Dissociation energies of CaI, SrI, and BaI from high temperature mass spectrometry

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(Received 9 September 1977)

Equilibrium effusion beams containing the gaseous molecules CaI, SrI, and BaI were generated by the reaction of HI with the corresponding metal oxides at 1500 to 1900 K. Beam composition data obtained by mass spectrometry were used to determine the equilibrium constants of gaseous reactions involving the monoiodides and certain reference molecules. Reaction enthalpies then were evaluated by second and third law methods, from which the dissociation energies $D_0°$(CaI) $= 62.1 \pm 2.5$, $D_0°$(SrI) $= 63.6 \pm 1.4$, and $D_0°$(BaI) $= 71.4 \pm 1.0$ kcal/mole were derived. The results are consistent with data obtained earlier for the diatomic metal fluorides, chlorides, and bromides, and they are compatible with the predictions of the Rittner polarizable-ion model. Various features of the chemical bonding are discussed. A correlation of the thermochemical properties across the entire halide series allows one to estimate reliable dissociation energies for BeBr, BeI, MgBr, and MgI.

INTRODUCTION

The dissociation energies $(D_0°)$ of the gaseous mono-iodides of the alkaline earth metals are quite uncertain, as noted in a recent critical review of the thermochemistry of these compounds.[1] There have been no direct thermochemical determinations of these quantities, but considerations based largely on Birge–Sponer extrapolations and bond energy correlations led to the selected values $D_0°$(BeI) $= 62 \pm 10$, $D_0°$(MgI) $= 54 \pm 10$, $D_0°$(CaI) $= 69 \pm 20$, $D_0°$(SrI) $= 72 \pm 20$, and $D_0°$(BaI) $= 78 \pm 20$ kcal/mole.[1] In an earlier review Gaydon[2] estimated $D_0°$(CaI) $= 69 \pm 23$ kcal/mole, but considered the experimental data for BaI and SrI to be inadequate and declined to give recommended values. Lower bounds to the dissociation energies of CaI, SrI, and BaI of 64, 65, and 66 kcal/mole, respectively, were deduced later from the threshold energies of crossed beam reactions of HI with the metals.[3] Subsequently, the value $D_0°$(BaI) $= 102 \pm 1$ kcal/mole was reported, based on chemiluminescent spectra resulting from the Ba + I$_2$ reaction.[4]

In a recent analysis of thermochemical data for the Ca, Sr, and Ba monobromides we reported some preliminary results and some projected values for the monoiodides that indicated $D_0°$(CaI) $\cong 62 \pm 5$, $D_0°$(SrI) $\cong 66 \pm 5$, and $D_0°$(BaI) $= 71 \pm 3$ kcal/mole.[5] We have now completed experimental determinations of these quantities by a thermochemical method and report the results here. The monoiodide dissociation energies follow smooth trends established by the other monohalides, and provide a good opportunity for testing modeling schemes used to predict binding energies.

EXPERIMENTAL

The thermochemical data were derived from equilibrium measurements made by means of high tempera-

ture mass spectrometry. A description of the instrument, the experimental technique, and the method of evaluating the results is given in previous publications.[6] For this work beams to be sampled by the mass spectrometer were generated by admitting gaseous HI to the base of a molybdenum effusion oven containing a mixture of metal oxides. The gas was introduced via a molybdenum gas inlet tube connected to an external reservoir; gas flow was controlled by a variable leak valve. In equilibrium studies of the Ca–Al–I and Sr–Al–I systems the corresponding IIA metal oxide was added to a mixture of Al$_2$O$_3$ and AlB$_{12}$. Unresolved overlap of AlI$^+$ and BaO$^+$ at nominal m/e 154 precluded the use of AlI as a reference for measurement of $D_0°$(BaI). Therefore, BaI was measured by reference to GaI, using beams produced by the reaction of HI with a mixture of BaO and Ga$_2$O$_3$. The oxide samples were placed in the lower half of the effusion oven and were covered with a thin molybdenum partition containing several 0.5 mm diameter holes to increase the number of reactive gas–solid collisions.

