant values of ΔH^*_{298} would not be expected to be independent of temperature. However, the variation of ΔH^*_{298}, where the asterisk indicates this is not the true heat of sublimation but one obtained through neglect of gas imperfections, should be a slowly varying function of temperature as indicated in figure 1,
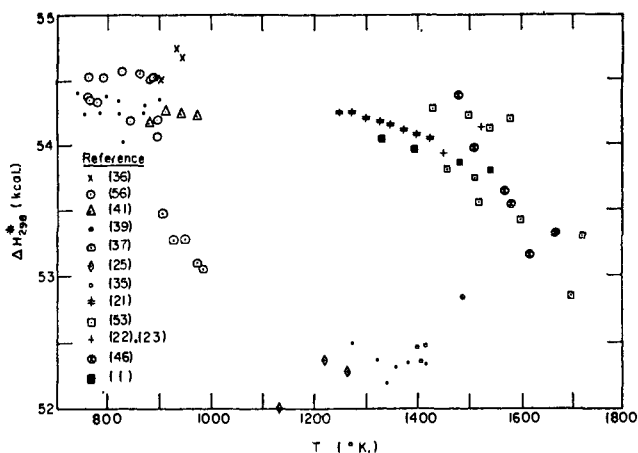

Fig. 1. ΔH^*_{298} versus T for sodium chloride.

where the data for sodium chloride are presented. A plot of this type allows one to make a very sensitive comparison of different data and particularly to make a good comparison of the consistency of vapor-pressure measurements for liquid and solid when the heats of fusion, and thus accurate values of $(F^\circ - H^\circ_{298})/T$ for the liquid, are known. Fortunately, the heats of fusion of virtually all the alkali halides have recently been determined (19). For sodium chloride there are a large number of concordant measurements. It is seen

that it is quite easy to draw a best curve of ΔH^* versus temperature, which in effect defines the best equilibrium vapor-pressure curves for both the solid and the liquid.

In correcting for gas imperfections there are two alternative procedures which are commonly used. One is to express an equation of state in terms of virial coefficients, and for virtually all the alkali halides at the pressures and temperatures of interest, a second virial coefficient would be adequate within the accuracy desired. One can equally well express the gas imperfection by a chemical approach which describes the gas in terms of monomers and dimers. Since most of the data which bear on the gas imperfections of alkali halides have been expressed in terms of monomer and dimer equilibria, the authors have followed this approach and have attempted to reconcile the various data which deal with the monomer–dimer equilibrium constant as a function of temperature. $\Delta C^\circ_P = -2$ cal./degree was assumed for the reaction $M_2X_2(g) = 2MX(g)$ for the temperature range above 1000°K.

Figure 2 shows the various data for sodium chloride
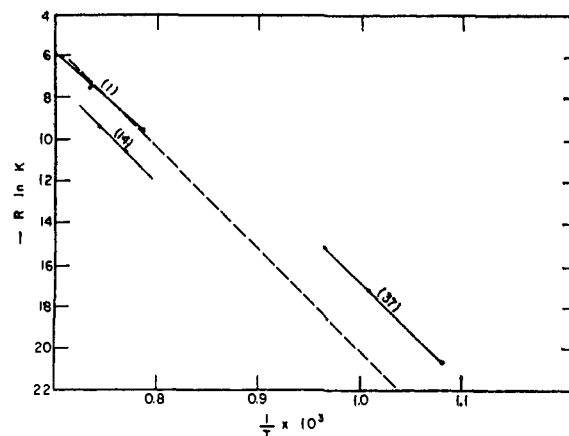

Fig. 2. Dimerization data for sodium chloride.

and the dashed line which has been chosen to best represent $R \ln K$ for $2NaCl(g) = Na_2Cl_2(g)$ as a function of $1/T$. The best line is seen not to be a simple average of the various measurements but a weighted average based on consideration of the magnitude of possible sources of error of the various types of measurements. With the value of the equilibrium constant for the monomer–dimer equilibrium established, one can calculate, for each equilibrium vapor pressure, the proportion of monomer and dimer and thus subtract from the equilibrium vapor pressure the partial pressure of dimer. This yields the partial pressure of monomer or the fugacity of the monomer if higher polymers are negligible. This value, which is expressed as f_{eq}, can now be substituted into equation 3.

