THERMODYNAMIC PROPERTIES OF GASEOUS METAL DIHALIDES

LEO BREWER, G. R. SOMAYAJULU,* AND ELIZABETH BRACKETT**

Department of Chemistry and Inorganic Materials Division of the Lawrence Radiation Laboratory, University of California, Berkeley, California

Received March 26, 1962

CONTENTS

I. INTRODUCTION

The three principal aims of this review are (1) the evaluation of entropies of gaseous metal dihalides through the treatment of vapor pressure data by the second law of thermodynamics, (2) the use of these experimental entropies to aid in the estimation of entropies that can be used for third law calculations, and (3) the evaluation of enthalpies of formation of gaseous metal dihalides by both methods.

To carry out the first aim, one must have vapor pressure data that are complete and reliable enough to yield enthalpies and entropies of vaporization when treated by a second law method. Often high temperature vapor pressure measurements are not sufficiently accurate or do not extend over a wide enough temperature range to yield reliable enthalpies and entropies when treated by a second law method. One may still obtain useful enthalpies of formation from such data if one can apply a third law method. The spectroscopic data necessary for calculation of the entropies of gaseous metal dihalides are not available. In an attempt to overcome this deficiency, the second aim of this paper is the development of a method of estimating entropies or free energy functions of the gaseous dihalides. The third law procedure that is developed here cannot yield accurate enthalpies of formation, but it should yield enthalpies of formation for various compounds which are consistent with one another; it should reflect trends as a function of electronic structure or position in the periodic table and it should yield reliable vapor pressures. The third aim of this paper includes the consideration of enthalpies of formation of the gaseous dihalides obtained from all sources from the point of view of electronic structures as a guide to the estimation of yet unmeasured enthalpies of formation. The application of these procedures allows one to gain a much more complete understanding of the vaporization processes of metal–halogen systems.

II. SECOND LAW TREATMENT OF VAPOR PRESSURE DATA

The second law treatment of vapor pressure data by the conventional Σ plot method is illustrated by Lewis, Randall, Pitzer, and Brewer (50). To apply this method it is necessary to know the fugacity of the gaseous species in equilibrium with a condensed phase over a range of temperature, and one must know ΔC_p^0 for the vaporization process. Within the accuracy of most of these data, ΔC_p^0 can be taken as a constant over the temperature range of measurements. The heat capacities of a number of condensed halides are given by Kelley (42). Estimated heat capacities are used for the other halides. The heat capacities of the gaseous molecules are calculated by use of estimated molecular constants that will be discussed in connection with the calculation of free energy functions. As both the rotational and vibrational contributions to the heat capacity are very close to the classical values in the temperature range of interest, the calculated heat capacities are insensitive to the choice of molecular constants.

The Σ plot treatment yields equations for ΔH^0 of the vaporization process over the temperature range of study. These values are reduced to values at 298.15°K., not by assuming constant ΔC_p^0 from the temperature studied down to room temperature, but by the use of actual enthalpy increments for the condensed phase and by use of calculated values for the gaseous species. The values of $\Delta H^0_{298.15}$ are then combined with values of ΔF^0 in the temperature range of study to obtain the experimental values of $(\Delta F^0 - \Delta H^0_{298.15})/T$. These values combined with values of $-(F^0 - H^0_{298.15})/T$

---

* Osmania University, India.
** Department of Chemistry, Rice University, Houston, Texas.

for the condensed phase give free energy functions for the gaseous species. The free energy functions for the condensed halides are recorded in Table I, along with references to sources of the data. When it has

TABLE I

FREE ENERGY FUNCTIONS OF CONDENSED METAL HALIDES BASED ON $H^0_{298.5}$

Values in parentheses are estimated; the symbol (l) indicates that the value is given for the liquid phase at the indicated temperature and at all higher temperatures.

	$(F^0 - H^0_{298.15})/T$, cal./deg. mole						$H^0_{298.15} - H_0^0$,	
Compound	298.15°	500°	1000°	1500°	2000°	2500°K.	cal./mole	References
BeF_2	(8.3)	10	17 (l)	23			(1650)	
$BeCl_2$	(16	18	25 (l)				(2550)	
$BeBr_2$	(22)	24	32 (l)				(2950)	
BeI_2	(25)	27	36 (l)				(3250)	
MgF_2	13.7	15.5	22.3	27.9	34.6 (l)	39.9	2370	(42, 43, 50)
$MgCl_2$	21.4	23.4	30.9 (l)	40.4			3291	(42, 43, 50)
$MgBr_2$	(27)	29	37 (l)	47			(3700)	(12)
MgI_2	(30)	32	40 (l)	49			(4000)	
CaF_2	16.5	18.4	25.7	31.8	37.9 (l)	43.2	2788	(42, 43, 50)
$CaCl_2$	27.2	29.3	36.6	44.6 (l)	50.9		3687	(42, 43, 50)
$CaBr_2$	(33)	35	43	51 (l)	57		(4100)	(12)
CaI_2	(36)	38	46	55 (l)			(4400)	(12)
SrF_2	(19.5)	21.5	28.5	34.5	40.5 (l)	45.5	(3200)	(43)
$SrCl_2$	(29.0)	31.0	38.9	47 (l)			(4100)	(42)
$SrBr_2$	(35.0)	37.2	44.5 (l)	53			(4500)	(42, 43)
SrI_2	(38.0)	40.2	48.5 (l)				(4800)	(42, 43)
BaF_2	23.0	25.1	32.7	39.3	45.8 (l)	51.1	3452	(42, 43)
$BaCl_2$	(32.0)	34.1	41.5	48.7 (l)	55.3		(4350)	(42)
$BaBr_2$	(38.0)	40.2	48	56 (l)			(4750)	
BaI_2	(41.0)	43.2	51 (l)	59			(5050)	
ZnF_2	17.6	19.4	26.2	33.4 (l)	39.4		2827	(42, 43)
$ZnCl_2$	26.7	28.7	40.4 (l)				3598	(17, 89)
$ZnBr_2$	32.5	34.6	45 (l)				(4000)	(43)
ZnI_2	(35.0)	37.1	47 (l)				(4300)	(43)
CdF_2	(19.5)	21.5	28.5	34.5 (l)	40.5		(2900)	(43)
$CdCl_2$	27.6	29.6	39.0 (l)	48.4			3791	(34, 85, 86)
$CdBr_2$	33.2	35.3	44.7 (l)				4235	(35, 85, 86)
CdI_2	37.7	39.8	50.7 (l)				4512	(34, 85, 86)
HgF_2	(27)	29	36 (l)				(3700)	
$HgCl_2$	(34.5)	36.5					(4600)	(43, 50, 85 86)
$HgBr_2$	(40.7)	42.7					(5000)	(43, 50)
HgI_2	(42.4)	44.9					(5300)	(42, 43, 50)
SnF_2	(21.5)	23.5	30.5				(3000)	
$SnCl_2$	(29)	31	42 (l)				(3900)	(42)
$SnBr_2$	(35)	37	48 (l)				(4300)	
SnI_2	(38)	40	52 (l)				(4600)	
PbF_2	(25.0)	27.0	34.4	41.9 (l)			(3200)	(42)
$PbCl_2$	32.5	34.6	44.4 (l)	53.6			(4100)	(42, 43, 50)
$PbBr_2$	38.6	40.8	51.7 (l)	60.7			(4600)	(33, 42, 43, 50)
PbI_2	41.8	44.0	55.6 (l)	65.9			(4700)	(42, 89)
$TiCl_2$	(24.3)	26.3	33.6				(3600)	(42, 44)
$TiBr_2$	(29.5)	31.7	39.3				(4200)	(42, 44)
TiI_2	(32.5)	34.9	43.2				(4500)	(42, 44)
VCl_2	23.2	25.2	32.5	41			(3600)	(42, 43, 50)
VBr_2	(29)	31	39				(4200)	(12)
VI_2	(32)	34	42				(4500)	(12)
CrF_2	(22)	24	31	38 (l)			(2800)	
$CrCl_2$	27.6	29.5	36.7	45.1 (l)			(3593)	(16, 50)
$CrBr_2$	(33)	35	43	51 (l)			(4100)	
CrI_2	(36)	38	46	54 (l)			(4400)	(12)
MnF_2	22.3	24.2	31.1	38.2 (l)			(3000)	(52)
$MnCl_2$	28.3	30.4	38.6 (l)	47.9			(3602)	(16, 52)
$MnBr_2$	(33.5)	35.6	43.6 (l)				(4300)	(52)
MnI_2	(36.5)	39.1	49.8 (l)				(4600)	(52)
FeF_2	20.8	22.8	29.8	36.8 (l)			3049	(43)
$FeCl_2$	26.6	28.8	37 (l)	47			(3550)	(42, 89)
$FeBr_2$	33.6	35.8	44.2 (l)	54.3			(4350)	(28, 89)
FeI_2	36.8	39.1	48.1 (l)	59.4			(4650)	(50, 57)
CoF_2	19.6	21.6	28.6	35.6 (l)			2978	(12, 43)
$CoCl_2$	26.1	28.4	37.1	47 (l)			(3375)	(16, 42)
$CoBr_2$	(32)	34	43 (l)	53			(4300)	(12)
CoI_2	(35)	37	46 (l)	56			(4600)	(12)
NiF_2	17.6	19.5	26.5	33.5 (l)			2729	(43, 50)
$NiCl_2$	23.3	25.3	32.7	40.6 (l)			(3439)	(42, 43, 50)
$NiBr_2$	(29)	31	39	47 (l)			(4000)	
NiI_2	(32)	34	42	50 (l)			(4300)	
CuF_2	(20)	22	29				(3000)	
$CuCl_2$	25.8	28.0	36.3				(3581)	(16, 42)
$CuBr_2$	(32)	34	42				(4300)	
CuI_2	(35)	37					(4600)	