Identification of neutrals in the collision–free effusion beam emerging from the oven was made from the masses, isotopic distribution, and threshold appearance potentials of ions formed by electron impact. The response of each signal to misalignment of the neutral beam defining slit was checked at all temperatures to correct for any background contributions; the latter were generally negligible. Some of the measurements on the Ba–Ga–I equilibria were made by both pulse counting and electrometer techniques, with no discernible difference in derived results. In general, pulse counting yields data of higher precision and accuracy. The conventional electrometer method was used in measurements on the Ca and Sr iodides.

The sample of HI was obtained from the Matheson Co. All of the metal and metal oxide samples were of reagent grade quality.

RESULTS

The IIA metals and their monoiodides, along with the Al and Ga reference species, were observed as com-

ponents of the effusion oven beams when HI was admitted at temperatures of 1600 to 1800 K. Identification is based primarily on the threshold appearance potentials of the resulting ions, shown in Table I. The threshold appearance potentials of the atomic ions are in agreement with the spectroscopic ionization potentials of the corresponding metals, as are those of CaI^+, SrI^+, and BaI^+. This latter observation is in accord with results for all of the other Group IIA monohalides, signifying that the ionization of MI occurs by removal of a nonbonding σ electron derived largely from the metal s orbital. On the other hand, the appearance potentials of AlI^+ and GaI^+ are higher than those of the metals, as expected for removal of a bonding electron from the $^1\Sigma$ ground state of AlI and GaI; similar results were observed for AlF, AlCl, and AlBr.[5,6] In any event, the observed threshold appearance potentials clearly identify the metals and metal monoiodides as constituents of the neutral effusion beams. Sharp second thresholds appeared in the ion yield curves of the IIA monoiodides, denoting the onset of di-iodide fragmentation; only the values for SrI^+ and BaI^+ were recorded, as shown in Table I. Interference from fragmentation was easily avoided by measuring the parent MI^+ signals below these second onsets. A weak BaI_2^+ parent ion signal was also observed, with threshold appearance potential of 7.5 eV; however, the measured ion abundances show that fragmentation is clearly the dominant ion production process in BaI_2, as it is in the other di-iodides. Several measurements of equilibria involving SrI_2 and BaI_2 were made by extrapolating the MI^+ parent ion curves to higher energies and estimating the MI^+/MI_2 fragment ion contributions.

The gaseous isomolecular exchange reactions

$$Ca + AlI = CaI + Al, \tag{1}$$

$$Sr + AlI = SrI + Al, \tag{2}$$

TABLE I. Threshold appearance potentials of ions formed from effusion beam species.

Ion	Appearance potential (eV)[a]	Neutral	Literature[b]
Ca^+	6.0	Ca	6.11
CaI^+	6.1	CaI	
Sr^+	5.5	Sr	5.69
SrI^+	5.5	SrI	
	9.5	SrI_2	
Ba^+	5.0	Ba	5.21
BaI^+	5.0	BaI	
	9.0	BaI_2	
Al^+	6.0	Al	5.98
AlI^+	9.3	AlI	
Ga^+	6.0	Ga	6.00
GaI^+	9.0	GaI	

[a]Uncertainty ±0.3 eV.
[b]Reference 26.

TABLE II. Change in free energy function for gaseous reactions.

