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# THERMODYNAMIC PROPERTIES OF GASEOUS METAL DIHALIDES

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CONTENTS

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## Abstract

The second and third law methods of thermodynamics are used to obtain the enthalpies of vaporization of the halides of Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Sn, Pb, Ti, V, Cr, Mn, Fe, Co, Ni and Cu. Molecular and free energy data necessary for such calculations are presented. The structure of bonding in these molecules is briefly discussed.

## 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 is the consideration of enthalpies of formation of the gaseous dihalides obtained from all sources from the point of view of electronic structures to develop a procedure for 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 $\Delta C_p^\circ$ for the vaporization process. Within the accuracy of these data, $\Delta C_p^\circ$ 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 $\Delta H^\circ$ of the vaporization process over the temperature range of study. These values are reduced to values at 298.15°K, not by assuming constant $\Delta C_p^\circ$ 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 $\Delta H^\circ_{298.15}$ are then combined with values of $\Delta F^\circ$ in the temperature range of study to obtain the experimental values of $(\Delta F^\circ - \Delta H^\circ_{298.15})/T$. These values combined with values of $-(F^\circ - H^\circ_{298.15})/T$ 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 been necessary to estimate $S^{\circ}_{298.15}$, the $-(F^{\circ} - H^{\circ}_{298.15})/T$ values at 298.15°K in Table I is given in parenthesis. In such cases, the values of $S^{\circ}_{298.15}$ 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 accurately calculated 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 treatment of bending frequencies described below is believed to be compensate for any error due to the assumption of a linear structure. The structures of the transition metal dihalides are not known, but in the present study they are assumed to be linear. Judging from the high values of the observed entropies, the gaseous transition metal dihalides could possibly have bent structures.

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 is then 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 0.5A in the internuclear distances would lead to an error of less than 1 cal/deg mole in the rotational contribution to the entropy. The molecu-

lar constants chosen for the gaseous dihalides are given in Tables IIa and IIb. In Table III are shown the calculated free energy functions compared with experimental free energy functions for some dihalides with no appreciable electronic contribution.

## 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 substantially change 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.

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 $(k\delta/\ell^2)/k_1$ 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.

In Table IV are given the electronic contributions of the $M^{++}$ ions. 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 III 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. Based on fragmen-

tary vapor pressure data, the third law calculations were made for the following compounds: calcium chloride, calcium bromide, strontium bromide, barium chloride, barium bromide, mercury (II) fluoride, manganese (II) bromide, cobalt (II) bromide, and nickel (II) iodide. The free energy functions of all the gaseous metal dihalides considered here are given in Table VI.

## V. Enthalpies of Dissociation

In Table VII are tabulated the enthalpies of sublimation at 298.15°K for all metal dihalides for which any sort of data exist. These data are combined with the enthalpies of formation of the solid halides, the enthalpies of sublimation of the metals, and the enthalpies of dissociation of the halogens to yield the dissociation or atomization energies of the gaseous metal dihalides to gaseous atoms. These are shown in the fourth column of Table VII. The ionization potentials of the metals as given by Moore[54] and the electron affinities as given by Brewer and Brackett[11] then yield the dissociation or ionization energies of the dihalides to gaseous ions as given in Table VIII.

Ionization energies of the alkaline earth metal dihalides as calculated by Cubicciotti[18] are compared with the experimentally determined values in Table IX. In the third column of the Table IX are given those values calculated on the basis of the Rittner potential function which employs an overlap repulsion term of the type: $A \exp(-r/\rho)$. The values calculated on the basis of an overlap repulsion term of the type $Ar^{-n}$ are given in the second column. The agreement of the values calculated on the basis of the reciprocal repulsion term with the experimental values is remarkably good.

A plot of the ionization energies 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 energies 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 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.[4,49,50]

It is known that the charge clouds overlap much more when they are assymetric; this may account for the enhanced stability of these halides over that expected on the basis of a simple ionic model with spherical ions. The deviation curve for the gaseous dihalides indicate maxima at vanadium and copper.

A plot of the atomization energies of gaseous dihalides of the metals from calcium through zinc is shown in Fig. 2. This shows maxima at titanium and iron, and minima at chromium and copper.

## VI. Fusion and Second Law Vaporization Data

The constants of the equations

$$\Delta C_p^o = \Delta a + \Delta b\, T + \Delta c\, T^2 \qquad (1)$$

and

$$\Delta F^o = \Delta H_I - \Delta a\, T \ln T - 1/2\, \Delta b\, T^2 - 1/2\, \Delta c\, T^{-1} - I\, T \qquad (2)$$

as obtained from second law treatment of the vapor pressure data are given in Table X. The free energy equation is applicable only in the temperature range of interest. The equations are not corrected to yield the required values of the melting point, enthalpy of fusion and entropy of fusion. These constants are tabulated in Table X only for the purpose of allowing 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 becomes known. In general, it is believed that more reliable vapor pressures can be calculated through the use of the tabulated free energy functions of Tables I and VI and the enthalpies of Table VII even in a large part of the experimental temperature range.

In Table XI are presented melting point and 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. Generally these values are given only for the temperature range for which measurements exist. In all cases including the halides of beryllium for which polymerization is known to be very extensive, the pressures in Table XI 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. These same tables can be used to extrapolate the values of Table XI for all of the halides beyond the experimental temperature range.

## 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 energies of the dihalides will be slightly large. 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 lack of a good third law check even when all molecular data are available as an indication that 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 substantially 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 dihalides of beryllium, zinc, copper and tin. Below and above limiting cation-anion ratios, the degree of polymerization should be much less extensive. Available mass spectrometer data is 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 correction is not expected to be more than a factor of two and has not been applied.

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 will thus limit the accuracy of the enthalpies of atomization recorded in the fourth column of Table VII.

The heats of atomization reported in this paper are, however, accurate enough to make a few conclusions about the structure of bonding in these molecules. The irregularities in the curve obtained when the heats of atomization are plotted against the atomic number (as shown in Fig. 2) for the transition metal dihalides may be traced to the participation of the d electrons in bonding. A transition metal with an $s^2$ outer electronic configuration is normally 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 characters present in the hybrids. Electron diffraction studies will help solve the problem. If the bond angles should show a strong alternation between transition elements with even and odd number of electrons, some error may be present in the free energy functions of Table VI which largely smooth out the values for the

transition metal halides.

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References


1. Allen, T.S.: J. Am. Chem. Soc. 78, 5476(1958).
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. New York Acad.Sci. 79,1073(1960).
6. Beusman, C.A., and Blankenship, F.F.: Oak Ridge National Laboratory Report 2323(1960).
7. Blocher, Jr., J.M.: 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 Welsch, B.J.: J. Phys. Chem. 62, 1594(1958).
10. Brewer, L.: Paper No. 7, Chemistry of Miscellaneous Materials, NNES-IV-19B, McGraw-Hill Book Company Inc., New York(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 Company Inc., New York(1950).
13. Brewer, L., and Somayajulu, G.R.: (unpublished results).
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. : Stanford Research Institute Technical Note No. 7(1960).
19. Desai, M.S.: Proc. Natl. Acad. Sci.(India) 2, 119(1933).
20. Ditte, A.: Compte 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. 59, 156(1955).

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. physikal 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. Herztog, A., and Pidgeon, L.M.: Canadian 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. physikal Chem. A147, 461(1930).