$$\frac{\Delta H^\circ_{298}}{T} = -\Delta \left(\frac{F^\circ - H^\circ_{298}}{T}\right) - R \ln f_{eq} \qquad (3)$$
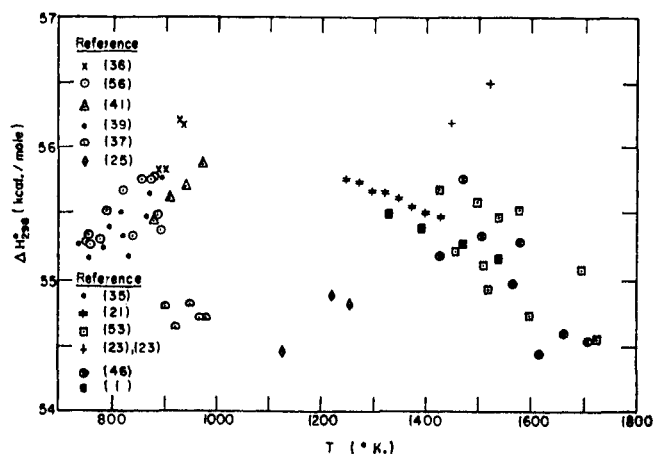
FIG. 3. ΔH°_{298} of sublimation of sodium chloride.

Now one should obtain the true value of ΔH°_{298} from each individual vapor-pressure measurement, and figure 3 shows the values of ΔH°_{298} as obtained from each individual vapor-pressure measurement for sodium chloride. It is obvious that there is some leeway in the fitting of the data by the curve of figure 2 and that slight shifts of the curve representing the monomer-dimer equilibrium will cause corresponding shifts in the ΔH°_{298} values of figure 3. The curve chosen in figure 2 represents the best fit of the data consistent with a reasonable entropy of dimerization.

There are inherent errors in the various measurements which are very difficult to avoid, and there are fairly serious discrepancies between measurements which must be reconciled in this type of procedure. This process was carried out for each of the alkali halides. Fortunately for those alkali halides with rela-

tively large cations, the degree of gas imperfection is rather small and the uncertainties in the monomer-dimer equilibrium did not have any large influence upon the final heat of sublimation that was adopted. Also, the thermodynamic data are known with rather high accuracy for most of the alkali halides. The uncertainties which are given after the final values of ΔH°_{298} in table 7 are based on consideration of the uncertainties in the free-energy functions as well as the uncertainties in the vapor-pressure measurements and the monomer-dimer equilibrium constants.

The treatment of the data for lithium halides is somewhat more difficult because of the very extensive gas imperfections. However, for purposes of comparison with theoretical calculations, these experimental values are quite adequate and are known to a relatively high degree of accuracy compared to most equilibrium measurements which have been carried out at such temperatures.

The available data for all the alkali halides were treated in the manner illustrated for sodium chloride. The free-energy functions of both the diatomic gaseous molecules and the condensed phases are given in tables 1 and 2 and are combined in table 3 in the form actually used in the calculations. Table 4 gives the molecular constants used to obtain the free-energy functions of table 1. Table 5 lists the melting points and enthalpies of fusion, together with references to all of the data required for the construction of table 2. Table 6 lists the data for the dimer which were necessary to correct for gas imperfection. Table 7 lists the resultant ΔH°_{298} values for the sublimation of MX(g) together with references to the vapor-pressure data considered.