been necessary to estimate $S^0_{298.15}$, the $-(F^0-H^0_{298.15})/T$ value at 298.15°K. in Table I is given in parentheses. In such cases, the values of $S^0_{298.15}$ are obtained by a modification of Latimer's rule using the melting points as described by Lewis, Randall, Pitzer and Brewer (50).

III. FREE ENERGY FUNCTIONS OF GASEOUS METAL DIHALIDES

The free energy functions of the gaseous dihalides are calculated on the basis of various assumptions concerning the molecular constants. For the dihalides of the alkaline earth metals and of the zinc and tin groups, the multiplicity of the ground electronic state is taken as unity and it is assumed that there are no low-lying electronic levels that would contribute appreciably to the partition function. The translational contribution to the entropy or free energy function can be calculated accurately from knowledge of the molecular weight. For the calculation of rotational and vibrational contributions to the partition function it is necessary to make an assumption about the structure of the dihalide. The available electron diffraction data indicate a linear structure (3) for the dihalides of the alkaline earth metals and of the zinc group, and bent structure (81) for the dihalides of tin and lead. The structures of the transition metal dihalides are not known, but in the present study they are assmed to be linear. Judging from the high values of the observed entropies, the gaseous transition metal dihalides could possibly have bent structures. The treatment of bending frequencies described below is believed to compensate for any error due to the assumption of a linear structure.

Vibrational frequencies are evaluated from the frequencies observed for the diatomic halides, where they are known, using the valence force model. Thus the stretching force constant is taken the same for the diatomic and triatomic molecules. In a few instances experimental frequencies are available for the unsymmetrical stretch and these experimental values are used. In a very few instances bending frequencies are available from the experimental spectroscopic data, and these are used as a guide in estimating the bending force constant for other molecules. As the doubly degenerate bending frequency is lower than the stretching frequencies, the bending frequency has the most important contribution to the partition function, and uncertainties in the estimation of other molecular properties are negligible compared to the uncertainty in the estimation of the bending frequency for those molecules where the electronic contribution is unimportant. Since the contribution of the bending frequency is the only one which cannot be estimated accurately, one may use the bending frequency as a parameter to determine what value of this bending frequency will yield agreement with the experimental free energy functions. Values obtained by this procedure together with the few experimental frequencies are used to obtain an average value of the ratio of bending force constant, $k\delta/l^2$, to stretching force constant, k_1, for related compounds. This average value then is used for the prediction of unknown values.

Internuclear distances are available (3, 81) for all of the dihalides considered here except for the transition metal dihalides and the difluorides of mercury, tin and lead for which estimated values are used. These are of sufficient accuracy for these calculations as an error as large as 0.5 Å. in the internuclear distances would lead to an error of less than 1 cal./deg. mole in the rotational contribution to the entropy. The molecular constants chosen for the gaseous dihalides are given in Tables II and III. In Table IV are shown the calculated free energy functions compared with experimental free energy functions for some dihalides with no appreciable electronic contribution. Where sufficient data are available for both the solid and liquid ranges, comparisons are given for second law values from each range.

TABLE II

MOLECULAR CONSTANTS OF METAL DIHALIDES (LINEAR MODEL)

Compound	r(M–X),[a] Å.	ν_1, cm.$^{-1}$	ν_2, cm.$^{-1}$	ν_3, cm.$^{-1}$	k, md./Å.	$k\delta/l^2$, md./Å.
BeF_2	1.40	668	825[b]	1520[b]	5.0[b]	0.73[b]
$BeCl_2$	1.75	373	482[b]	1113[b]	2.9[b]	.27[b]
$BeBr_2$	1.91	230	446	997	2.5	.25
BeI_2	2.10	164	395	883	2.0	.20
MgF_2	1.77	535	479	858	3.2	.50
$MgCl_2$	2.18	302	295[b]	597[b]	1.9[b]	.23[b]
$MgBr_2$	2.34	179	220	491[c]	1.5[c]	.15
MgI_2	2.52	132	199	446	1.3	.13
CaF_2	2.10	484	95	675	2.62	.0262
$CaCl_2$	2.51	268	63	446	1.5	.015
$CaBr_2$	2.67	164	52	367	1.27	.0127
CaI_2	2.88	118	45	321	1.05	.0105
SrF_2	2.20	454	77	543	2.3	.023
$SrCl_2$	2.67	254	48	342	1.35	.0135
$SrBr_2$	2.82	156	37	262	1.15	.0115
SrI_2	3.03	111	31	219	0.92	.0092
BaF_2	2.32	439	70	496	2.16	.0216
$BaCl_2$	2.82	248	43	302	1.28	.0128
$BaBr_2$	2.99	154	32	226	1.11	.0111
BaI_2	3.20	109	26	184	0.89	.0089
ZnF_2	1.81	551	385	687	3.4	.57
$ZnCl_2$	2.05	358	295[d]	516[e]	2.67[e]	.44[d]
$ZnBr_2$	2.21	222	225[d]	413[e]	2.33[e]	.35[d]
ZnI_2	2.38	154	180	340[e]	1.77[e]	.25
CdF_2	1.97	500	129	580	2.8	.07
$CdCl_2$	2.21	330	94	422[e]	2.28[e]	.057
$CdBr_2$	2.37	202[e]	70	315[e]	1.93[e]	.048
CdI_2	2.55	147	59	265[e]	1.61[e]	.04
HgF_2	2.00	560	113	610	3.5	.06
$HgCl_2$	2.29	360[f]	70[f]	413[f]	2.67[f]	.038[f]
$HgBr_2$	2.41	225[f]	41[f]	293[f]	2.32[f]	.023[f]
HgI_2	2.59	156[f]	33[f]	237[f]	1.83[f]	.018[f]
TiF_2	1.88	535	72	716	3.2	.016
$TiCl_2$	2.25	310	49	487	2.0	.010
$TiBr_2$	2.40	184	38	385	1.6	.008
TiI_2	2.59	137	34	344	1.4	.007
VF_2	1.76	535	70	706	3.2	.016
VCl_2	2.13	310	48	478	2.0	.010
VBr_2	2.28	184	38	375	1.6	.008
VI_2	2.47	137	33	335	1.4	.007
CrF_2	1.72	535	70	704	3.2	.016