37. Jellinek, K., and Koop, R.: Z. physikal Chem. A145, 305(1929).

38. Jellinek, K., and Rudat, A.: Z. physikal 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 (N.B.S.) 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. Kolosov, 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 Company Inc., New York (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(1925).

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. Am. Chem. Soc. 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., Stone, R.W., and Filbert, Jr., R.B.: Battelle Memorial Institute Report, BMI-1186(1957).

75. Shchukarev, S.A., Oranskaya, M.A., Tomacheva, 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., Heynemann, H.: Chem. Ber. 42, 2088(1909).

80. Stock, A., Zimmerman, W.: Monatshefte, 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. Topal, L.E., and Ransom, L.D.: J. Phys. Chem. 64, 1339(1960).

86. Topal, L.E., and Ransom, L.D.: (Unpublished results).

87. Völmer, F.: Physikal Z. 30, 590(1929).

88. Wartenberg, H. von, and Bosse, O.: Z. Electrochem. 28, 384(1922).

89. Westrum, E.F.: Unpublished results.

90. Wiedemann, E.: Ber. Deutsch Physikal Gesell, 3, 159(1905).

Table I

Free energy functions of condensed metal halides based on $H^{\circ}_{298.15}$ [a]

| Compound | $-(F^{\circ} - H^{\circ}_{298.15})/T$, cal/deg mole | | | | | | $H^{\circ}_{298.15} - H^{\circ}_{0}$ cal/mole | References |
|---|---|---|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500° | 2000° | 2500° K | | |
| $BeF_2$ | (8.3) | 10.0 | 17.0 | 23.0 | | | (1650) | |
| $BeCl_2$ | (16.0) | 18.0 | 25.0 | | | | (2550) | |
| $BeBr_2$ | (22.0) | 24.0 | 32.0 | | | | (2950) | |
| $BeI_2$ | (25.0) | 27.0 | 36.0 | | | | (3250) | |
| $MgF_2$ | 13.7 | 15.5 | 22.3 | 27.9 | 34.6 | 39.9 | 2370 | (50) |
| $MgCl_2$ | 21.4 | 23.4 | 30.9 | 40.4 | | | 3291 | (50) |
| $MgBr_2$ | (27.0) | 29.0 | 37.0 | 47.0 | | | (3700) | (12) |
| $MgI_2$ | (30.0) | 32.0 | 40.0 | 49.0 | | | (4000) | |
| $CaF_2$ | 16.5 | 18.4 | 25.7 | 31.8 | 37.9 | 43.2 | 2788 | (50) |
| $CaCl_2$ | 27.2 | 29.3 | 36.6 | 44.6 | 50.9 | | 3687 | (50) |
| $CaBr_2$ | (33.0) | 35.0 | 43.0 | 51.0 | 57.0 | | (4100) | (12) |
| $CaI_2$ | (36.0) | 38.0 | 46.0 | 54.0 | | | (4400) | (12) |
| $SrF_2$ | (19.5) | 21.5 | 28.5 | 34.5 | 40.5 | 45.5 | (3200) | (43) |
| $SrCl_2$ | (29.0) | 31.0 | 38.9 | 47.0 | | | (4100) | (42) |
| $SrBr_2$ | (35.0) | 37.2 | 44.5 | 53.6 | | | (4500) | (42) |
| $SrI_2$ | (38.0) | 40.2 | 48.5 | | | | (4800) | (42) |
| $BaF_2$ | 23.0 | 25.1 | 32.7 | 39.3 | 45.8 | 51.1 | 3452 | (42)(43) |
| $BaCl_2$ | (32.0) | 34.1 | 41.5 | 48.7 | 55.3 | | (4350) | (42) |
| $BaBr_2$ | (38.0) | 40.2 | 48.0 | 56.0 | | | (4750) | |
| $BaI_2$ | (41.0) | 43.2 | 51.0 | 59.0 | | | (5050) | |

Table I

Free energy functions of condensed metal halides based on $H^{\circ}_{298.15}$ [a]

| Compound | $-(F^{\circ} - H^{\circ}_{298.15})/T$, cal/deg mole | | | | | $H^{\circ}_{298.15} - H^{\circ}_{0}$ cal/mole | References |
|---|---|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500° | 2000°K | | |
| $ZnF_2$ | 17.6 | 19.4 | 26.2 | 33.4 | 39.4 | 2827 | (42)(43) |
| $ZnCl_2$ | 26.7 | 28.7 | 40.4 | | | 3598 | (17)(89) |
| $ZnBr_2$ | 32.5 | 34.6 | 44.5 | | | (4000) | |
| $ZnI_2$ | 35.0 | 37.1 | 47.0 | | | (4300) | |
| $CdF_2$ | (19.5) | 21.5 | 28.5 | 34.5 | 40.5 | (2900) | (43) |
| $CdCl_2$ | 27.6 | 29.6 | 39.0 | 48.4 | | 3791 | (34)(85)(86) |
| $CdBr_2$ | 33.2 | 35.3 | 44.7 | | | 4235 | (35)(85)(86) |
| $CdI_2$ | 37.7 | 39.8 | 50.7 | | | 4512 | (34)(85)(86) |
| $HgF_2$ | (27.0) | 29.0 | 36.0 | | | (3700) | |
| $HgCl_2$ | (34.5) | 36.5 | | | | (4600) | (50) |
| $HgBr_2$ | (40.7) | 42.7 | | | | (5000) | (50) |
| $HgI_2$ | (42.4) | 44.9 | | | | (5300) | (50) |
| $SnF_2$ | (21.5) | 23.5 | 30.5 | | | (3000) | |
| $SnCl_2$ | (29.0) | 31.0 | 42.0 | | | (3900) | |
| $SnBr_2$ | (35.0) | 37.0 | 48.0 | | | (4300) | |
| $SnI_2$ | (38.0) | 40.0 | 52.0 | | | (4600) | |
| $PbF_2$ | (25.0) | 27.0 | 34.4 | 41.9 | | (3200) | (42) |
| $PbCl_2$ | 32.5 | 34.6 | 44.4 | 53.6 | | (4100) | (42)(50) |
| $PbBr_2$ | 38.6 | 40.8 | 51.7 | 60.7 | | (4500) | (33)(42)(50) |
| $PbI_2$ | 41.8 | 44.0 | 55.6 | 65.9 | | (4800) | (42)(89) |

Table I

Free energy functions of condensed metal halides based on $H^{\circ}_{298.15}$ [a]