TABLE 1

Free-energy functions for gaseous diatomic alkali halides

Halide	$-\left(\dfrac{F^\circ_T - H^\circ_{298}}{T}\right)$ in calories per degree mole								
	298	400	600	800	1000	1250	1500	1750	2000°K.
LiF	47.77	48.06	49.29	50.61	51.83	53.19	54.41	55.48	56.43
LiCl	50.80	51.12	52.41	53.77	55.04	56.45	57.69	58.78	59.74
LiBr*	53.58	53.91	55.22	56.62	57.91	59.32	60.59		62.72
LiI*	55.48	55.81	57.13	58.56	59.86	61.31	62.57		64.66
NaF	51.98	52.30	53.65	55.06	56.36	57.78	59.05	60.15	61.14
NaCl*	54.87	55.20	56.55	57.97	59.34	60.80	62.08	63.19	64.23
NaBr*	57.60	57.94	59.32	60.76	62.10	63.58	64.85	65.97	67.02
NaI*	59.48	59.83	61.22	62.68	64.01	65.49	66.78	67.90	68.93
KF	54.19	54.52	55.87	57.30	58.61	60.05	61.30	62.42	63.40
KCl*	56.98	57.35	58.80	60.23	61.57	63.04	64.33		66.50
KBr*	59.89	60.24	61.64	63.10	64.44	65.93	67.22		69.38
KI	61.78	62.14	63.53	64.98	66.30	67.76	69.03	70.15	71.16
RbF	56.61	56.94	58.30	59.73	61.03	62.47	63.73	64.85	65.84
RbCl*	59.85	60.20	61.60	63.06	64.40	65.88	67.16		69.34
RbBr	62.36	62.71	64.10	65.56	66.87	68.34	69.61	70.74	71.74
RbI	64.33	64.67	66.07	67.53	68.85	70.32	71.59	72.72	73.72
CsF	58.03	58.37	59.73	61.15	62.47	63.90	65.17	66.28	67.27
CsCl*	61.19	61.54	62.94	64.40	65.74	67.21	68.51		70.68
CsBr	63.99	64.34	65.74	67.20	68.52	69.98	71.26	72.37	73.36
CsI	66.01	66.38	67.78	69.24	70.57	72.03	73.30	74.43	75.41

* Calculated from data given by Rice and Klemperer (45).

TABLE 2

*Free-energy function for condensed alkali halides**

Halide	$-\left(\dfrac{F_T^\circ - H_{298}^\circ}{T}\right)$ in calories per degree mole								
	298	400	600	800	1000	1250	1500	1750	2000°K.
LiF	8.52	8.93	10.67	12.58	14.39	17.10	(19.84)		(24.24)
LiCl	14.17	14.63	16.55	18.63	21.25	24.46	(27.12)	(29.37)	
LiBr	(16.6)	(17.1)	(19.0)	(21.1)	(23.9)	(27.1)	(29.8)		
LiI	(19.8)	(20.3)	(22.2)	(24.7)	(27.6)	(30.7)	(33.3)		
NaF	12.26	12.71	14.57	16.56	18.42	20.56	23.38	(25.93)	(28.12)
NaCl	17.33	17.81	19.77	21.87	23.85	26.97	29.90	(32.37)	
NaBr	(20.8)	(21.30)	(23.29)	(25.42)	(27.42)	(30.83)	(33.75)	(36.22)	
NaI	23.55	24.07	26.17	28.30	(30.80)	(34.21)	(37.01)		
KF	15.91	16.38	18.30	20.37	22.29	25.01	(27.89)	(30.33)	
KCl	19.72	20.21	22.20	24.34	26.34	29.67	(32.65)		
KBr	22.96	23.47	25.51	27.66	29.68	33.16	(36.05)		
KI	25.2	25.70	27.78	29.96	(32.29)	(35.77)	(38.63)		
RbF	(18.6)	(19.09)	(21.05)	(23.20)	(25.31)	(28.54)	(31.51)	(34.03)	
RbCl	(22.9)	(23.4)	(25.4)	(27.5)	(29.5)	(33.0)	(35.8)	(38.2)	
RbBr	26.0	26.50	28.49	30.61	(32.77)	(36.12)	(38.88)	(41.25)	
RbI	28.2	28.69	30.68	32.79	(35.11)	(38.45)	(41.22)	(43.58)	
CsF	(20.3)	(20.8)	(22.7)	(24.9)	(27.1)	(30.6)	(33.4)		
CsCl	(24.5)	(25.0)	(27.1)	(29.2)	(31.7)	(35.1)	(37.8)		
CsBr	(27.9)	(28.4)	(30.5)	(32.6)	(35.3)	(38.8)	(41.7)		
CsI	(30.2)	(30.7)	(32.8)	(34.9)	(37.7)	(41.2)	(44.0)		

* Values in parentheses are estimated.