Continued

TABLE II (*Concluded*)

Compound	r(M–X),[a] Å.	ν_1, cm.$^{-1}$	ν_2, cm.$^{-1}$	ν_3, cm.$^{-1}$	k, md./Å.	$k\delta/l^2$, md./Å.
$CrCl_2$	2.09	310	48	475	2.0	.010
$CrBr_2$	2.24	184	37	373	1.6	.008
CrI_2	2.43	137	33	332	1.4	.007
MnF_2	1.72	535	70	696	3.2	.016
$MnCl_2$	2.09	309	47	467[g]	1.99[g]	.010
$MnBr_2$	2.24	184	36	365	1.6	.008
MnI_2	2.43	137	32	324	1.4	.007
FeF_2	1.72	550	71	714	3.4	.017
$FeCl_2$	2.09	327	49	492[g]	2.23[g]	.0112
$FeBr_2$	2.24	206	40	405	2.0	.01
FeI_2	2.43	150	35	355	1.7	.0085
CoF_2	1.72	550	71	707	3.4	.017
$CoCl_2$	2.09	332	49	493[g]	2.3[g]	.0115
$CoBr_2$	2.24	206	40	397[g]	2.0[g]	.01
CoI_2	2.43	150	35	348	1.7	.0085
NiF_2	1.72	550	71	707	3.4	.017
$NiCl_2$	2.09	346	51	515[g]	2.5[g]	.0125
$NiBr_2$	2.24	206	40	397	2.0	.010
NiI_2	2.43	150	35	348	1.7	.0085
CuF_2	1.72	550	71	697	3.4	.017
$CuCl_2$	2.09	340	50	496[g]	2.43[g]	.0122
$CuBr_2$	2.24	206	39	386	2.0	.010
CuI_2	2.43	150	34	338	1.7	.0085

[a] The internuclear distances in the halides of the second group elements with the exception of HgF_2 are from Akishin and his coworkers (3). All other values have been estimated by the authors. [b] From Büchler and Klemperer (15). [c] From Randall, Greene and Margrave (61). [d] From Büchler (14). [e] From Klemperer (46). [f] See Klemperer and Lindeman (47). [g] From Leroi (49).

TABLE III

MOLECULAR CONSTANTS OF DIHALIDES OF Sn AND Pb (ASSUMING 95° BOND ANGLE)

Compound	r(M–X), Å.	ν_1, cm.$^{-1}$	ν_2, cm.$^{-1}$	ν_3, cm.$^{-1}$	k, md./Å.	$k\delta/{}^{f}{}_{2}$, md./Å.
SnF_2	2.04	607	157	614	3.6	0.12
$SnCl_2$	2.40	398	102	406	2.6	.0865
$SnBr_2$	2.55	282	68	291	2.3	.0765
SnI_2	2.74	232	52	240	2.0	.0665
PbF_2	2.08	574	149	578	3.4	.1135
$PbCl_2$	2.45	365	94	369	2.4	.08
$PbBr_2$	2.60	247	59	251	2.1	.07
PbI_2	2.79	200	49	206	1.9	.0635

The lengths of the Sn–F and Pb–F bonds have been estimated. All other bond lengths are from Sutton (81).

TABLE IV

COMPARISON OF FREE ENERGY FUNCTIONS OF GASEOUS METAL DIHALIDES OBTAINED FROM SECOND LAW AND CALCULATED FROM ESTIMATED MOLECULAR CONSTANTS

Compound	$-(F^0 - H^0_{298.15})/T$, cal./deg mole Second law[b]	Estd.[a]	T,°K.
MgF_2	69.8	66.3	1500
	73.8	69.7	2000
$MgCl_2$	68.0	68.6	1000
CaF_2	78.6	78.0	2000
SrF_2	(81.2)	80.7	2000
ZnF_2	69.7	69.0	1500
$ZnCl_2$	66.3	63.7	500
$ZnBr_2$	(67.8)	69.3	500
ZnI_2	(67.2)	73.3	500
CdF_2	(78.2)	78.5	2000
$CdCl_2$	70.0	69.6	500
	77.8	75.4	1000
$CdBr_2$	73.6	75.2	500
	81.6	81.0	1000
CdI_2	86.4	84.7	1000
PbF_2	(75.9)	76.4	1000
$PbCl_2$	83.2	81.8	1000
$PbBr_2$	88.2	87.4	1000
PbI_2	85.1	85.3	500
	91.0	90.7	1000

[a] A linear model has been assumed except for the lead halides where a bond angle of 95° was assumed. [b] Column 2 values in parentheses are based on estimated free energy functions for the condensed phase.

IV. ELECTRONIC CONTRIBUTION FOR TRANSITION METAL DIHALIDES

In treating the transition metal dihalides, one has the additional complication that the electronic contribution to the partition function can be quite appreciable and thus one has to evaluate two large terms, *viz.*, the electronic contribution and the bending frequency contribution. It is not feasible to use both of these quantities as parameters. No data are available on the ground states of the gaseous transition metal dihalides, and in addition many low-lying levels are to be expected. The following recipe is used to estimate the electronic contribution to the partition function. The electronic contribution to the partition function is calculated for the doubly charged gaseous metal ion from the electronic levels tabulated by Moore (54). It is assumed that the electronic partition function for the MX_2 molecule is close to the value for the M^{++} ion. This assumes that perturbations of the electronic levels of the divalent metal ion by the approach of two halide ions are not large enough to change substantially the partition function at high temperatures. The procedure is a straightforward one which gives an unambiguous value for the electronic contribution to the partition functions. Berg and Sinanoglu (4) and Leroi (49) have used the ligand-field theory to predict the order of low-lying electronic states of the divalent oxides and halides of the transition elements. Electronic partition functions based on their predictions would be essentially equivalent to those given here. The electronic contributions to the free energy functions (13) vary from 3.5 to 4.6 cal./deg. mole at 298°K. and range up to 6 cal./deg. mole at 1500°K.

This procedure then leaves only a single parameter, the bending frequency, to consider in comparing the experimental entropies with those calculated on the basis of the proposed model. The best fit for the transition metal dihalide is generally obtained by assuming the ratio $(k\delta/l^2)/k_1$ to be 1/200, if the assumption is made that the molecules are linear. If the calculations are repeated on the basis of a bent molecule with an angle of 110°, the ratio of the force constants must be taken at about $^1/_{30}$ to obtain agreement with the experimental entropies. Thus the procedure proposed here would yield the same free energy values if the molecules were assumed to be bent as for the linear molecule. The only difference would be in the ratio of the force constants used. With either model the calculated bending frequencies are so low that their experimental determination by conventional infrared methods does not seem feasible at the moment except for the fluorides. Leroi (49) was unable to detect the bending frequencies of the transition metal dihalides even at frequencies as low as 200 cm.$^{-1}$. Possibly the structure of these molecules may be resolved by electron diffraction measurements. Due to the almost complete lack of data for dihalides of transition metals beyond the first transition period, only transition compounds involving 3d electrons are considered here. In Table V are shown the experimental values of the free energy functions of the transition metal dihalides obtained from a second law treatment of vapor pressure data along with the calculated free energy functions for comparison. Except for titanium(II) chloride and iodide the agreement is excellent.

The agreement between the experimental and calculated values in Tables IV and V is considered to be good enough to justify the use of the recipe for calculation of free energy functions of the gaseous dihalides and for the use of these calculated values in approximate third law calculations for data which are not sufficiently extended over temperature or which are not sufficiently accurate to be subject to second law calculations. The free energy functions of all the gaseous metal dihalides considered here are given in Table VI.