| Compound | $-(F^{\circ} - H^{\circ}_{298.15})/T$, cal deg mole | | | | $H^{\circ}_{298.15} - H^{\circ}_{0}$ | References |
|---|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500°K | cal/mole | |
| $TiF_2$ | (18.6) | 20.6 | 27.6 | 34.6 | (2900) | |
| $TiCl_2$ | (24.3) | 26.3 | 33.6 | | (3800) | (42)(44) |
| $TiBr_2$ | (29.5) | 31.7 | 39.3 | | (4200) | (42)(44) |
| $TiI_2$ | (32.5) | 34.9 | 43.2 | | (4500) | (42)(44) |
| $VF_2$ | (17.5) | 19.5 | 26.5 | 33.5 | (2900) | |
| $VCl_2$ | 23.2 | 25.2 | 32.5 | 41.0 | (3800) | (42)(43) |
| $VBr_2$ | (29.0) | 31.0 | 39.0 | | (4200) | (12) |
| $VI_2$ | (32.0) | 34.0 | 42.0 | | (4500) | (12) |
| $CrF_2$ | (22.0) | 24.0 | 31.0 | 38.0 | (2800) | |
| $CrCl_2$ | 27.6 | 29.5 | 36.7 | 45.1 | (3700) | (16)(50) |
| $CrBr_2$ | (33.0) | 35.0 | 43.0 | 51.0 | (4100) | |
| $CrI_2$ | (36.0) | 38.0 | 46.0 | 54.0 | (4400) | |
| $MnF_2$ | 22.3 | 24.2 | 31.1 | 38.2 | (3000) | (52) |
| $MnCl_2$ | 28.3 | 30.4 | 38.6 | 47.9 | (3900) | (16)(52) |
| $MnBr_2$ | (33.5) | 35.6 | 43.5 | | (4300) | (52) |
| $MnI_2$ | (36.5) | 39.1 | 49.4 | | (4600) | (52) |
| $FeF_2$ | 20.8 | 22.8 | 29.8 | 36.8 | 3049 | (43) |
| $FeCl_2$ | 26.6 | 28.8 | 37.0 | 47.0 | (3950) | (42)(89) |
| $FeBr_2$ | 33.6 | 35.8 | 44.2 | 54.3 | (4350) | (28)(89) |
| $FeI_2$ | 36.8 | 39.1 | 48.1 | 59.4 | (4650) | (50)(57) |

Table 1

Free energy functions of condensed metal halides based on $H^{\circ}_{298.15}$ [a]

| Compound | $-(F^{\circ}-H^{\circ}_{298.15})/T$, cal/deg mole | | | | | $H^{\circ}_{298.15}-H^{\circ}_{0}$ kcal/mole | References |
|---|---|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500° | K | | |
| $CoF_2$ | 19.6 | 21.6 | 28.6 | 35.6 | | 2978 | (12)(43) |
| $CoCl_2$ | 26.1 | 28.4 | 37.1 | 47.0 | | (3900) | (16)(42) |
| $CoBr_2$ | (32.0) | 34.0 | 43.0 | 53.0 | | (4300) | (12) |
| $CoI_2$ | (35.0) | 37.0 | 46.0 | 56.0 | | (4600) | (12) |
| $NiF_2$ | 17.6 | 19.5 | 26.5 | 33.5 | | 2729 | (50) |
| $NiCl_2$ | 23.3 | 25.3 | 32.7 | 40.6 | | (3600) | (50) |
| $NiBr_2$ | (29.0) | 31.0 | 39.0 | 47.0 | | (4000) | |
| $NiI_2$ | (32.0) | 34.0 | 42.0 | 50.0 | | (4300) | |
| $CuF_2$ | (20.0) | 22.0 | 29.0 | | | (3000) | |
| $CuCl_2$ | 25.8 | 28.0 | 36.3 | | | (3900) | (16)(42) |
| $CuBr_2$ | (32.0) | 34.0 | 42.0 | | | (4300) | |
| $CuI_2$ | (35.0) | 37.0 | | | | (4600) | |

(a) Values in parentheses are estimated.

Table II a

Molecular constants of metal dihalides (linear model)

| Compound | r(M-X)[a] A | $\nu_1$ $cm^{-1}$ | $\nu_2$ $cm^{-1}$ | $\nu_3$ $cm^{-1}$ | k md/A | $k\delta/r^2$ md/A |
|---|---|---|---|---|---|---|
| $BeF_2$ | 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] | 0.27[b] |
| $BeBr_2$ | 1.91 | 230 | 446 | 997 | 2.5 | 0.25 |
| $BeI_2$ | 2.10 | 164 | 395 | 883 | 2.0 | 0.20 |
| $MgF_2$ | 1.77 | 535 | 479 | 858 | 3.2 | 0.50 |
| $MgCl_2$ | 2.18 | 302 | 295[b] | 597[b] | 1.9[b] | 0.23[b] |
| $MgBr_2$ | 2.34 | 179 | 220 | 491[c] | 1.5[c] | 0.15 |
| $MgI_2$ | 2.52 | 132 | 199 | 446 | 1.3 | 0.13 |
| $CaF_2$ | 2.10 | 484 | 95 | 675 | 2.62 | 0.0262 |
| $CaCl_2$ | 2.51 | 268 | 63 | 446 | 1.5 | 0.015 |
| $CaBr_2$ | 2.67 | 164 | 52 | 367 | 1.27 | 0.0127 |
| $CaI_2$ | 2.88 | 118 | 45 | 321 | 1.05 | 0.0105 |
| $SrF_2$ | 2.20 | 454 | 77 | 543 | 2.3 | 0.023 |
| $SrCl_2$ | 2.67 | 254 | 48 | 342 | 1.35 | 0.0135 |
| $SrBr_2$ | 2.82 | 156 | 37 | 262 | 1.15 | 0.0115 |
| $SrI_2$ | 3.03 | 111 | 31 | 219 | 0.92 | 0.0092 |
| $BaF_2$ | 2.32 | 439 | 70 | 496 | 2.16 | 0.0216 |
| $BaCl_2$ | 2.82 | 248 | 43 | 302 | 1.28 | 0.0128 |
| $BaBr_2$ | 2.99 | 154 | 32 | 226 | 1.11 | 0.0111 |
| $BaI_2$ | 3.20 | 109 | 26 | 184 | 0.89 | 0.0089 |

Table IIa

Molecular constants of metal dihalides (linear model)

| Compound | r(M-X)[a] A | $\nu_1$ $cm^{-1}$ | $\nu_2$ $cm^{-1}$ | $\nu_3$ $cm^{-1}$ | k md/A | $k\delta/r^2$ md/A |
|---|---|---|---|---|---|---|
| $ZnF_2$ | 1.81 | 551 | 385 | 687 | 3.4 | 0.57 |
| $ZnCl_2$ | 2.05 | 358 | 295[d] | 516[e] | 2.67[e] | 0.44[d] |
| $ZnBr_2$ | 2.21 | 222 | 225[d] | 413[e] | 2.33[e] | 0.35[d] |
| $ZnI_2$ | 2.38 | 154 | 180 | 340[e] | 1.77[e] | 0.25 |
| $CdF_2$ | 1.97 | 500 | 129 | 580 | 2.8 | 0.07 |
| $CdCl_2$ | 2.21 | 330 | 94 | 422[e] | 2.28[e] | 0.057 |
| $CdBr_2$ | 2.37 | 202[e] | 70 | 315[e] | 1.93[e] | 0.048 |
| $CdI_2$ | 2.55 | 147 | 59 | 265[e] | 1.61[e] | 0.04 |
| $HgF_2$ | 2.00 | 560 | 113 | 610 | 3.5 | 0.06 |
| $HgCl_2$ | 2.29 | 360[f] | 70[f] | 413[f] | 2.67[f] | 0.038[f] |
| $HgBr_2$ | 2.41 | 225[f] | 41[f] | 293[f] | 2.32[f] | 0.023[f] |
| $HgI_2$ | 2.59 | 156[f] | 33[f] | 237[f] | 1.83[f] | 0.018[f] |
| $TiF_2$ | 1.88 | 535 | 72 | 716 | 3.2 | 0.016 |
| $TiCl_2$ | 2.25 | 310 | 49 | 487 | 2.0 | 0.010 |
| $TiBr_2$ | 2.40 | 184 | 38 | 385 | 1.6 | 0.008 |
| $TiI_2$ | 2.59 | 137 | 34 | 344 | 1.4 | 0.007 |
| $VF_2$ | 1.76 | 535 | 70 | 706 | 3.2 | 0.016 |
| $VCl_2$ | 2.13 | 310 | 48 | 478 | 2.0 | 0.010 |
| $VBr_2$ | 2.28 | 184 | 38 | 375 | 1.6 | 0.008 |
| $VI_2$ | 2.47 | 137 | 33 | 335 | 1.4 | 0.007 |