	$-\Delta(G° - H°_{298})/T$ (cal/mole deg)			
Gaseous reaction	1400 K	1600 K	1800 K	2000 K
$Ca + AlI = CaI + Al$	5.68	5.69	5.70	5.71
$Sr + AlI = SrI + Al$	6.02	6.04	6.06	6.08
$Sr + SrI_2 = 2\ SrI$	8.24	8.06	7.89	7.74
$Ba + GaI = BaI + Ga$	5.33	5.43	5.51	5.57
$Ba + BaI_2 = 2\ BaI$	8.70	8.62	8.54	8.46

and

$$Ba + GaI = BaI + Ga \tag{3}$$

were studied at a series of temperatures by measuring the corresponding parent ion abundances at equal excess energy increments (3 eV) above threshold. In addition, the two monoiodide disproportionation reactions

$$Sr + SrI_2 = 2\ SrI, \tag{4}$$

$$Ba + BaI_2 = 2\ BaI \tag{5}$$

were studied in a limited fashion by evaluating the MI_2 molecular abundances from the MI^+/MI_2 fragment ion signals, as described above. These measurements were sufficient to provide reliable equilibrium constants for use in third law calculations. Equilibrium constants were evaluated from the ion abundance ratios without further correction, and were analyzed by second and third law methods. For each species the intensity of the major isotopic peak was measured; since iodine is monoisotopic, the derived equilibrium constants need not be corrected for isotopic distribution. For these calculations the thermodynamic functions of all gaseous species except Ga and GaI were taken from the JANAF Tables[1]; see the Appendix for the pertinent table date of issue. A small correction was applied to the tabulated functions for AlI to be consistent with the internuclear distance of 2.537 Å determined by microwave spectroscopy.[7] The functions of Ga compiled by Stull and Sinke[8] were used in the analyses, while those of GaI were calculated from available spectroscopic constants.[9,10] Values of the change in free energy function $-\Delta(G° - H°_{298})/T$ for the various reactions are summarized in Table II. The equilibrium data and the derived thermochemical results are given in Tables III–V. The agreement between second and third law heats is quite satisfactory for the monoiodide gaseous exchange reactions. Since the spectroscopic constants of the diatomic metal iodides are known accurately, the third law heats are preferred.

Several measurements showed the derived equilibrium constants to be independent of changes in gas composition effected by varying the HI flow rate. Consider, for example, the two data points for the Sr–Al–I system at 1762 K, obtained at different HI flow rates. The parent ion intensities of Sr^+, SrI^+, Al^+, and AlI^+ changed by factors of 1.2, 36, 0.87, and 25, respectively, yet the two derived equilibrium constants for Reaction (2) are in good agreement. Likewise, for the Ba–Ga–I system

TABLE III. Ion abundances and derived equilibrium data for the gaseous reaction $Ca + AlI = CaI + Al$ (1).

$T(K)$	$I(Ca^+)$ (9.0 eV)	$I(CaI^+)$ (9.0 eV)	$I(Al^+)$ (9.0 eV)	$I(AlI^+)$ (12.0 eV)	$K_{eq}(1) \times 10^2$	$\Delta H^\circ_{298}(1)$ (kcal/mole)
1541	1.16	0.315	1.74	50.7	0.932	23.1
1573	2.84	1.04	6.42	223	1.05	23.2
1573	3.75	0.76	5.64	105	1.09	23.1
1575	2.72	1.05	6.84	290	0.910	23.7
1576	2.55	1.07	6.57	287	0.961	23.5
1589	4.98	1.40	8.16	200	1.15	23.1
1618	6.96	1.96	11.3	248	1.28	23.2
1643	13.9	1.66	20.7	153	1.62	22.8
1646	13.7	1.52	20.2	159	1.41	23.3
1674	25.6	3.45	33.6	302	1.50	23.5
					Average	23.2
					Second law	22.9 ± 3.0

at 1711 K, HI flow rate variations led to changes in the Ba^+, BaI^+, Ba^+, and GaI^+ parent ion abundances by factors of 0.43, 2.4, 4.4, and 25, respectively; despite these variations, the derived equilibrium constants of Reaction (3) for the two different conditions are in good accord. Similar statements can be made about the Ba–Ga–I data points at 1722 K. The invariance of K_{eq} with these substantial changes in neutral abundance is a good indication of the attainment of gaseous equilibrium.