TABLE V

COMPARISON OF FREE ENERGY FUNCTIONS OF GASEOUS METAL DIHALIDES OBTAINED FROM SECOND LAW AND CALCULATED FROM ESTIMATED MOLECULAR CONSTANTS INCLUDING ELECTRONIC CONTRIBUTION

Compound	$-(F^0 - H_{298.15})/T$, cal./deg. mole Second law^a	Estd.	T,°K.
$TiCl_2$	(61.6)	74.8	298.15
TiI_2	(67.8)	84.1	298.15
$CrCl_2$	73.2	74.8	298.15
CrI_2	(84.8)	84.2	298.15
$MnCl_2$	80.3	80.2	1000
MnI_2	(92.3)	89.8	1000
$FeCl_2$	77.1	82.0	1000
$FeBr_2$	79.2	79.5	298.15
FeI_2	82.4	83.2	298.15
$CoCl_2$	75.3	73.9	298.15
$NiCl_2$	75.5	73.2	298.15
$NiBr_2$	(81.3)	78.9	298.15
$CuCl_2$	71.8	72.4	298.15

[a] Values in parentheses are based on estimated free energy functions for the condensed phase.

V. ENTHALPIES OF DISSOCIATION

In Table VII are presented the enthalpies of sublimation at 298.15°K. for all metal dihalides for which any sort of data exist. Estimated values are given in parentheses. These data are combined with ΔH_f^0(solid), the enthalpies of formation of the solid halides, the enthalpies of sublimation of the metals (50) and the enthalpies of dissociation of the halogens (50) to yield the dissociation or atomization enthalpies, ΔH^0_{Atom}(gas), of the gaseous metal dihalides to gaseous atoms. These are shown in the fourth column of Table VII. The

TABLE VI

FREE ENERGY FUNCTIONS OF GASEOUS METAL DIHALIDES BASED ON $H^0_{298.15}$

	$-(F^0 - H^0_{298.15})/T$, cal./deg. mole						$H^0_{298.15} - H_0^0$, kcal./mole
Compound	298.15°	500°	1000°	1500°	2000°	2500°K.	
BeF_2	52.36	53.49	57.98	61.82	64.96	67.58	2.245
$BeCl_2$	57.87	59.23	64.34	68.53	71.85		2.597
$BeBr_2$	63.1	64.5	69.8	74.0	77.4		2.76
BeI_2	66.8	68.2	73.6	77.9	81.3		2.89
MgF_2	55.6	56.9	62.1	66.3	69.7	72.4	2.54
$MgCl_2$	61.49	63.02	68.56	72.96	76.42		2.973
$MgBr_2$	67.53	69.12	74.79	79.26	82.73		3.256
MgI_2	71.1	72.7	78.4	82.8	86.4		3.37
CaF_2	62.9	64.4	70.1	74.3	78.0	80.6	3.23
$CaCl_2$	68.9	70.5	76.3	80.7	84.3		3.55
$CaBr_2$	74.4	76.1	81.9	86.4	89.9		3.72
CaI_2	78.2	79.9	85.7	90.2	93.8		3.82
SrF_2	65.6	67.2	72.8	77.2	80.7	83.6	3.34
$SrCl_2$	71.7	73.3	79.1	83.6	87.1		3.66
$SrBr_2$	77.3	79.0	84.8	89.4	92.8		3.85
SrI_2	81.1	82.8	88.6	93.2	96.8		3.95
BaF_2	67.4	69.0	74.6	79.0	82.5	85.4	3.38
$BaCl_2$	73.5	75.1	80.9	85.5	89.0		3.71
$BaBr_2$	78.9	80.6	86.4	91.0	94.5		3.90
BaI_2	82.8	84.5	90.3	94.9	98.3		4.00
ZnF_2	57.90	59.33	64.65	68.95	73.35		2.673
$ZnCl_2$	62.20	63.74	69.30	73.71	77.17		2.964
$ZnBr_2$	67.66	69.25	74.95	79.43	82.92		3.244
ZnI_2	71.71	73.34	79.10	83.60	87.13		3.450
CdF_2	63.5	65.1	70.6	75.0	78.5		3.18
$CdCl_2$	68.03	69.64	75.35	79.83	83.06		3.432
$CdBr_2$	73.56	75.22	81.03	85.54	89.08		3.671
CdI_2	77.22	78.88	84.71	89.22	92.72		3.797
HgF_2	65.3	66.8	72.3	76.7			3.18
$HgCl_2$	70.39	72.07	77.69	82.20			3.473
$HgBr_2$	76.51	78.15	83.95	88.51			3.742
HgI_2	80.32	81.98	87.86	92.31			3.882
SnF_2	67.9	69.3	74.4	78.4			2.96
$SnCl_2$	73.1	74.6	79.8	84.0			3.22
$SnBr_2$	78.4	79.9	85.3	89.5			3.42
SnI_2	81.9	83.4	88.9	93.1			3.53
PbF_2	69.9	71.3	76.4	80.5			2.99
$PbCl_2$	75.0	76.5	81.8	86.0			3.27
$PbBr_2$	80.4	82.0	87.4	91.6			3.49
PbI_2	83.7	85.3	90.7	94.9			3.59
TiF_2	69.1	70.7	76.4	80.9			3.58
$TiCl_2$	74.8	76.5	82.3	86.9			3.85
$TiBr_2$	80.6	82.3	88.2	92.9			4.05
TiI_2	84.1	85.8	91.8	96.4			4.14
VF_2	69.4	71.0	76.8	81.3			3.67
VCl_2	75.0	76.7	82.7	87.3			3.94
VBr_2	80.7	82.4	88.5	93.2			4.14
VI_2	84.4	86.1	92.1	96.8			4.23
CrF_2	69.2	70.9	76.6	81.1			3.78
$CrCl_2$	74.8	76.6	82.5	87.1			4.05
$CrBr_2$	80.7	82.5	88.5	93.1			4.25
CrI_2	84.2	86.0	92.0	96.6			4.34
MnF_2	67.2	68.8	74.3	78.6			3.27
$MnCl_2$	73.0	74.6	80.2	84.8			3.54
$MnBr_2$	78.8	80.4	86.2	90.7			3.74
MnI_2	82.3	84.0	89.8	94.3			3.83
FeF_2	68.7	70.3	76.2	80.8			3.40
$FeCl_2$	74.2	75.9	82.0	86.6			3.66
$FeBr_2$	79.5	81.3	87.4	92.2			3.83
FeI_2	83.2	85.0	91.1	95.9			3.93
CoF_2	68.4	70.0	75.9	80.6			3.29
$CoCl_2$	73.9	75.6	81.6	86.4			3.54
$CoBr_2$	79.2	80.9	87.1	91.9			3.73
CoI_2	82.9	84.6	90.8	95.7			3.83
NiF_2	68.1	69.6	75.3	79.9			3.26
$NiCl_2$	73.2	74.9	80.7	85.4			3.49
$NiBr_2$	78.9	80.6	86.5	91.3			3.69
NiI_2	82.5	84.2	90.2	95.0			3.80
CuF_2	67.5	69.0	74.5	79.0			3.26
$CuCl_2$	72.4	74.2	80.0	84.6			3.49
$CuBr_2$	78.3	79.9	85.8	90.4			3.70
CuI_2	81.9	83.6	89.4	94.0			3.80

Based on molecular constants of Tables II and III with a linear model for all dihalides except those of tin and lead for which a bond angle of 95° was assumed.

electron affinities tabulated by Cubicciotti (18) were increased slightly on the basis that the deviations of the values from potassium and rubidium salts were due to errors in the enthalpies of formation of the aqueous ions. The electron affinities of the gaseous halogen atoms at 0°K. were taken as: F, 80; Cl, 86; Br, 81; and I, 74 kcal./gram atom. ΔH^0_{298} was taken equal to ΔH_0^0 for the reaction $M(g) + 2X(g) = M^{++}(g) + 2X^-(g)$. The ionization potentials of the metals as given by Moore (54) then yield the dissociation or ionization enthalpies of the dihalides to gaseous ions as given in Table VIII.