Table IIa

Molecular constants of metal dihalides (linear model)

| Compound | r(M-X)[a] A | $\nu_1$ $cm^{-1}$ | $\nu_2$ $cm^{-1}$ | $\nu_3$ $cm^{-1}$ | k md/A | $k\delta/r^2$ md/A |
|---|---|---|---|---|---|---|
| $CrF_2$ | 1.72 | 535 | 70 | 704 | 3.2 | 0.016 |
| $CrCl_2$ | 2.09 | 310 | 48 | 475 | 2.0 | 0.010 |
| $CrBr_2$ | 2.24 | 184 | 37 | 373 | 1.6 | 0.008 |
| $CrI_2$ | 2.43 | 137 | 33 | 332 | 1.4 | 0.007 |
| $MnF_2$ | 1.72 | 535 | 70 | 696 | 3.2 | 0.016 |
| $MnCl_2$ | 2.09 | 309 | 47 | 467[g] | 1.99[g] | 0.010 |
| $MnBr_2$ | 2.24 | 184 | 30 | 365 | 1.6 | 0.008 |
| $MnI_2$ | 2.43 | 137 | 32 | 324 | 1.4 | 0.007 |
| $FeF_2$ | 1.72 | 550 | 71 | 714 | 3.4 | 0.017 |
| $FeCl_2$ | 2.09 | 327 | 49 | 492[g] | 2.23[g] | 0.0112 |
| $FeBr_2$ | 2.24 | 206 | 40 | 405 | 2.0 | 0.01 |
| $FeI_2$ | 2.43 | 150 | 35 | 355 | 1.7 | 0.0085 |
| $CoF_2$ | 1.72 | 550 | 71 | 707 | 3.4 | 0.017 |
| $CoCl_2$ | 2.09 | 332 | 49 | 493[g] | 2.3[g] | 0.0115 |
| $CoBr_2$ | 2.24 | 206 | 40 | 397[g] | 2.0[g] | 0.01 |
| $CoI_2$ | 2.43 | 150 | 35 | 348 | 1.7 | 0.0085 |
| $NiF_2$ | 1.72 | 550 | 71 | 707 | 3.4 | 0.017 |
| $NiCl_2$ | 2.09 | 346 | 51 | 515[g] | 2.5[g] | 0.0125 |
| $NiBr_2$ | 2.24 | 206 | 40 | 397 | 2.0 | 0.010 |
| $NiI_2$ | 2.43 | 150 | 35 | 348 | 1.7 | 0.0085 |

Table IIa

Molecular constants of metal dihalides (linear model)

| Compound | r(M-X)[a] Å | $\nu_1$ $cm^{-1}$ | $\nu_2$ $cm^{-1}$ | $\nu_3$ $cm^{-1}$ | k md/A | $k\delta/s^2$ md/A |
|---|---|---|---|---|---|---|
| $CuF_2$ | 1.72 | 550 | 71 | 697 | 3.4 | 0.017 |
| $CuCl_2$ | 2.09 | 340 | 50 | 496[f] | 2.43[f] | 0.0122 |
| $CuBr_2$ | 2.24 | 206 | 39 | 386 | 2.0 | 0.010 |
| $CuI_2$ | 2.43 | 150 | 34 | 338 | 1.7 | 0.0085 |

(a) The internuclear distances in the halides of the second Group elements with the exception of $HgF_2$ are from Akishin and his coworkers.[13] 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 IIb

Molecular constants of dihalides of Sn and Pb (assuming 95° bond angle)

| Compound | r(M-X)[a] Å | $\nu_1$ $cm^{-1}$ | $\nu_2$ $cm^{-1}$ | $\nu_3$ $cm^{-1}$ | k md/Å | $k\delta/\ell^2$ md/Å |
|---|---|---|---|---|---|---|
| $SnF_2$ | 2.04 | 607 | 157 | 614 | 3.6 | 0.12 |
| $SnCl_2$ | 2.40 | 398 | 102 | 406 | 2.6 | 0.0865 |
| $SnBr_2$ | 2.55 | 282 | 68 | 291 | 2.3 | 0.0765 |
| $SnI_2$ | 2.74 | 232 | 52 | 240 | 2.0 | 0.0665 |
| $PbF_2$ | 2.08 | 574 | 149 | 578 | 3.4 | 0.1135 |
| $PbCl_2$ | 2.45 | 365 | 94 | 369 | 2.4 | 0.08 |
| $PbBr_2$ | 2.60 | 247 | 59 | 251 | 2.1 | 0.07 |
| $PbI_2$ | 2.79 | 200 | 49 | 206 | 1.9 | 0.0635 |

a) The lengths of the Sn-F and Pb-F bonds have been estimated. All other bond lengths are from Sutton (51).

Table III

Comparison of free energy functions of gaseous metal dihalides obtained from second law and calculated from estimated molecular constants.[a]

| Compound | $-(F^\circ - H_{298.15})/T$ in cal/deg mole | | $T^\circ K$ |
|---|---|---|---|
| | Second law[b] | Estimated | |
| $MgF_2$ | 59.1 | 55.6 | 298.15 |
| | 73.8 | 69.7 | 2000 |
| $MgCl_2$ | 68.0 | 68.6 | 1000 |
| $CeF_2$ | 78.6 | 78.0 | 2000 |
| $SrF_2$ | (81.2) | 80.7 | 2000 |
| $ZnF_2$ | 69.7 | 69.0 | 1500 |
| $ZnCl_2$ | 64.8 | 62.2 | 298.15 |
| $ZnBr_2$ | (66.2) | 67.7 | 298.15 |
| $ZnI_2$ | (65.6) | 71.7 | 298.15 |
| $CdF_2$ | (78.2) | 78.5 | 2000 |
| $CdCl_2$ | 68.4 | 68.0 | 298.15 |
| | 77.8 | 75.4 | 1000 |
| $CdBr_2$ | 71.9 | 73.6 | 298.15 |
| | 81.6 | 81.0 | 1000 |
| $CdI_2$ | 86.4 | 84.7 | 1000 |
| $PbF_2$ | (69.4) | 69.9 | 298.15 |
| $PbCl_2$ | 83.2 | 81.8 | 1000 |
| $PbBr_2$ | 88.2 | 87.4 | 1000 |
| $PbI_2$ | 83.5 | 83.7 | 298.15 |
| | 91.0 | 90.7 | 1000 |

(a) A linear model has been assumed except for the lead halides where a bond angle of $95^\circ$ was assumed.

(b) Values in parentheses are based on estimated free energy functions for the condensed phase.