DISCUSSION

Derived dissociation energies of CaI, SrI, and BaI

The resulting thermochemical data for Reactions (1)–(5) can be combined with available data for the reference molecules AlI, GaI, SrI₂, and BaI₂ to yield the dissociation energies of the IIA metal iodides CaI, SrI, and BaI. Sources of data and selected thermochemical properties of the reference molecules are discussed in the Appendix. A summary of the reaction thermochemistry obtained from this work, along with the derived dissociation energies, is given in Table VI. The values of $D_0^\circ(SrI)$ and $D_0^\circ(BaI)$ derived from the two independent reactions are in excellent agreement, in-

dicating good internal consistency between the AlI–SrI₂ data and between the GaI–BaI₂ data, thereby providing strong support for the selected properties of these reference molecules.

Our new experimental data for CaI, SrI, and BaI are in good agreement with the D_0° values obtained by extrapolating the experimental bond strengths from the corresponding fluorides, chlorides, and bromides.[5] Within the uncertainties they are also consistent with the lower bounds to D_0° derived from the $M + HI \rightarrow MI + H$ crossed beam experiments of Mims et al.[3]; from the agreement of these lower bounds with the thermochemical values of D_0° it seems reasonable to conclude that product recoil energy and internal excitation are relatively minor in the crossed beam experiments.

The results of Dickson et al.,[4] which yielded $D_0^\circ(BaI)$ = 102 ± 1 kcal/mole from chemiluminescent studies of the reaction $Ba + I_2$, seem on the surface difficult to reconcile with our thermochemical data. It now appears, however, that the Ba beam in those chemiluminescence experiments contained a significant population of metastable $Ba(^3D)$ atoms, and that reactions of these metastables with I_2 were responsible for the observed spectra.[11] A recalculation of the energy balance to account for the excitation energy of the ^3D state now yields $D_0^\circ(BaI) = 73.0 ± 1$ kcal/mole, in good agreement with our thermochemical value. As confirmation of this interpretation, similar studies of the $Ba + Br_2$ reaction yielded $D_0^\circ(BaBr) = 85.8 ± 1.0$ kcal/mole, again in close agreement with our thermochemical result of 85.5 ± 2.2 kcal/mole.[5] Intercomparison of the results from the two different methods thus provides valuable insight into the mechanism of the elementary chemiluminescent process. This is important in that the chemiluminescent technique is a valuable new tool for determining molecular energy quantities.

Comparison with model calculations

It has been noted previously[5,6] that the Rittner electrostatic model[12] and the ionicity-corrected Birge–

TABLE IV. Ion abundances and derived equilibrium data for the gaseous reactions $Sr + AlI = SrI + Al$ (2), $Sr + SrI_2 = 2 SrI$ (4).

$T(K)$	$I(Sr^+)$ (8.5 eV)	$I(SrI^+)$ (8.5 eV)	$I(SrI^+)^a$ (12.0 eV)	$I(Al^+)$ (9.0 eV)	$I(AlI^+)$ (12.0 eV)	$K_{eq}(2) \times 10^2$	$\Delta H^\circ_{298}(2)$ (kcal/mole)	$K_{eq}(4) \times 10^2$	$\Delta H^\circ_{298}(4)$ (kcal/mole)
1626	0.27	0.025	0.23	0.48	2.0	2.22	22.1	1.62	26.4
1671	4.1	0.265	2.2	8.55	20.0	2.76	22.0	1.35	27.7
1674	1.0	0.09	0.87	18.0	64.0	2.53	22.4	1.46	27.4
1693	6.45	0.57	5.85	12.0	36.0	2.94	22.1	1.31	28.1
1696	0.285	0.12		0.45	6.90	2.75	22.4		
1707	0.39	0.09		0.80	5.85	3.16	22.0		
1726	5.55	0.69	8.25	45.0	168.0	3.33	22.1	1.47	28.2
1760	0.95	0.205	2.10	2.00	10.0	4.32	21.6	3.20	26.0
1762	2.30	0.54	9.60	5.85	36.5	3.76	22.2	1.64	28.3
1762	1.90	0.015		6.75	1.45	3.68	22.2		
1782	13.35	0.22		75.0	28.0	4.41	21.8		
1787	1.40	0.33	3.75	2.85	17.0	3.95	22.3	3.00	26.6
1810	5.70	0.09		34.0	11.0	4.88	21.8		
					Average		22.1		27.3
					Second law		24.5 ± 1.7		