III. DISSOCIATION ENERGIES

The enthalpies of sublimation of table 7 were combined with enthalpies of formation of the solid alkali halides and the gaseous monatomic elements as given by Lewis, Randall, Pitzer, and Brewer (34) to obtain the ΔH_{298}° values for $MX(g) = M(g) + X(g)$ that are given in table 8. ΔH_0° values were obtained by subtracting 0.4 to 0.9 kcal. from LiF to CsI. The values were converted to ΔH_0° values for $MX(g) = M^+(g) + X^-(g)$ by use of the ionization energies given by Moore (38)

and the following electron affinities: F, 80.6 kcal.; Cl, 85.3 kcal.; Br, 80.2 kcal.; and I, 73.0 kcal. The electron affinities were obtained by repeating the lattice-energy calculations of Cubicciotti (12) with use of more recent data (34).

IV. COMPARISON WITH THEORETICAL CALULATIONS

In carrying out the theoretical calculations of expected dissociation energies of alkali halides to gaseous ions, one of the main uncertainties is the calculation of

TABLE 3

Change in free-energy function for MX(s, l) = MX(g)

Halide	$-\left(\dfrac{\Delta F^\circ - \Delta H_{298}^\circ}{T}\right)$ in calories per degree mole								
	298	400	600	800	1000	1250	1500	1750	2000°K.
LiF	39.25	39.13	38.62	38.03	37.44	36.09	34.57	33.27	32.19
LiCl	36.63	36.49	35.86	35.14	33.79	31.99	30.53	29.37	
LiBr	37.0	36.8	36.2	35.5	34.0	32.2	30.8		
LiI	35.7	35.5	34.9	33.9	32.3	30.6	29.3		
NaF	39.72	39.59	39.08	38.50	37.94	37.22	35.67	34.22	33.02
NaCl	37.54	37.39	36.78	36.10	35.49	33.83	32.18	30.82	
NaBr	36.80	36.64	36.03	35.34	34.68	32.75	31.10	29.75	
NaI	35.93	35.76	35.05	34.38	33.21	31.28	29.77		
KF	38.28	38.14	37.57	36.93	36.32	35.03	33.41	32.09	
KCl	37.26	37.14	36.60	35.89	35.23	33.37	31.68		
KBr	36.93	36.77	36.13	35.44	34.76	32.77	31.17		
KI	36.58	36.44	35.75	35.02	34.01	31.99	30.40		
RbF	38.0	37.85	37.25	36.53	35.72	33.93	32.22	30.82	
RbCl	37.0	36.8	36.2	35.6	34.9	32.9	31.4	30.1	
RbBr	36.36	36.21	35.61	34.95	34.10	32.22	30.73	29.49	
RbI	36.13	35.98	35.39	34.74	33.74	31.87	30.37	29.14	
CsF	37.7	37.6	37.0	36.3	35.4	33.3	31.8		
CsCl	36.7	36.5	35.8	35.2	34.0	32.1	30.7		
CsBr	36.1	35.9	35.2	34.6	33.2	31.2	29.6		
CsI	35.8	35.7	35.0	34.3	32.9	30.8	29.3		

TABLE 4

Data used in calculating free-energy functions
for gaseous diatomic alkali halides*

Alkali Halide	r_e	ω
	A.	cm.$^{-1}$
LiF	1.547	(900)
LiCl	(2.022)	650
LiBr	2.1704	576
LiI	2.3919	501
NaF	(1.840)	(450)
NaCl	2.3606	366
NaBr	2.5020	302
NaI	2.7115	258
KF	(2.129)	(378)
KCl	2.6666	281
KBr	2.8207	213
KI	3.0478	173
RbF	2.2655	(370)
RbCl	2.7868	228
RbBr	2.9448	166
RbI	3.1769	128
CsF	2.3453	(360)
CsCl	2.9062	209
CsBr	3.0720	139
CsI	3.3150	101

* All internuclear distances, with the exception of those for RbF (33) and LiF (8). are from Honig. Mandel, Stitch, and Townes (24). Their estimates of r_e should be good to 1 per cent, which contributes an uncertainty of 0.04 in the free-energy function. The vibrational frequencies are from Klemperer (30, 31, 44) except those for NaF and KF, which are estimated by Berkowitz (5).

the contribution to the energy due to the repulsive forces between the ions caused by interpenetration of electron clouds. The proper functional form of the repulsive force as a function of internuclear distance is not well established. Berkowitz (5) has recently repeated the calculations of Rittner, using an exponential form to represent the repulsive contribution.

Table 9 shows the comparison of the experimental enthalpies of dissociation to the free ions with the calculated values based on the classical electrostatic model which considers dipole polarization of the ions.