Table IV

Electronic contribution of $M^{++}$ ions

| $M^{++}$ | $-(F^{\circ}-H^{\circ}_0)/T$, cal/deg mole | | | | $H^{\circ}_{298.15}-H^{\circ}_0$ |
|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500° K | cal/mole |
| $Ti^{++}$ | 4.377 | 4.907 | 5.411 | 5.622 | 324 |
| $V^{++}$ | 4.396 | 4.990 | 5.717 | 5.999 | 410 |
| $Cr^{++}$ | 3.906 | 4.772 | 5.478 | 5.768 | 515 |
| $Mn^{++}$ | 3.561 | 3.561 | 3.561 | 3.561 | 0 |
| $Fe^{++}$ | 4.582 | 4.912 | 5.436 | 5.706 | 146 |
| $Co^{++}$ | 4.603 | 4.732 | 5.157 | 5.475 | 35 |
| $Ni^{++}$ | 4.368 | 4.420 | 4.610 | 4.847 | 4 |
| $Cu^{++}$ | 3.561 | 3.564 | 3.626 | 3.734 | 0.2 |

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 | $-(F^{\circ}-H_{298.15})/T$ in cal/deg mole | | $T^{\circ}K$ |
|---|---|---|---|
| | Second law[(a)] | Estimated | |
| $TiCl_2$ | (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 parenthesis are based on estimated free energy functions for the condensed phase.

Table VI

Free energy functions of gaseous metal dihalides based on $H^{\circ}_{298.15}$ [a]

| Compound | $-(F^{\circ}-H^{\circ}_{298.15})$ cal/deg mole | | | | | | $H^{\circ}_{298.15} - H^{\circ}_{0}$ |
|---|---|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500° | 2000° | 2500°K | kcal/mole |
| $BeF_2$ | 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 |
| $BeBr_2$ | 63.12 | 64.53 | 69.77 | 74.02 | 77.39 | | 2.755 |
| $BeI_2$ | 66.76 | 68.21 | 73.57 | 77.89 | 81.29 | | 2.892 |
| $MgF_2$ | 55.57 | 56.93 | 62.10 | 66.31 | 69.67 | 72.42 | 2.540 |
| $MgCl_2$ | 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 |
| $MgI_2$ | 71.05 | 72.66 | 78.37 | 82.84 | 86.36 | | 3.372 |
| $CaF_2$ | 62.90 | 64.[illegible] | 70.10 | 74.34 | 78.01 | 80.59 | 3.234 |
| $CaCl_2$ | 68.89 | 70.[illegible] | 76.26 | 80.72 | 84.25 | | 3.545 |
| $CaBr_2$ | 74.44 | 76.07 | 81.86 | 86.38 | 89.85 | | 3.720 |
| $CaI_2$ | 78.22 | 79.89 | 85.67 | 90.24 | 93.79 | | 3.821 |
| $SrF_2$ | 65.63 | 67.18 | 72.79 | 77.22 | 80.66 | 83.57 | 3.337 |
| $SrCl_2$ | 71.69 | 73.33 | 79.11 | 83.62 | 87.08 | | 3.660 |
| $SrBr_2$ | 77.28 | 78.97 | 84.79 | 89.37 | 92.77 | | 3.848 |
| $SrI_2$ | 81.12 | 82.81 | 88.61 | 93.17 | 96.77 | | 3.953 |
| $BaF_2$ | 67.36 | 68.95 | 74.60 | 79.03 | 82.53 | 85.37 | 3.384 |
| $BaCl_2$ | 73.48 | 75.11 | 80.90 | 85.45 | 88.95 | | 3.709 |
| $BaBr_2$ | 78.94 | 80.60 | 86.44 | 90.98 | 94.51 | | 3.896 |
| $BaI_2$ | 82.82 | 84.47 | 90.27 | 94.87 | 98.34 | | 4.004 |

Table VI

Free energy functions of gaseous metal dihalides based on $H^{\circ}_{298.15}$ [a]

| Compound | $-(F^{\circ}-H^{\circ}_{298.15})$ cal/deg mole | | | | | $H^{\circ}_{298.15} - H^{\circ}_{0}$ |
|---|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500° | 2000°K | kcal/mole |
| $ZnF_2$ | 57.90 | 59.33 | 64.65 | 68.95 | 72.35 | 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 |
| $CdF_2$ | 63.52 | 65.06 | 70.60 | 75.00 | 78.46 | 3.176 |
| $CdCl_2$ | 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 |
| $HgF_2$ | 65.28 | 66.80 | 72.30 | 76.71 | | 3.175 |
| $HgCl_2$ | 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 |
| $SnF_2$ | 67.87 | 69.27 | 74.36 | 78.43 | | 2.960 |
| $SnCl_2$ | 73.06 | 74.55 | 79.84 | 84.01 | | 3.215 |
| $SnBr_2$ | 78.37 | 79.89 | 85.28 | 89.50 | | 3.419 |
| $SnI_2$ | 81.89 | 83.43 | 88.86 | 93.08 | | 3.527 |
| $PbF_2$ | 69.86 | 71.27 | 76.40 | 80.49 | | 2.993 |
| $PbCl_2$ | 74.99 | 76.49 | 81.82 | 86.00 | | 3.269 |
| $PbBr_2$ | 80.42 | 81.96 | 87.38 | 91.59 | | 3.494 |
| $PbI_2$ | 83.72 | 85.28 | 90.72 | 94.94 | | 3.593 |

Table VI

Free energy functions of gaseous metal dihalides based on $H^{\circ}_{298.15}$ [a]

| Compound | $-(F^{\circ}-H^{\circ}_{298.15})$ cal/deg mole | | | | $H^{\circ}_{298.15} - H^{\circ}_{0}$ |
|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500°K | kcal/mole |
| $TiF_2$ | 69.12 | 70.72 | 76.37 | 80.86 | 3.580 |
| $TiCl_2$ | 74.76 | 76.47 | 82.34 | 86.90 | 3.853 |
| $TiBr_2$ | 80.56 | 82.29 | 88.21 | 92.90 | 4.050 |
| $TiI_2$ | 84.06 | 85.79 | 91.77 | 96.37 | 4.137 |
| $VF_2$ | 69.39 | 70.95 | 76.77 | 81.27 | 3.674 |
| $VCl_2$ | 75.02 | 76.67 | 82.68 | 87.31 | 3.944 |
| $VBr_2$ | 80.74 | 82.42 | 88.48 | 93.22 | 4.140 |
| $VI_2$ | 84.37 | 86.05 | 92.14 | 96.81 | 4.230 |
| $CrF_2$ | 69.20 | 70.89 | 76.59 | 81.06 | 3.779 |
| $CrCl_2$ | 74.84 | 76.61 | 82.51 | 87.10 | 4.050 |
| $CrBr_2$ | 80.65 | 82.48 | 88.45 | 93.12 | 4.250 |
| $CrI_2$ | 84.19 | 86.01 | 91.96 | 96.62 | 4.339 |
| $MnF_2$ | 67.23 | 68.75 | 74.26 | 78.62 | 3.266 |
| $MnCl_2$ | 72.95 | 74.56 | 80.24 | 84.75 | 3.543 |
| $MnBr_2$ | 78.76 | 80.39 | 86.17 | 90.66 | 3.743 |
| $MnI_2$ | 82.32 | 83.96 | 89.78 | 94.26 | 3.833 |
| $FeF_2$ | 68.66 | 70.31 | 76.16 | 80.75 | 3.400 |
| $FeCl_2$ | 74.17 | 75.91 | 81.98 | 86.64 | 3.658 |
| $FeBr_2$ | 79.51 | 81.27 | 87.38 | 92.17 | 3.831 |
| $FeI_2$ | 83.15 | 84.95 | 91.13 | 95.91 | 3.934 |