$^a I(SrI^+/SrI_2) = I(SrI^+)_{12.0} - 3.5\, I(SrI^+)_{8.5}$.

TABLE V. Ion abundances and derived equilibrium data for the gaseous reactions $Ba + GaI = BaI + Ga$ (3), $Ba + BaI_2 = 2\,BaI$ (5).

$T(K)$	$I(Ba^+)$ (8.0 eV)	$I(BaI^+)$ (8.0 eV)	$I(BaI^+)^b$ (12.0 eV)	$I(Ga^+)$ (9.0 eV)	$I(GaI^+)$ (12.0 eV)	$K_{eq}(3)$	$\Delta H^\circ_{298}(3)$ (kcal/mole)	$K_{eq}(5)$	$\Delta H^\circ_{298}(5)$ (kcal/mole)
1711[a]	111	46		126	74	0.702	10.6		
1711[a]	180	66		165	84	0.720	10.5		
1711[a]	69	75		280	430	0.708	10.6		
1711[a]	160	31		63	17.5	0.698	10.6		
1722	0.05	0.067		0.71	1.25	0.762	10.4		
1722	2.76	1.65		9.96	8.13	0.732	10.5		
1765[a]	487	61.2		79.1	12.1	0.821	10.4		
1768[a]	270	57		130	33	0.832	10.4		
1775	8.19	2.65		11.94	4.41	0.876	10.2		
1785	0.261	0.178		1.88	1.61	0.796	10.6		
1828	24.4	4.89		22.5	5.64	0.800	10.9		
1886	1.66	0.309		3.75	0.76	0.918	10.8		
1873	0.18	0.09	0.61					0.152	23.0
1899	0.29	0.084	0.44					0.167	22.9
1927	0.46	0.16	0.92					0.155	23.5
1956	0.58	0.14	0.64					0.225	22.4
1986	0.66	0.12	0.54					0.182	23.5
2011	0.60	0.08	0.32					0.267	22.3
Average							10.5		22.9
Second law							8.9 ± 1.5		

[a]Detection by ion pulse counting.   [b]$I(BaI^+/BaI_2) = I(BaI^+)_{12.0} - 3.5\,I(BaI^+)_{8.0}$.

Sponer extrapolation[13] give calculated binding energies in fairly good agreement with the thermochemical values for most of the IIA metal diatomic fluorides, chlorides, and bromides. Since the data for the Ca, Sr, and Ba monohalides are now complete, it is of interest to compare experimental results with model calculations for the entire series.

In these analyses the parameter r_x/r_e is used as a measure of the degree of ionic character in the diatomic metal halide molecule. This parameter, in which r_x is the hypothetical crossing point of ionic (coulombic) and covalent potential energy curves and r_e is the equilibrium internuclear distance, has been used to differentiate between the two extremes of chemical bonding.[14] Numerical values of r_x can be calculated readily from the expression

$$r_x(\text{Å}) = \frac{14.40}{(\text{I.P.} - \text{E.A.})},\qquad (6)$$

where I.P. is the first ionization potential of the metal and E.A. is the electron affinity of the halogen, both in eV. It can be shown[14] that molecules in which $r_x/r_e > 2.0$

TABLE VI. Summary of reaction thermochemistry.