TABLE VII

THERMODYNAMIC PROPERTIES (IN KCAL./MOLE) OF METAL DIHALIDES AT 298.15°K.[a]

Compound	$\Delta H^0_{\text{Subl.}}$	ΔH^0_f(solid)[b]	ΔH^0_f(gas)	$\Delta H^0_{\text{Atom.}}$(gas)	Sources for vapor pressure data
BeF_2	56.8	− 241.2[c]	−184.4	300	(5, 45, 73, 74)
$BeCl_2$	32	− 118[d]	− 86	222	(12, 60)
$BeBr_2$	31	− 88.8	− 58	189	(12, 60)
BeI_2	30	− 50.6	− 20.6	150	(41, 60)
MgF_2	87	− 268[e]	−181	254	(30, 31, 65)
$MgCl_2$	53	− 153.2[e]	−100	194	(53)
$MgBr_2$	(51)	− 123.7	− 73	(162)	(10)
MgI_2	46.5	− 86	− 39.5	126	(7)
CaF_2	102	− 290.3	−188	268	(65)
$CaCl_2$	(71.5)	− 190.0	−118.5	(219)	(10, 88)
$CaBr_2$	66	− 161.3	− 95	191	(79, 88)
CaI_2	(65)	− 127.8	− 63	(156)	(10)
SrF_2	102	− 290.3	−188	265	(65)
$SrCl_2$	(71)	− 198.0	−127	(224)	
$SrBr_2$	70	− 171.1	−101	194	(79)
SrI_2	(65)	− 135.5	− 71	(161)	(10)
BaF_2	88	− 286.9	−199	279	(65)
$BaCl_2$	70	− 205.6	−136	236	(53, 88)
$BaBr_2$	71	− 180.4	−109	205	(79)
BaI_2	(66)	− 144	− 78	(172)	(10)
ZnF_2	61	−(176)[f]	−115	184	(65)
$ZnCl_2$	31.5	− 99.6[e]	− 68	157	(8, 9, 37, 53, 56, 83)
$ZnBr_2$	31	− 78.4[e]	− 47.4	132	(8, 19, 56)
ZnI_2	32	− 49.8[e]	− 18	100	(56)
CdF_2	76	− 164.9	− 89	153	(65)
$CdCl_2$	43	− 93.0	− 50	135	(2, 9, 29, 53, 56, 83)
$CdBr_2$	39	− 75.8[e]	− 36.8	117	(8, 29, 56, 84)
CdI_2	35	− 48.4[e]	− 13.4	91	(8, 56, 70, 84)
HgF_2	33	−(105)[f]	− 72	125	(56, 76)
$HgCl_2$	20	− 53.4[e]	− 33.4	106	(25, 39, 41, 53, 59, 62, 70, 76, 80, 90)
$HgBr_2$	20	− 40.7[e]	− 20.7	89	(39, 41, 59, 63, 76, 80, 90)
HgI_2	21.8	− 25.3[e]	− 3.5	69	(20, 39, 41, 59, 63, 76, 80, 90)
SnF_2	(50)	−(158)[f]	−108	218	
$SnCl_2$	35	− 83.6	− 49	179	(26, 53)
$SnBr_2$	35	− 63.6	− 29	154	(26)
SnI_2	36	− 34.4	2	121	(26)
PbF_2	58	− 158.5	−101	185	(53, 55, 88)
$PbCl_2$	43.5	− 85.7[e]	− 42	146	(2, 22, 29, 36, 53, 56, 83, 87, 88)
$PbBr_2$	40.5	− 66.3[e]	− 25.8	126	(8, 29, 56, 83, 87, 88)
PbI_2	39	− 41.6[e]	− 3	101	(29, 38, 56)
$TiCl_2$	63	− 123[g]	− 60	231	(23)
$TiBr_2$	(62)	− 95	− 33	(199)	(10)
TiI_2	62	− 66[g]	− 4	168	(32)
VCl_2	(63)	− 110[h]	− 47	(228)	(10)
VBr_2	(62)	− 82[f]	− 20	(196)	(10)
VI_2	(60)	− 53[f]	7	(167)	(10)
CrF_2	(85)	− 181	− 96	(229)	
$CrCl_2$	64.8	− 95	− 30	183	(21, 72)
$CrBr_2$	63.3	− 70[f]	− 6.7	155	(72, 78)
CrI_2	62	− 37.8[i]	24	122	(1, 7)
MnF_2	(75)	− 190[e]	−115	(220)	
$MnCl_2$	54.5	− 115.2[e]	− 60.7	186	(53, 66, 72)
$MnBr_2$	52.5	− 90.7	− 38	159	(72)
MnI_2	49	− 59.3	− 10	128	(7)
FeF_2	(75)	− 168	− 93	(230)	
$FeCl_2$	52	− 81.9[e]	− 30	187	(6, 53, 66, 77)
$FeBr_2$	48.8	− 60	− 11	164	(51, 77)
FeI_2	47	− 30	17	134	(7, 67, 72, 77)
CoF_2	(75)	− 159	− 84	(223)	
$CoCl_2$	54	− 75[e]	− 21	180	(53, 66, 72)
$CoBr_2$	53	− 53[f]	0	155	(72)
CoI_2	(50)	− 22[f]	28	(125)	(10)
NiF_2	78.5	− 158[f]	− 79.5	220	(24)
$NiCl_2$	58.7	− 73[e]	− 14.3	175	(53, 66)
$NiBr_2$	56	− 52[f]	4	152	(68)
NiI_2	53	− 22[f]	31	123	(69)
CuF_2	(66)	− 126.9	− 61	(180)	(10)
$CuCl_2$	47	− 49.2	− 2	141	(82)
$CuBr_2$	(45)	− 33.2	12	(123)	(10)

[a] Values in parentheses are estimated. [b] From N.B.S. Circular 500 if not indicated otherwise (see ref. 64). [c] From Kolesov, Popov and Skuratov (48). [d] From Johnson and Gilliland (40). [e] From Lewis, Randall, Pitzer and Brewer (50). [f] From Brewer, Bromley, Gilles and Lofgren (12). [g] From Kelley and Mah (44). [h] From Shchukarev, Oranskaya, Tolmacheva and Il'inski (75). [i] From Gregory and Burton (27).

TABLE VIII

$\Delta H^0_{298.15}$ IN KCAL./MOLE FOR $MX_2(g) = M^{++}(g) + 2X^-(g)$. Values in parentheses are estimated.

M	MF_2	MCl_2	MBr_2	MI_2
Be	775	685	662	636
Mg	617	545	(523)	501
Ca	523	461	444	(423)
Sr	491	(438)	417	(398)
Ba	470	415	394	(374)
Zn	655	616	601	583
Cd	591	560	552	540
Hg	637	607	600	594
Sn	(565)	514	499	480
Pb	543	493	480	470
Ti	(575)	529	(507)	490
V	(590)	(549)	(527)	(512)
Cr	(605)	547	530	510
Mn	(592)	546	529	512
Fe	(625)	570	557	540
Co	(638)	583	568	(551)
Ni	(655)	598	585	569
Cu	(666)	615	(607)	(589)

A plot of the ionization enthalpies of the gaseous and solid dichlorides in the horizontal row of the periodic table from calcium through zinc is shown in Fig. 1. On the basis of a simple ionic model, the ionization enthalpies of the dihalides of the above metals are expected to fall on a smooth curve (see the dotted curve in Fig. 1). It can be seen, however, that among the transition metal dichlorides, only manganous chloride

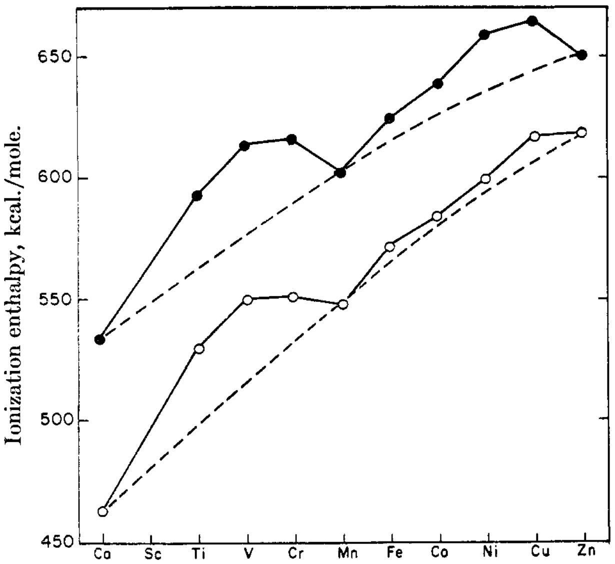

Fig. 1.—(●) $\Delta H^0_{298.15}$ in kcal./mole for $MCl_2(s) = M^{++}(g) + 2Cl^-(g)$; (○) $\Delta H^0_{298.15}$ in kcal./mole for $MCl_2(g) = M^{++}(g) + 2Cl^-(g)$.

behaves as expected, the points for calcium chloride, manganous chloride and zinc chloride falling on a smooth curve, while the others show large deviations. The reason for this may be traced to the spherical symmetry of the d-electrons of the manganous ion, which has a half-filled d-shell; the d-electrons of the other transition metal ions do not have spherical symmetry and the deviations are explained readily by crystal-field theory (4, 49, 50). The deviation curves for the gaseous dihalides indicate maxima at vanadium and copper.