The agreement is most remarkable. With the exception of lithium fluoride, for which the experimental value is 8.5 kcal. larger than the calculated value, all other values agree well within experimental error. The problem, in fact, is to explain the closeness of the agreement. On one hand, the theoretical values are certainly incomplete in considering only dipole polarization. On the other hand, the experimental values include uncertainties due not only to the enthalpies of vaporization which have been derived in this paper but also uncertainties of the enthalpies of formation of the solid halides, of the enthalpies of sublimation of the elements, and particularly of the electron affinities of the halogens.

The experimental values for the potassium halides are uniformly 1 kcal./mole low, while those for the rubidium salts are 2 kcal./mole low. The most likely source of these uniform differences is an error in the enthalpy of formation of the aqueous ion, which probably should be more negative by as much as 0.5 kcal. for potassium and as much as 1-2 kcal./mole for rubidium, with some error also due to the enthalpy of sublimation of rubidium metal. The calculation of electron affinities from the lattice energies of the solids also indicates similar errors in the data for potassium and rubidium. One might expect uniform differences to be shown for the salts of a given halogen, owing to error in the electron affinity of the halogen. No such differences are shown for any of the halogens.

TABLE 5

Fusion data and references to heat-capacity and entropy data of condensed alkali halides

Halide	References for ΔS_{298}°	References for C_p° at High Temperatures	T_f	ΔH_f°	References for Fusion Data
			$^{\circ}K.$	kcal./mole	
LiF	(16)	(16, 18)	1121	6.47	(16, 18)
LiCl	(49)	(17, 18)	880	4.72	(17, 18)
LiBr	—	—	823	4.22	(19)
LiI	—	—	742	3.50	(19)
NaF	(29)	(42)	1268	8.03	(19, 42)
NaCl	(11, 50)	(27)	1073	6.69	(19)
NaBr	—	(27)	1020	6.24	(19)
NaI	(4)	(27)	933	3.64	(19)
KF	(55)	(27)	1131	6.75	(19, 27)
KCl	(4, 28, 51)	(27)	1044	6.27	(27)
KBr	(4, 11, 32)	(10)	1007	6.10	(19)
KI	(4. 11. 32)	(10)	954	5.74	(19)
RbF	—	(26)	1068	5.82	(19. 26)
RbCl	—	—	995	5.67	(19)
RbBr	(11. 32)	(27)	965	5.57	(19)
RbI	(11. 32)	(27)	920	5.27	(19)
CsF	—	—	976	5.19	(19)
CsCl	—	—	918	4.84	(19)
CsBr	—	—	909	5.64	(19)
CsI	—	—	899	5.64	(19)

TABLE 6

Thermodynamic data for $M_2X_2(g) = 2MX(g)$

Halide	ΔH°_{1000}	References	ΔS°_{1000}	References	P_2/P_1 (T = 1000°K.)	References
	kcal./mole		cal./degree mole			
LiF*	61.5	(20)	34.0	—	0.74	(20)
LiCl	52.1	(6, 37)	32.1	—	0.3	(6, 37)
LiBr	46.6	—	31.6	(3)	1.4	(37)
LiI	43.4	—	(31.3)	—	(1.2)	—
NaF	56.9	(20)	31.6	—	0.15	(20)
NaCl	48.5	(2, 14, 37)	29	(2, 14, 37)	1.0	—
NaBr	46.1	(14)	29.3	(14)	0.9	—
NaI	41.2	(13, 14, 37)	27	(13, 14, 37)	1.0	—
KF	49.6	(20)	32.4	—	0.14	(20)
KCl	44.5	(2, 6, 14. 37)	28.4	(2, 3. 6, 14)	0.35	—
KBr	(40.6)		(27.7)		0.2	—
KI	37.5	(14. 37)	26.3	(3, 14)	0.2	—
RbF	43.9	(20)	29.4	—	0.14	(20)
RbCl	41.7	(14. 37)	28.1	(3, 14)	0.3	—
RbBr	(37.2)		(27)		0.06	
RbI	(34.4)		(27)		0.04	
CsF	39.2	(20)	30.5	—	0.12	(20)
CsCl	39.0	(3, 14, 37)	28.0	(3, 14, 37)	0.22	—
CsBr	(35.7)		(27)		0.10	
CsI	(32.0)		(27)		0.02	

* Trimers were considered only for LiF. At 1000°K. $\Delta H^\circ_3 = 40.5$ kcal./mole (20), $\Delta S^\circ_3 = 18.2$ kcal./degree mole, and $P_3/P_1 = 0.04$ (20). At 1800°K. $P_3/P_1 = 0.35$.