Table VI

Free energy functions of gaseous metal dihalides based on $H^{\circ}_{298.15}$ [a]

| Compound | $-(F^{\circ}-H^{\circ}_{298.15})$ cal/deg mole | | | | $H^{\circ}_{298.15}-H^{\circ}_{0}$ |
|---|---|---|---|---|---|
| | 298.15° | 500° | 1000° | 1500° K | kcal/mole |
| $CoF_2$ | 68.41 | 70.01 | 75.88 | 80.55 | 3.290 |
| $CoCl_2$ | 73.86 | 75.56 | 81.63 | 86.38 | 3.543 |
| $CoBr_2$ | 79.23 | 80.94 | 87.07 | 91.94 | 3.725 |
| $CoI_2$ | 82.86 | 84.61 | 90.81 | 95.67 | 3.828 |
| $NiF_2$ | 68.07 | 69.63 | 75.29 | 79.90 | 3.260 |
| $NiCl_2$ | 73.23 | 74.88 | 80.74 | 85.41 | 3.486 |
| $NiBr_2$ | 78.88 | 80.57 | 86.49 | 91.29 | 3.694 |
| $NiI_2$ | 82.51 | 84.24 | 90.23 | 95.02 | 3.797 |
| $CuF_2$ | 67.45 | 68.96 | 74.51 | 78.99 | 3.258 |
| $CuCl_2$ | 72.38 | 74.24 | 79.98 | 84.57 | 3.488 |
| $CuBr_2$ | 78.28 | 79.92 | 85.75 | 90.40 | 3.700 |
| $CuI_2$ | 81.91 | 83.55 | 89.42 | 94.01 | 3.803 |

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

Table VII

Thermodynamic properties of metal dihalides at 298.15°K [a]

| Compound | $\Delta H^\circ_{Subl.}$ | $\Delta H^\circ_f$(solid)[b] | $\Delta H^\circ_f$(gas) | $\Delta H^\circ_{Atom.}$(gas) | Sources for vapor pressure data |
|---|---|---|---|---|---|
| $BeF_2$ | 56.8 | -241.2[c] | -184.4 | 300.1 | (5)(45)(73)(74) |
| $BeCl_2$ | 32.0 | -118.0[d] | - 86.0 | 221.8 | (12)(60) |
| $BeBr_2$ | 31.0 | - 88.8 | - 57.8 | 189.2 | (12)(60) |
| $BeI_2$ | 30.0 | - 50.6 | - 20.6 | 150.0 | (60)(41) |
| $MgF_2$ | 87.0 | -268.0[e] | -181.0 | 254.4 | (30)(31)(65) |
| $MgCl_2$ | 52.7 | -153.2[e] | -100.5 | 194.0 | (53) |
| $MgBr_2$ | (51.0) | -123.7 | - 72.7 | (161.8) | |
| $MgI_2$ | 46.5 | - 86.0 | - 39.5 | 126.6 | (7) |
| $CaF_2$ | 102.3 | -290.3 | -188.0 | 268.0 | (65) |
| $CaCl_2$ | 71.5 | -190.0 | -118.5 | 218.6 | (88) |
| $CaBr_2$ | 66.0 | -161.3 | - 95.3 | 191.0 | (79)(88) |
| $CaI_2$ | (65.0) | -127.8 | - 62.8 | (156.0) | |
| $SrF_2$ | 101.6 | -290.3 | -188.7 | 265.2 | (65) |
| $SrCl_2$ | (71.0) | -198.0 | -127.0 | (224.0) | |
| $SrBr_2$ | 69.5 | -171.1 | -101.6 | 194.2 | (79) |
| $SrI_2$ | (65.0) | -135.5 | - 70.5 | (160.6) | |
| $BaF_2$ | 87.6 | -286.9 | -199.3 | 279.6 | (65) |
| $BaCl_2$ | 71.5 | -205.6 | -134.1 | 234.5 | (53)(88) |
| $BaBr_2$ | 71.0 | -180.4 | -109.4 | 205.4 | (79) |
| $BaI_2$ | (65.0) | -144.0 | - 79.0 | (172.5) | |

Table VII

Thermodynamic properties of metal dihalides at 298.15°K [a]

| Compound | $\Delta H^\circ_{subl}$ | $\Delta H^\circ_f(s)$ | $\Delta H^\circ_f(g)$ | $\Delta H^\circ_{Atom}(gas)$ | Sources for vapor pressure data |
|---|---|---|---|---|---|
| $ZnF_2$ | 60.7 | -(176.0)[f] | -115.3 | 184.3 | (65) |
| $ZnCl_2$ | 31.5 | - 99.6[e] | - 68.1 | 157.2 | (8)(9)(37)(53)(56)(83) |
| $ZnBr_2$ | 31.0 | - 78.4[e] | - 47.4 | 132.1 | (8)(19)(56) |
| $ZnI_2$ | 31.5 | - 49.8[e] | - 18.3 | 100.5 | (56) |
| $CdF_2$ | 76.2 | - 164.9 | - 88.7 | 153.3 | (65) |
| $CdCl_2$ | 42.6 | - 93.0 | - 50.4 | 135.0 | (2)(9)(29)(53)(56)(83) |
| $CdBr_2$ | 39.0 | - 75.8[e] | - 36.8 | 117.1 | (8)(29)(56)(84) |
| $CdI_2$ | 35.0 | - 48.4[e] | - 13.4 | 91.2 | (8)(56)(70)(84) |
| $HgF_2$ | 33.0 | -(105.0)[f] | - 72.0 | 124.5 | (56) |
| $HgCl_2$ | 20.0 | - 53.4 | - 33.4 | 105.9 | (25)(39)(41)(53)(59)(62)(70)(76)(80)(90) |
| $HgBr_2$ | 20.0 | - 40.7 | - 20.7 | 88.9 | (39)(41)(59)(63)(76)(80)(90) |
| $HgI_2$ | 21.8 | - 25.3 | - 3.5 | 69.2 | (20)(39)(41)(59)(63)(76)(80)(90) |
| $SnF_2$ | (50.0) | -(158.0)[f] | -108.0 | 217.8 | |
| $SnCl_2$ | 35.0 | - 83.6 | - 48.6 | 178.5 | (26)(53) |
| $SnBr_2$ | 34.9 | - 63.6 | - 28.7 | 154.2 | (26) |
| $SnI_2$ | 36.4 | - 34.4 | 2.0 | 121.5 | (26) |
| $PbF_2$ | 57.9 | - 158.5 | -100.6 | 185.2 | (53)(55)(88) |
| $PbCl_2$ | 43.0 | - 85.7[e] | - 42.7 | 147.4 | (2)(22)(29)(36)(53)(56)(83)(87)(88) |
| $PbBr_2$ | 40.5 | - 66.3[e] | - 25.8 | 126.2 | (8)(29)(56)(83)(87)(88) |
| $PbI_2$ | 39.6 | - 41.6[e] | - 2.0 | 100.3 | (29)(38)(56) |