Reaction source	Gaseous reaction studied	ΔH°_{298} (kcal/mole)	Derived result (kcal/mole)
$CaO(s) + Al_2O_3(s) + HI(g)$	$Ca + AlI = CaI + Al$	23.2 ± 1.5	$D^\circ_0(CaI) = 62.1 ± 2.5$
$SrO(s) + Al_2O_3(s) + HI(g)$	$Sr + AlI = SrI + Al$	22.1 ± 1.5	$D^\circ_0(SrI) = 63.6 ± 2.5$
	$Sr + SrI_2 = 2\,SrI$	27.3 ± 1.5	$D^\circ_0(SrI) = 63.7 ± 1.1$
$BaO(s) + Ga_2O_3(s) + HI(g)$	$Ba + GaI = BaI + Ga$	10.5 ± 1.5	$D^\circ_0(BaI) = 71.6 ± 1.8$
	$Ba + BaI_2 = 2\,BaI$	22.9 ± 1.5	$D^\circ_0(BaI) = 71.2 ± 1.1$

will have predominately ionic binding, while those with $r_x/r_e < 1.5$ are largely covalent; both types of binding will contribute substantially in the range between 1.5 and 2.0. For those molecules in which $r_x/r_e > 2.0$, a purely electrostatic model would therefore be expected to account for many features of the bonding, including the binding energy. The Rittner polarizable-ion model,[12] which in its simplified form considers contributions from charge–charge, charge–dipole, dipole–dipole, and repulsive interactions, reproduces the established binding energies of the diatomic alkali halides quantitatively.[15] The dissociation energy can be evaluated from the relatively simple expression

$$D^\circ_0(MX) = (e^2/r^2)(r - \rho) + (e^2/2r^5)[(\alpha_1 + \alpha_2)(r - 4\rho)]$$
$$+ (2e^2\alpha_1\alpha_2/r^8)(r - 7\rho) - (\text{I.P.} - \text{E.A.}),\qquad (7)$$

where e is the electronic charge, r is the internuclear distance (taken to be the equilibrium value), ρ is the repulsion parameter in the exponential repulsion term, and α_1 and α_2 are the dipole polarizabilities of M^+ and X^-, respectively. ρ is evaluated from the vibrational force constant as described by Rittner. The internuclear distances in the monoiodides were taken to be 3% shorter than the measured di-iodide values. The dipole polarizabilities of Ca^+, Sr^+, and Ba^+ used in the calculations were 7, 9, and 12 Å^3, respectively, obtained as described previously[6]; our $\alpha(M^+)$ values agree closely with those estimated by Krasnov and Karaseva[16] using a different method. $\alpha(I^-)$ was taken to be 7.6 Å^3 as given by Dalgarno.[17] In converting the calculated binding energies of the ion pairs $M^+ + X^-$ to those of the

TABLE VII. Comparison of experimental and calculated dissociation energies.

MX	Exptl.	Ionic model	LBX	LBX (corr.)	r_x/r_e
CaF	126.4	120	90	125	2.68
CaCl	94.2	87	75	95	2.36
CaBr	73.4	75	67	77	2.04
CaI	62.1	58	66	68	1.71
SrF	128.7	127	80	124	3.10
SrCl	95.9	92	69	97	2.72
SrBr	78.7	78	65	81	2.28
SrI	63.6	61	52	57	1.88
BaF	139.5	137	87	157	3.79
BaCl	104.4	99	62	102	3.36
BaBr	85.5	84	64	90	2.71
BaI	71.6	68	57	69	2.18

(Header: $D_0^o(MX)$ (kcal/mole))

ground state neutrals $M + X^-$ the value E.A. (I) = 3.06 eV was used.