A plot of the atomization enthalpies of gaseous dihalides of the metals from calcium through zinc is given in Fig. 2, and shows maxima at titanium and iron, and minima at chromium and copper. In contrast to the direct explanation of the variation of ionization enthalpies by crystal field theory, an explanation on the basis of the valence bond theory is difficult. A transition metal with an s^2-outer electronic configuration normally is expected to form two sp-hybrids which make the molecule linear. However, participation of the d-electrons in bonding leads to hybrids which are expected to make the dihalide molecule bent. The actual bond angle will depend on the amounts of s-, p- and d-character present in the hybrids. Electron diffraction studies will help solve this problem. If the bond angles should show a strong alternation between transition elements with even and odd numbers of electrons, some error would be present in the free energy functions of Table VI which largely smooth out the values for the transition metal halides and some additional irregularity should appear in Figs. 1 and 2.

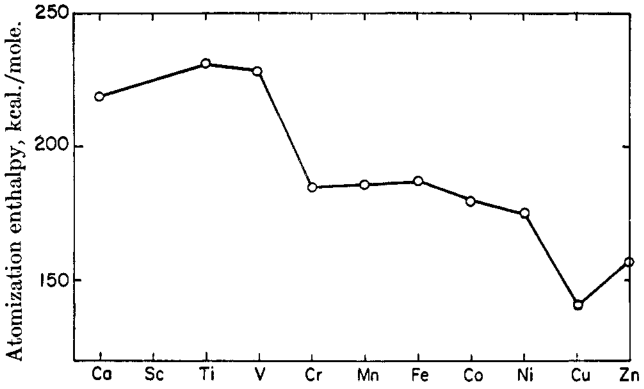

Fig. 2.—$\Delta H^0_{298.15}$ in kcal./mole for $MCl_2(g) = M(g) + 2Cl(g)$.

VI. SECOND LAW VAPORIZATION DATA

The constants of the equations

$$\Delta C_p^0 = \Delta a + \Delta bT + \Delta cT^{-2} \quad (1)$$

and

$$\Delta F^0 = \Delta H_I - \Delta aT \ln T - {}^1/_2\Delta bT^2 - {}^1/_2\Delta cT^{-1} - IT \quad (2)$$

as obtained from second law treatment of the vapor pressure data are tabulated by Brewer, Somayajulu and Brackett (13) and are thus available to allow a ready re-examination of the second law *versus* third law checks at a later date when more complete data on the structures and the extent of polymerization become known.

In Table IX are presented melting points and enthalpy of fusion data and the temperatures in degrees Kelvin at which the vapor pressures have the values 10^{-6}, 10^{-4}, 10^{-2} and 1 atm. References to sources of the data are given in Tables I and VII. In all cases including the halides of beryllium, for which polymerization is known to be very extensive, the pressures in Table IX are taken as closely as possible to represent the total vapor pressure. The partial pressures of the beryllium halide monomers may be calculated from the data of Tables I, VI and VII.

The recent evaluation of the vapor pressure data of the alkali halides (11) was a rigorous thermodynamic treatment with correction for gas imperfections and with use of reliable free energy functions for both condensed and gaseous phases. A table of vapor pressures of the alkali halides similar to Table IX was not necessary since the tabulated thermodynamic data could be used to obtain reliable values for any equilibrium conditions. In contrast, the present treatment of the vapor pressure data of the metal dihalides is not rigorous since most of the free energy functions must be estimated and data on gas imperfections are very rare. In addition, Tables IV and V show that there are differences between the second and third law treatments due to temperature-dependent errors in the vapor pressure data in some instances, to errors in the free energy functions in other instances, and to polymerization for others. In general, it is believed that more reliable

TABLE IX

FUSION AND VAPORIZATION DATA FOR METAL DIHALIDES[a]

Compound	ΔH^0_m, kcal./mole	ΔS^0_m, cal./deg. mole	T_m, °K.	T, °K. at pressures of (atm.)			
				10^{-6}	10^{-4}	10^{-2}	1
BeF_2			816	820	954	1148	1460
$BeCl_2$[b]			678	443	514	610	760
$BeBr_2$[b]			761	443	513	608	747
BeI_2[b]			753	432	504	607	760
MgF_2	13.9	9.05	1536	1323	1530	1900	(2600)
$MgCl_2$	10.3	10.44	987	800	937	1170	(1700)
$MgBr_2$	8.3	8.4	984		(900)	(1120)	(1600)
MgI_2			923			980	(1300)
CaF_2	7.1	4.2	1691		(1710)	2100	(2800)
$CaCl_2$	6.78	6.42	1055	(1070)	(1270)	(1600)	(2200)
$CaBr_2$			1033	990	1180	1480	(2000)
CaI_2			1057	(960)	(1140)		(1900)
SrF_2			1673		(1700)	2080	(2750)
$SrCl_2$	(7)	(6)	1145	(1060)	(1260)		(2150)
$SrBr_2$	(5.5)	(6)	926	1040	(1240)	(1560)	(2150)
SrI_2	(4.7)	(6)	788	(970)	(1150)		(1950)
BaF_2	(6.4)	(4)	1593		(1510)	1880	(2550)
$BaCl_2$	(8.6)	(7)	1235		1230	1520	(2100)
$BaBr_2$			1120	1090	(1300)		(2250)
BaI_2			984	(990)	(1180)		(2000)
ZnF_2	(7)	(6)	1145			1320	1780
$ZnCl_2$	5.5	9.3	591	540	610	760	(1000)
$ZnBr_2$			667	515	600	715	930
ZnI_2			719	494	590		(970)
CdF_2			1322			1530	2010
$CdCl_2$	7.22	8.58	842	650	760	914	1235
$CdBr_2$	7.97	9.48	841	590	690	835	(1100)
CdI_2	4.95	7.49	661	535	620	750	1017
HgF_2			918			700	920
$HgCl_2$	4.64	8.4	553	315	369	447	580
$HgBr_2$	4.0	7.7	511	316	371	450	592
HgI_2	4.5	8.6	523	333	389	470	627
SnF_2			>900				>1000
$SnCl_2$	3	6	500		540	660	930
$SnBr_2$			505		560	690	910
SnI_2			593			730	990
PbF_2	5.54	5.04	1097	820	955	1160	1570
$PbCl_2$	5.8	7.52	771	650	745	910	1225
$PbBr_2$	4.43	6.89	643	610	700	870	1180
PbI_2	6.01	8.77	685	585	685	830	1170
$TiCl_2$			1308	820	938		
$TiBr_2$			>1100	(805)	(920)		
TiI_2			>1100	806	922		
VCl_2			>1273	(810)	(920)	(1070)	(1300)
VBr_2			(1100)	(800)	(910)		(1300)
VI_2			(1050)	(765)	(870)		(1250)
CrF_2			1144	(1180)	(1370)		(2200)
$CrCl_2$	(9.4)	(8.6)	1093	881	1013	1217	(1570)
$CrBr_2$			1155	850	990		(1500)
CrI_2	(9)	(8)	1123	840	965	1140	1440
MnF_2	(5.5)	(5)	1129	(1070)	(1250)	(1515)	
$MnCl_2$	8.97	9.72	923	776	901	1093	1500
$MnBr_2$	(10)	(10)	971	737	852	1016	(1300)
MnI_2	(10)	(10)	911	700	820	1000	(1290)
FeF_2			1375	(1020)	(1175)		
$FeCl_2$	10.28	10.92	950	700	810	960	1280
$FeBr_2$	(11)	11.5	962	680	780	930	1230
FeI_2	(10)	(12)	867	650	750	880	1200
CoF_2			1475	(1000)	(1160)	(1370)	
$CoCl_2$	(11)	(11)	1013	740	850	1000	(1330)
$CoBr_2$			951	730	840		(1300)
CoI_2			790	(675)	(780)		(1150)
NiF_2			>1365	1030	1190	(1400)	
$NiCl_2$	18.47	14.18	1303	(770)	880	1030	1250
$NiBr_2$			1236	(750)	860	1000	1192
NiI_2			1070	690	790	920	(1100)
$CuCl_2$				640	740	880	