Table VII

Thermodynamic properties of metal dihalides at 298.15°K [a]

| Compound | $\Delta H^\circ_{subl}$ | $\Delta H^\circ_f$(solid) | $\Delta H^\circ_f$(gas) | $\Delta H^\circ_A$(gas) | Sources for vapor pressure data |
|---|---|---|---|---|---|
| $TiCl_2$ | 63.0 | -123.0[g] | - 60.0 | 230.6 | (23) |
| $TiBr_2$ | (62.0) | - 95.0 | - 33.0 | (199.2) | |
| $TiI_2$ | 62.0 | - 66.0[g] | - 4.0 | 167.7 | (32) |
| $VCl_2$ | (63.0) | -110.0[h] | - 47.0 | (227.7) | |
| $VBr_2$ | (62.0) | - 82.0[f] | - 20.0 | (196.3) | |
| $VI_2$ | (60.0) | - 53.0[f] | 7.0 | (166.8) | |
| $CrF_2$ | (85.0) | -181.0 | - 96.0 | (228.8) | |
| $CrCl_2$ | 64.8 | - 97.0 | - 32.2 | 185.2 | (21)(72) |
| $CrBr_2$ | 63.3 | - 70.0[f] | - 6.7 | 155.2 | (72)(78) |
| $CrI_2$ | 61.3 | - 37.8[i] | 23.5 | 123.0 | (1)(7) |
| $MnF_2$ | (75.0) | -190.0 | -115.0 | (220.0) | |
| $MnCl_2$ | 54.5 | -115.2 | - 60.7 | 185.8 | (53)(66)(72) |
| $MnBr_2$ | 52.5 | - 90.7 | - 38.2 | 158.9 | (72) |
| $MnI_2$ | 49.3 | - 59.3 | - 10.0 | 128.7 | (7) |
| $FeF_2$ | (75.0) | -168.0 | - 93.0 | (230.3) | |
| $FeCl_2$ | 52.0 | - 81.9[e] | - 29.9 | 187.3 | (6)(53)(66)(77) |
| $FeBr_2$ | 48.8 | - 60.0 | - 11.2 | 164.2 | (51)(77) |
| $FeI_2$ | 47.4 | - 30.0 | 17.4 | 133.1 | (7)(67)(72)(77) |

Table VII

Thermodynamic properties of metal dihalides at 298.15°K [a]

| Compound | $\Delta H^{\circ}_{subl}$ | $\Delta H^{\circ}_{f}$(solid) | $\Delta H^{\circ}_{f}$(gas) | $\Delta H^{\circ}_{A}$(gas) | Sources for vapor pressure data |
|---|---|---|---|---|---|
| $CoF_2$ | (75.0) | -159.0 | -84.0 | (223.4) | |
| $CoCl_2$ | 54.6 | - 75.0 | -20.4 | 179.9 | (53)(66)(72) |
| $CoBr_2$ | 53.1 | - 55.5 | - 2.4 | 157.5 | (72) |
| $CoI_2$ | (50.0) | - 24.4 | -25.6 | (127.5) | |
| $NiF_2$ | 78.5 | -158.0 | -79.5 | 220.1 | (24) |
| $NiCl_2$ | 58.7 | - 73.0 | -14.3 | 175.0 | (53)(66) |
| $NiBr_2$ | 57.3 | - 52.0 | 5.3 | 151.0 | (68) |
| $NiI_2$ | 53.0 | - 22.0[f] | 21.0 | 122.8 | (69) |
| $CuF_2$ | (66.0) | -126.9 | -60.9 | (179.8) | |
| $CuCl_2$ | 47.8 | - 49.2 | - 1.4 | 140.4 | (82) |
| $CuBr_2$ | (45.0) | - 33.2 | 11.8 | (122.8) | |

(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 (10).

(g) From Kelley and Mah (44).

(h) From Shchukarev, Oranskaya, Tolmacheva and Il'inski (75).

(i) From Gregory and Burton (27).

Table VIII

$\Delta H^{\circ}_{298.15}$ [a] in kcal/mole for $MX_2(g) = M^{++}(g) + 2X^{-}(g)$

| M | $MF_2$ | $MCl_2$ | $MBr_2$ | $MI_2$ |
|---|---|---|---|---|
| Be | 774 | 687 | 665 | 641 |
| Mg | 616 | 546 | (524) | 506 |
| Ca | 521 | 463 | 445 | (427) |
| Sr | 490 | (439) | 419 | (402) |
| Ba | 469 | 415 | 396 | (379) |
| Zn | 654 | 617 | 602 | 587 |
| Cd | 589 | 562 | 554 | 544 |
| Hg | (636) | 608 | 601 | 598 |
| Sn | (563) | 515 | 500 | 484 |
| Pb | 542 | 494 | 483 | 474 |
| Ti | (574) | 530 | (509) | 494 |
| V | (590) | (550) | (529) | (516) |
| Cr | (604) | 551 | 531 | 515 |
| Mn | (591) | 547 | 531 | 517 |
| Fe | (624) | 571 | 558 | 544 |
| Co | (637) | 584 | 572 | (558) |
| Ni | (653) | 599 | 585 | 573 |
| Cu | (665) | 616 | (608) | (593) |

(a) Values in parentheses are estimated.

Table IX

Comparison of the experimental heats of ionization of gaseous metal dihalides with those calculated on the basis of empirical potential functions.

| Compound | $\Delta H_0^o$ in kcal/mole for $MX_2(g) = M^{++}(g) + 2X^-(g)$ | | |
|---|---|---|---|
| | Experimental[a] | Calc.[b] | Calc.[c] |
| $BeF_2$ | 771 | 748 | 662 |
| $BeCl_2$ | 685 | 707 | 623 |
| $BeBr_2$ | 664 | 675 | 606 |
| $BeI_2$ | 640 | 624 | 565 |
| $MgF_2$ | 614 | 591 | 560 |
| $MgCl_2$ | 545 | 533 | 511 |
| $MgBr_2$ | (523) | 513 | 490 |
| $MgI_2$ | 506 | 500 | 473 |
| $CaF_2$ | 519 | 502 | 484 |
| $CaCl_2$ | 462 | 455 | 442 |
| $CaBr_2$ | 445 | 438 | 426 |
| $CaI_2$ | (427) | 425 | 409 |
| $SrF_2$ | 489 | 482 | 465 |
| $SrCl_2$ | (439) | 427 | 416 |
| $SrBr_2$ | 419 | 413 | 402 |
| $SrI_2$ | (402) | 400 | 386 |
| $BaF_2$ | 468 | 463 | 445 |
| $BaCl_2$ | 415 | 404 | 393 |
| $BaBr_2$ | 396 | 389 | 377 |
| $BaI_2$ | (379) | 377 | 363 |

(a) Values in parentheses are based on estimated $\Delta H$ of atomization values from Table VII.

(b) Values calculated by Cubicciotti (18) based on a potential function which has an overlap repulsion term of the type : $Ar^{-n}$.

(c) Values calculated by Cubicciotti (18) based on a potential function which has an overlap repulsion term of the type: $A \exp(-r/\rho)$.

Table X

Constants for vaporization equations (1) and (2)