In Table VII the experimental values of $D_0^o(MI)$ are compared with values calculated from the Rittner model, along with results reported earlier[5,6] for the fluorides, chlorides, and bromides. It is evident that the Rittner model yields binding energies which are in excellent agreement with experiment throughout the entire Ca,Sr,Ba halide series. As further support, the independent ionic model calculations of Krasnov and Karaseva,[6] made with slightly different atomic and molecular parameters, generally agree to within a few kcal/mole with the $D_0^o(MX)$ values presented here, after both sets of data are normalized to the same halogen electron affinity values. As the r_x/r_e values indicate, the degree of ionic character drops markedly in going to the heavier halogens and the lighter metals, because of the increase in r_e and I.P.(M). Thus, the Rittner model is not applicable to most of the Be and Mg halides, where $r_x/r_e < 1.6$. As noted previously,[5] the IIA metal halides constitute a much more stringent test of the Rittner model than the alkali halides, since the IIA M^+ ions are substantially more polarizable than the alkali ions; the polarization terms contribute up to 20% of the total binding energy in the IIA halides, compared to only a few percent in the alkali halides. It should be noted that the Rittner model does require fairly reliable input parameters, particularly r_e and $\alpha(M^+)$ values; the lack of these data limits the extension of the model to other metal halide systems of interest, e.g., lanthanide and actinide halides.

Another type of model that has proved useful in estimating dissociation energies when direct measurements are lacking is the ionicity-corrected Birge–Sponer extrapolation of vibrational energy levels.[13] The ionicity correction removes the objection to arbitrary use of the linear Birge–Sponer extrapolation (LBX), and provides generally good agreement with experimental thermochemical values. A correlation of the thermochemical D_0^o values with $D_0^o(LBX)$ values for

a number of diatomic halides over a wide range of ionic character shows that the relation

$$[D_0^o/D_0^o(LBX)] \cong 0.390 + 0.374(r_x/r_e) \qquad (8)$$

represents the data quite well.[13] In Table VII the values of $D_0^o(LBX)$ and those corrected by means of Eq. (8) are compared with the experimental results. On the whole the corrected $D_0^o(LBX)$ values agree remarkably well with the thermochemical values, lending a fair degree of confidence to this approach. Bear in mind, however, that the accuracy of the linear extrapolation is sensitive to the quality of the spectroscopic constants used in the analysis. In particular, reliable values of the anharmonic constant $\omega_e x_e$ are required; instances of poor correlation usually can be traced to inadequate spectroscopic data.

Since the correction procedure produces satisfactory results over a wide range of ionic character, it therefore removes much of the stigma associated with the Birge–Sponer extrapolation. Gaydon[2] cautioned that the extrapolation might be unreliable for ionic molecules because of the nature of the coulombic potential function, and also that molecules containing an atom with a $^1S_0$ ground state might show an unusual form of the extrapolation because of the contribution of excited atomic states to the binding. The data for the IIA monohalides, in which both factors are operative, show that no such unusual features are encountered.

Correlation of bond strengths in mono- and dihalides

An analysis of earlier bond strength data on the IIA fluorides seemed to indicate that the energies of dissociation to gaseous atoms of the mono- and difluorides were related by the expression $D(MX)/D(MX_2) = 0.45 \pm 0.03$.[18,19] This generalization has in fact been used as a guide in estimating other monohalide bond strengths from available data on dihalides.[1] Now that rather complete results are in hand for the Ca, Sr, and Ba halides and for the Be and Mg fluorides and chlorides, it is of interest to examine variations in the above heat of dissociation ratio for the entire series. Data for the dihalides used in these evaluations are available in the JANAF Tables[1]; dates of issue of the tables are given in the Appendix. The data in Table VIII illustrate that the ratio varies rather systematically with metal and halogen, and that an approximately constant value does not represent the data adequately. It seems clear that the bond strength ratio increases with increasing ionic character in the molecule, in line with expectations; as the degree of covalency increases, the effects of valence excitation on the monohalide bond strength become more pronounced, and the difference between the two bond strengths grows.