The method of obtaining the electron affinities through use of the theoretical value for the lattice energy of the solid salt essentially insures agreement.

The main reason for the extraordinary agreement between the calculated and experimental values of table 9 must lie in the use of the constant of the exponential repulsive term as a parameter. The theoretical treatment is certainly incomplete, in that it only considers dipole polarization of the ions. Inclusion of higher terms will certainly increase the calculated force of

TABLE 7

Enthalpy of sublimation at 298.15°K. for the diatomic gas

Halide	ΔH°_{298}	Vapor-pressure Data Used for Evaluation of ΔH°_{298}
	kcal./mole	
LiF	65.5 ± 1	(43, 47, 54)
LiCl	51.5 ± 2	(6, 25, 35, 37, 40, 41)
LiBr	48.7 ± 2	(37, 46, 54)
LiI	44.2 ± 2	(46, 54)
NaF	67.1 ± 1	(41, 43, 47, 48, 54)
NaCl	55.5 ± 0.5	(1, 21, 22, 23, 36, 39, 41, 46, 53, 56)
NaBr	52.0 ± 1	(9, 36, 41, 46, 53)
NaI	47.5 ± 1	(9, 22, 37, 46, 54)
KF	57.3 ± 1	(43, 47, 54)
KCl	53.3 ± 0.5	(1, 6, 7, 15, 21, 22, 23, 36, 41, 43, 46, 52, 53, 56)
KBr	51.0 ± 0.5	(21, 23, 36, 41, 46, 53, 56)
KI	48.5 ± 0.5	(21, 22, 41, 46, 53, 56)
RbF	54.1 ± 1	(43)
RbCl	51.1 ± 1	(36, 52, 54)
RbBr	49.4 ± 1	(36, 46, 54)
RbI	47.3 ± 1	(41, 46, 54)
CsF	48.3 ± 1	(43, 47, 54)
CsCl	48.3 ± 1	(21, 25, 46, 52, 54)
CsBr	46.6 ± 1	(9, 41, 46, 54)
CsI	46.7 ± 1	(9, 15, 46, 54)

TABLE 8

Dissociation enthalpies of alkali halides
$$MX(g) = M(g) + X(g)$$

ΔH°_{298} in kilocalories

LiF 137.5	LiCl 111.9	LiBr 100.2	LiI 84.6
NaF 114.0	NaCl 97.5	NaBr 86.7	NaI 72.7
KF 117.6	KCl 101.3	KBr 90.9	KI 76.8
RbF 116.1	RbCl 100.7	RbBr 90.4	RbI 76.7
CsF 119.6	CsCl 106.2	CsBr 96.5	CsI 82.4

TABLE 9

Comparison of experimental and calculated values of enthalpies of dissociation to the free ions
$$MX(g) = M^+(g) + X^-(g)$$

	ΔH°_0				
	Li	Na	K	Rb	Cs
	kcal.	kcal.	kcal.	kcal.	kcal.
F { calculated	172	151	137	—	128
F { experimental	180.5	151	136	131	128
Cl { calculated	148	129	117	113	110
Cl { experimental	150	130	115	110	110
Br { calculated	141	124	111	107	105
Br { experimental	144	124	110	105.5	106
I { calculated	133	117	105	102	99
I { experimental	135	117.5	104	99.5	99

attraction between the ions. However, the experimental interionic distances are used in the calculations and an increase in the calculated attractive force will require a corresponding increase in the repulsive force to maintain the same distance.

The agreement shown in table 9 then does not necessarily testify to the adequacy of the particular theoretical model, but is more a confirmation of the consistency of the experimental data. The contribution due to the point charge interactions is fixed by the experimental interionic distances. The other attractive and repulsive contributions are smaller and largely cancel one another. As long as the repulsive term cannot be fixed independently instead of being used as a parameter, one can expect agreement of the type shown in table 9 for a variety of models with varying polarization treatments. One must look to properties other than the energy—such as dipole moment, for example—to test the adequacy of the treatment of the polarization of the ions.

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