[a] Values in parentheses are estimated or extrapolated values. [b] For these beryllium halides, pressures given are total pressures including polymers.

partial pressures can be calculated through the use of the tabulated free energy functions of Tables I and VI and the enthalpies of Table VII than through the use of second law equations such as eq. 2, and use of these tables is recommended for most equilibrium calculations. Table IX represents an alternative presentation of the data, not necessarily consistent with Tables I, VI and VII, in which considerable weight is given to the actual measurements in the temperature range of measurements. Where values have been extrapolated beyond the temperature range of the measurements, more weight is given to the third law calculations than to the extrapolation of equations of the type of eq. 2. Table IX is recommended when saturated vapor pressures of pure halides in the temperature range of existing measurements are desired while the third law calculations are recommended for all other calculations.

VII. CONCLUSION

In the present treatment of the vapor pressure data by the second law and third law methods, the polymerization of the dihalide vapors is not taken into account except for the beryllium halides. In most instances one would expect from the available (5, 58, 71) mass spectrometer examinations that the monomer is the major species and that the dimer or other polymeric species will be present to a minor extent which will increase with increasing temperature. As a result of the neglect of this contribution by polymers, the enthalpies of vaporization obtained by the third law method will be slightly low and atomization enthalpies of the dihalides will be slightly high. When the tabulated enthalpies of vaporization are used together with the free energy functions to calculate the vapor pressure data, the calculated vapor pressure will correspond to the actual total vapor pressure in the range of temperature corresponding to the original experimental measurements. At temperatures below that range the calculated pressures will be slightly high. At temperatures above the range of experimental measurements, the calculated pressures will generally be lower than the true total pressures due to the fact that the proportion of dimer will be larger at higher temperatures than in the temperature range of measurements. In some instances such as zinc chloride, the polymeric species may predominate over the monomer species. In those instances, the tabulated enthalpies of vaporization may be from 2 to 5 kcal. too small although the tabulated enthalpies of vaporization when combined with the free energy functions will yield vapor pressures in agreement with the experimental data in the middle of the experimental range, but substantial deviations will occur between the actual total pressures and those calculated at temperatures substantially below or above the range in which measurements have been made.

Brewer (10) has associated extensive polymerization of the gaseous phase with a rather narrow range of cation–anion radius ratios. This treatment would predict extensive polymerization for the non-fluoride dihalides of beryllium, zinc, copper and also tin because of its bent shape. Below and above limiting cation–anion ratios, the degree of polymerization should be much less extensive. Available mass spectrometer data are in agreement with this. Vapor density data are available to correct for polymerization only for beryllium halides. For dihalides of zinc, copper, and tin, the ratio of total pressure to monomer pressure is not expected to be more than a factor of two and has not been applied to the values of $H^0_{\text{subl.}}$ in Table VII.

The tabulated enthalpies of vaporization may also be in error in some instances due to the uncertainties in the estimated free energy functions for the gases and the solids. In many cases, however, where the second law and the third law gave essentially the same result, the error probably is less than 1 to 2 kcal. For compounds such as titanium(II) chloride, titanium(II) iodide, etc., where the agreement between the second law and third law calculations is poor, this error may be as large as 5 kcal. The estimated enthalpies of vaporization enclosed in parentheses are probably accurate to within 10 kcal. In a few cases, the enthalpies of formation of the solid dihalides are not known accurately and thus limit the accuracy of the enthalpies of atomization recorded in the fourth column of Table VII. The heats of atomization and ionization reported in this paper are, however, accurate enough to recognize significant trends as noted in section V.

ACKNOWLEDGMENT.—The authors are grateful to Drs. J. W. Stout and E. F. Westrum, Jr., for release of new entropy determinations prior to publication. Drs. K. K. Kelley and E. G. King greatly aided the progress of this work by allowing access to the manuscript of U. S. Mines Bulletin 592, "Entropies of Inorganic Substances," prior to publication. Dr. L. E. Topol kindly supplied unpublished high temperature enthalpy measurements and Dr. J. M. Blocher, Jr., provided unpublished vapor pressure data. Dr. W. Klemperer and Dr. George Leroi were particularly helpful in supplying results of spectral studies prior to publication. This work was supported by the United States Atomic Energy Commission.

VIII. REFERENCES

(1) Allen, T. L., *J. Am. Chem. Soc.*, **78**, 5476 (1956).
(2) Barton, J. L., and Bloom, H., *J. Phys. Chem.*, **60**, 1413 (1956).
(3) Bastiansen, O., and Lund, E. W., *Ann. Rev. Phys. Chem.*, **10**, 31 (1959).
(4) Berg, R. A., and Sinanoglu, O., *J. Chem. Phys.*, **32**, 1082 (1960).
(5) Berkowitz, J., and Chupka, W. A., *Ann. N. Y. Acad. Sci.*, **79**, 1073 (1960).
(6) Beusman, C. A., and Blankenship, F. F., Oak Ridge National Laboratory Report 2323 (1960).
(7) Blocher, J. M., Jr., Battelle Memorial Institute (unpublished data).
(8) Bloom, H., Bockris, J. O'M., Richards, N. E., and Taylor, R. G., *J. Am. Chem. Soc.*, **80**, 2044 (1958).
(9) Bloom, H., and Welch, B. J., *J. Phys. Chem.*, **62**, 1594 (1958).
(10) Brewer, L., Paper No. 7, "Chemistry of Miscellaneous Materials," NNES-IV-19B, McGraw-Hill Book Co. Inc., New York, N. Y., 1950.

(11) Brewer, L., and Brackett, E., *Chem. Rev.*, **61,** 425 (1961).

(12) Brewer, L., Bromley, L. A., Gilles, P. W., and Lofgren, N. L., Paper No. 6, "Chemistry and Metallurgy of Miscellaneous Materials," NNES-IV-19B, McGraw-Hill Book Co. Inc., New York, N. Y., 1950.

(13) Brewer, L., Somayajulu, G. R., and Brackett, E., U.C.R.L. 9840 (1961).

(14) Büchler, A., Thesis, Harvard University, Cambridge (1960).

(15) Büchler, A., and Klemperer, W., *J. Chem. Phys.*, **29,** 121 (1958).

(16) Chisholm, R. C., and Stout, J. W., private communication.

(17) Craw, D. A., and Rogers, J. L., *J. Chem. Soc.*, 217 (1956).

(18) Cubicciotti, D., *J. Chem. Phys.*, **34,** 2189 (1961).

(19) Desai, M. S., *Proc. Natl. Acad. Sci.* (India), **2,** 119 (1933).

(20) Ditte, A., *Compt. Rend.*, **140,** 1162 (1903).

(21) Doerner, H. A., U. S. Bur. Mines Technical Paper 577 (1937).

(22) Eastman, E. D., and Duschak, L. H., U. S. Bur. Mines Technical Paper 225 (1919).

(23) Farber, M., and Darnell, A. J., *J. Chem. Phys.*, **25,** 526 (1956).

(24) Farber, M., Meyer, R. T., and Margrave, J. L., *J. Phys. Chem.*, **62,** 883 (1958).