One can use the observed trends through the series to estimate the ratio $D(MX)/D(MX_2)$ for the Be–Br, Be–I, Mg–Br, and Mg–I systems, where the dissociation energies of the monohalides have not been measured. By combining these extrapolated ratios, shown parenthetically in Table VIII, with data for the dihalides[1] one can estimate $D_0^o(BeBr) = 71$, $D_0^o(BeI) = 57$, $D_0^o(MgBr) = 58$, and $D_0^o(MgI) = 45$ kcal/mole, with prob-

TABLE VIII. Ratio of heats of dissociation for
IIA metal mono- and dihalides $D^{\circ}_{298}(MX)/D^{\circ}_{298}(MX_2)$.[a]

	Halogen			
Metal	F	Cl	Br	I
Be	0.45	0.42	(0.38)	(0.38)
Mg	0.45	0.40	(0.36)	(0.36)
Ca	0.47	0.44	0.40	0.40
Sr	0.49	0.46	0.42	0.41
Ba	0.51	0.48	0.44	0.43

[a]Values in parentheses are estimated from trends
across the series.

able uncertainties of about 5 kcal/mole. We prefer
these values to the estimates in the JANAF Tables,
which are about 5 kcal/mole higher for the Be halides
and 10 kcal/mole higher for the Mg halides; the latter
are based partly on the expected constancy of the ratio
$D(MX)/D(MX_2)$. Completion of these studies on the
iodides brings to a close an interesting chapter in high
temperature chemistry and puts the thermochemistry
of the IIA metal gaseous halides on a reasonably firm
footing.

APPENDIX

Auxiliary thermochemical data used in deriving the
properties of the IIA iodides were taken from the fol-
lowing sources:

AlI—From an extrapolation of vibrational levels of
the $^1\pi$ state, Barrow[20] derived $D^{\circ}_0(AlI) = 87$ kcal/mole,
as part of a systematic analysis of spectroscopic data
for the IIIA metal monohalides. With other members
of this series for which data are now complete these
excited state extrapolations have proved to come in
several kcal high, because of maxima in the upper
state potential curves. An ionicity-corrected Birge–
Sponer extrapolation of the ground state levels leads to
a corresponding value of 84 kcal/mole. We adopt the
value D°_0 (AlI) = 85.0 ± 2 kcal/mole.

GaI—A third law analysis of the equilibrium data for
the reaction $2\,Ga(l) + GaI_3(g) = 3\,GaI(g)$ reported by Sil-
vestri and Lyons,[21] using recent spectroscopic data[22]
for GaI_3, leads to $\Delta H_{298} = 57.81$ kcal/mole, in close
agreement with the second law value. On combining
this result with the standard heats of formation of
$Ga(g)$ and $GaI_3(g)$,[23] one obtains $D^{\circ}_0(GaI) = 82.0 ± 1.0$
kcal/mole, which is adopted. This selected value is in
accord with Barrow's estimate of 80 kcal/mole, based
largely on short extrapolations of vibrational levels of
the $^3\pi$ states.

SrI_2, BaI_2—The heats of dissociation of these mole-
cules were taken from recently evaluated JANAF
Tables.[1] Vaporization data obtained in this laboratory[24]
agree closely with published results[25] used in deriving

the thermochemical data, and provide support for the
molecular constant assignments. The selected values
are $D^{\circ}_{298}(SrI_2) = 155.6 ± 1.5$, and $D^{\circ}_{298}(BaI_2) = 166.3 ± 1.5$
kcal/mole.

The thermodynamic functions used in the analysis of
the iodide equilibrium data, and the dihalide dissocia-
tion energies employed in evaluating the data in Table
VIII, were taken from JANAF Tables with the following
dates of issue: Al, 12/65; AlI, 9/64; Ca, CaF₂, 12/68;
CaI, SrI, CaI₂, SrI₂, BaI₂, CaBr₂, SrBr₂, MgBr₂, 6/74; Sr,
Ba, 12/70; BaI, BaBr₂, MgI₂, 12/74; BeF₂, CaCl₂, 6/70;
BeBr₂, MgF₂, 6/75; SrF₂, SrCl₂, BaF₂, BaCl₂, 12/72;
BeCl₂, 6/65; BeI₂, 12/75; and MgCl₂, 12/69.

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