(25) Fischer, W., and Biltz, W., *Z. anorg. u. allgem. Chem.*, **176,** 81 (1928).

(26) Fischer, W., and Gewecher, R., *Z. anorg. u. allgem. Chem.*, **222,** 303 (1935).

(27) Gregory, N. W., and Burton, P. R., *J. Am. Chem. Soc.*, **75,** 6054 (1953).

(28) Gregory, N. W., and O'Neal, H. E., *J. Am. Chem. Soc.*, **81,** 2649 (1959).

(29) Greiner, B., and Jellinek, K., *Z. physik. Chem.*, **A165,** 97 (1933).

(30) Gunther, K. G., *Glastech. Ber.*, **31,** 9 (1958).

(31) Hammer, R. R., Messier, D. R., and Pask, J. A., University of California Ceramic Laboratories, Ser. 18, Issue 8 (1960).

(32) Herczog, A., and Pidgeon, L. M., *Can. J. Chem.*, **34,** 1687 (1956).

(33) Hyde, J. L., *J. Am. Chem. Soc.*, **73,** 1860 (1951).

(34) Itskevich, E. S., and Strelkov, P. G., *Russ. J. Phys. Chem.*, **33,** 60 (1959).

(35) Itskevich, E. S., and Strelkov, P. G., *Russ. J. Phys. Chem.*, **34,** 627 (1960).

(36) Jellinek, K., and Golubowski, A., *Z. physik. Chem.*, **A147,** 461 (1930).

(37) Jellinek, K., and Koop, R., *Z. physik. Chem.*, **A145,** 305 (1929).

(38) Jellinek, K., and Rudat, A., *Z. physik. Chem.*, **A143,** 55 (1929).

(39) Johnson, F. M. G., *J. Am. Chem. Soc.*, **33,** 777 (1911).

(40) Johnson, W. J., and Gilliland, A. A., *J. Research Natl. Bur. Standards*, **65A,** 59 (1961).

(41) Kelley, K. K., U. S. Bur. Mines Bull. 383 (1935).

(42) Kelley, K. K., U. S. Bur. Mines Bull. 584 (1960).

(43) Kelley, K. K., and King, E. G., U. S. Bur. Mines Bull. 592 (1961).

(44) Kelley, K. K., and Mah, A. D., U. S. Bur. Mines Rept. of Investigation 5490 (1959).

(45) Khandamirova, N. E., Evseev, A. M., Pozharskaya, G. V., Borisov, E. A., Nesmeyanov, An. N., and Gerasimov, Ya. I., *Russ. J. Inorg. Chem.*, **4,** 998 (1959).

(46) Klemperer, W., *J. Chem. Phys.*, **25,** 1066 (1956).

(47) Klemperer, W., and Lindeman, L., *J. Chem. Phys.*, **25,** 397 (1956).

(48) Kolesov, V. P., Popov, M. M., and Skuratov, S. M., *Russ. J. Inorg. Chem.*, **4,** 557 (1959).

(49) Leroi, G., Thesis, Harvard University, Cambridge (1960).

(50) Lewis, G. N., Randall, M., Pitzer, K. S., and Brewer, L., "Thermodynamics," 2nd Ed., McGraw-Hill Book Co. Inc., New York, N. Y., 1961.

(51) MacLaren, R. O., and Gregory, N. W., *J. Phys. Chem.*, **59,** 184 (1955).

(52) Mah, A. D., U. S. Bur. Mines Rept. of Investigation 5600 (1960).

(53) Maier, C. G., U. S. Bur. Mines Technical Paper 360 (1929).

(54) Moore, C. E., Atomic Energy Levels, Natl. Bur. Stands. Circ. 467, Vol. III (1958).

(55) Nesmeyanov, An. N., and Iofa, B. Z., *Russ. J. Inorg. Chem.*, **4,** 219 (1959).

(56) Niwa, K., *J. Fac. Sci. Hokkaido Uni. Ser. III,* **3,** 17 (1940).

(57) Oetting, F. L., and Gregory, N. W., *J. Phys. Chem.*, **65,** 173 (1961).

(58) Porter, R. F., and Schoonmaker, R. C., *J. Phys. Chem.*, **63,** 626 (1959).

(59) Prideaux, E. B. R., *J. Chem. Soc.*, **97,** 2032 (1910).

(60) Rahlfs, O., and Fischer, W., *Z. anorg. u. allgem. Chem.*, **211,** 349 (1933).

(61) Randall, S. P., Greene, F. T., and Margrave, J. L., *J. Phys. Chem.*, **63,** 758 (1959).

(62) Richter, V., *Ber. Deutsch. Chem. Gesell.* **19,** 1057 (1886).

(63) Rinse, J., *Rec. trav. chim.*, **47,** 33 (1928).

(64) Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, I., Natl. Bur. Stands. Circ. 500 (1952).

(65) Ruff, O., and LeBoucher, L., *Z. anorg. u. allgem. Chem.*, **219,** 376 (1934).

(66) Schäfer, H., Bayer, L., Breil, G., Etzel, K., and Krehl, K., *Z. anorg. u. allgem. Chem.*, **278,** 300 (1955).

(67) Schäfer, H., and Hönes, W. J., *Z. anorg. u. allgem. Chem.*, **288,** 62 (1956).

(68) Schäfer, H., and Jacob, H., *Z. anorg. u. allgem. Chem.*, **286,** 56 (1956).

(69) Schäfer, H., Jacob, H., and Etzel, K., *Z. anorg. u. allgem. Chem.*, **286,** 42 (1956).

(70) Schmidt, G. C., and Walter, R., *Ann. Physik,* **72,** 565 (1923).

(71) Schoonmaker, R. C., and Porter, R. F., *J. Chem. Phys.*, **29,** 116 (1958).

(72) Schoonmaker, R. C., Friedman, A. H., and Porter, R. F., *J. Chem. Phys.*, **31,** 1586 (1959).

(73) Sense, K. A., Snyder, M. J., and Clegg, J. W., *J. Phys. Chem.*, **58,** 223 (1954).

(74) Sense, K. A., and Stone, R. W., *J. Phys. Chem.*, **62,** 453 (1958).

(75) Shchukarev, S. A., Oranskaya, M. A., Tolmacheva, T. A., and Il'inski, Yu. S., *Russ. J. Inorg. Chem.*, **5,** 3 (1960).

(76) Shibata, Z., and Niwa, K., *J. Fac. Sci. Hokkaido Uni. Ser. III,* **2,** 183 (1938).

(77) Sime, R. J., and Gregory, N. W., *J. Phys. Chem.*, **64,** 86 (1960).

(78) Sime, R. J., and Gregory, N. W., *J. Am. Chem. Soc.*, **82,** 800 (1960).

(79) Stock, A., and Heynemann, H., *Chem. Ber.*, **42,** 4088 (1909).

(80) Stock, A., and Zimmerman, W., *Monatsh.*, **53-54,** 786 (1929).

(81) Sutton, L. E., Special Publication No. 11, The Chemical Society, London (1958).

(82) Tarasenkov, D. N., and Klyacho-Gurvich, L. L., *J. Gen. Chem.* (*U.S.S.R.*), **6,** 305 (1936).

(83) Tarasenkov, D. N., and Skulkova, G. V., *J. Gen. Chem.* (*U.S.S.R.*), **7,** 1721 (1937).

(84) Tolmacheva, T. A., and Andrinovskaya, T. L., *Vestnik Leningrad Uni.*, **15,** No. 10, Ser. Fiz. and Khim. No. 2, 131 (1960).

(85) Topol, L. E., and Ransom, L. D., *J. Phys. Chem.* **64,** 1339 (1960).

(86) Topol, L. E., and Ransom, L. D., *J. Phys. Chem.*, **65**, 2267 (1961).
(87) Völmer, F., *Phys. Z.*, **30**, 590 (1929).
(88) Wartenberg, H. von, and Bosse, O., *Z. Elektrochem.*, **28**, 384 (1922).
(89) Westrum, E. F., unpublished results.
(90) Wiedemann, E., *Ber. Deutsch. Physik. Gesell.*, **3**, 159 (1905).