| Compound [a] | $\Delta H_I$ cal/mole | $-\Delta$ a | $-\Delta$ b | I | Temp. range ($^{\circ}$K) |
|---|---|---|---|---|---|
| | | | cal/deg mole | | |
| $BeF_2$(s) | 55,520 | | | 39.88 | 846-950 |
| $BeF_2$(l) | 58,330 | (7.0) | | 91.2 | 1075-1300 |
| $BeCl_2$(s) | 29,510 | | | 39.14 | 613-678 |
| $BeCl_2$(l) | 33,460 | (7.0) | | 43.63 | 678-733 |
| $BeBr_2$(s) | 29,930 | | | 40.06 | 624-695 |
| $BeI_2$(s) | 27,410 | | | 36.07 | 578-703 |
| $MgF_2$(s) [b] | 95,450 | 2.13 | 2.52 | 61.63 | 1137-1536 |
| $MgF_2$(l) | 85,220 | 7.8 | | 94.57 | 1934-2129 |
| $MgCl_2$(l) | 46,230 | 7.35 | | 82.00 | 1056-1400 |
| $MgI_2$(l) | 45,950 | (7.0) | | 85.75 | 1000-1200 |
| $CaF_2$(l) | 100,000 | 9.05 | | 107.7 | 2086-2208 |
| $SrF_2$(l) | 100,000 | (10.0) | | 115.4 | 2095-2232 |
| $BaF_2$(l) | 103,500 | (10.0) | | 120.5 | 1960-2206 |
| $BaCl_2$(l) | 75,000 | (10.0) | | 114.6 | 1343-1487 |
| $ZnF_2$(l) | 60,000 | (9.0) | | 101.1 | 1429-1738 |
| $ZnCl_2$(s) | 35,920 | 0.5 | 10.85 | 44.75 | 543-593 |
| $ZnCl_2$(l) | 34,480 | (10.0) | | 102.47 | 779-1034 |
| $ZnBr_2$(s) | 31,840 | 0.35 | 8.9 | 38.7 | 513-583 |
| $ZnBr_2$(l) | 28,340 | | | 30.5 | 701-922 |
| $ZnI_2$(s) | 29,000 | 0.2 | 9.9 | 34.98 | 493-553 |
| $CdF_2$(l) | 72,730 | (9.0) | | 104.55 | 1638-2023 |
| $CdCl_2$(s) | 44,400 | 0.11 | 10.18 | 44.55 | 643-753 |
| $CdCl_2$(l) | 44,030 | 11.6 | | 118.13 | 1001-1240 |
| $CdBr_2$(s) | 40,500 | 1.27 | 7.55 | 49.44 | 593-683 |
| $CdBr_2$(l) | 36,770 | 9.5 | | 99.48 | 841-998 |
| $CdI_2$(l) | 35,630 | 9.6 | | 101.47 | 773-928 |

Table X

Constants for vaporization equations (1) and (2)

| Compound [a] | $\Delta H_I$ cal/mole | $-\Delta a$ | $-\Delta b$ cal/deg mole | I | Temp. range (°K) |
|---|---|---|---|---|---|
| $HgCl_2(s)$ | 20,770 | 1.3 | 10.3 | 45.57 | 273-553 |
| $HgCl_2(l)$ | 19,850 | (10.0) | | 97.9 | 553-577 |
| $HgBr_2(s)$ | 20,590 | -0.1 | 13.8 | 39.26 | 273-511 |
| $HgBr_2(l)$ | 20,000 | (10.0) | | 97.54 | 511-592 |
| $HgI_2(\alpha)$ | 22,960 | 3.41 | 4.0 | 61.93 | 273-403 |
| $HgI_2(\beta)$ | 23,150 | 6.2 | | 78.4 | 403-524 |
| $HgI_2(l)$ | 21,160 | (11.0) | | 104.51 | 524-627 |
| $SnCl_2(l)$ | 29,170 | (12.0) | | 113.25 | 715-907 |
| $SnBr_2(l)$ | 32,810 | (10.0) | | 104.14 | 729-884 |
| $SnI_2(l)$ | 33,330 | (10.0) | | 102.66 | 711-956 |
| $PbF_2(s)$ | 58,700 | 2.85 | 4.1 | 64.7 | 792-988 |
| $PbF_2(l)$ | 54,000 | (10.0) | | 107.96 | 1351-1562 |
| $PbCl_2(s)$ | 46,650 | | | 43.93 | 653-733 |
| $PbCl_2(l)$ | 45,800 | 13.2 | | 131.22 | 771-1227 |
| $PbBr_2(s)$ | 31,590 | | | 24.22 | 603-633 |
| $PbBr_2(l)$ | 43,310 | 13.7 | | 133.44 | 1008-1189 |
| $PbI_2(s)$ | 41,380 | 4.1 | 4.7 | 70.55 | 579-650 |
| $PbI_2(l)$ | 42,860 | 18.5 | | 167.36 | 923-1073 |
| $TiCl_2(s)$ | 52,600 | 1.25 | 4.52 | 47.0 | 793-893 |
| $TiI_2(s)$ | 50,000 | 5.23 | 1.74 | 70.8 | 750-900 |
| $CrCl_2(s)$ | 63,640 | 0.43 | 5.3 | 50.05 | 998-1088 |
| $CrCl_2(l)$ | 61.540 | (10.0) | | 112.37 | 1088-1270 |
| $CrBr_2(s)$ | 55,100 | | | 37.4 | 837-1083 |
| $CrI_2(s)$ | 63,330 | (5.0) | | 82.3 | 1045-1123 |
| $CrI_2(l)$ | 59,890 | (10.0) | | 114.38 | 1123-1260 |

Table X

Constants for vaporization equations (1) and (2)

| Compound [a] | $\Delta H_I$ cal/mole | $-\Delta a$ | $-\Delta b$ cal/deg mole | I | Temp. range (°K) |
|---|---|---|---|---|---|
| $MnCl_2(l)$ | 47,580 | 7.83 | | 88.93 | 999-1216 |
| $MnI_2(l)$ | 47,620 | (9.0) | | 100.4 | 1000-1200 |
| $FeCl_2(s)$ [c] | 50,390 | 4.14 | 2.08 | 72.77 | 670-740 |
| $FeCl_2(l)$ | 42,330 | 9.6 | | 101.6 | 981-1107 |
| $FeBr_2$ | 50,280 | 2.8 | 5.32 | 65.9 | 670-740 |
| $FeI_2(s)$ | 48,440 | 5.03 | 0.58 | 79.4 | 670-740 |
| $FeI_2(l)$ | 38,910 | 9.55 | | 100.1 | 874-959 |
| $CoCl_2(s)$ | 55,560 | -0.34 | 14.6 | 51.28 | 925-1000 |
| $NiF_2(s)$ | 59,940 | | | 31.11 | 1026-1349 |
| $NiCl_2(s)$ [d] | 59,100 | 2.75 | 3.16 | 68.9 | 973-1056 |
| $NiBr_2(s)$ | 60,000 | (2.75) | (3.16) | 71.0 | 1073-1191 |
| $CuCl_2(s)$ | 46,880 | 0.72 | 12.0 | 54.44 | 773-893 |

(a) Values in parentheses are assumed.

(b) $\Delta c = 2.2 \times 10^{-5}$ for this compound.

(c) $\Delta c = 1.17 \times 10^{-5}$ for this compound.

(d) $\Delta c = 1.19 \times 10^{-5}$ for this compound.

Table XI

Fusion and vaporization data for metal dihalides [a]

| Compound | $\Delta H^\circ_m$ kcal/mole | $\Delta S^\circ_m$ cal/deg mole | $T_m$ °K | T°K at pressures of $10^{-6}$ | $10^{-4}$ | $10^{-2}$ | 1 atm. |
|---|---|---|---|---|---|---|---|
| $BeF_2$ | | | 1070 | 819 | 954 | 1148 | 1456 |
| $BeCl_2$ [b] | | | 678 | 443 | 514 | 611 | 760 |
| $BeBr_2$ [b] | | | 761 | 443 | 513 | 608 | 747 |
| $BeI_2$ [b] | | | 753 | 431.5 | 504 | 606.5 | 760 |
| $MgF_2$ | 13.9 | 9.05 | 1536 | 1323 | 1529 | 1900 | 2550 |
| $MgCl_2$ | 10.3 | 10.44 | 987 | 800 | 937 | 1168 | |
| $MgBr_2$ | | | 984 | | (901) | (1117) | |
| $MgI_2$ | | | 923 | | | 976 | 1308 |
| $CaF_2$ | 7.1 | 4.2 | 1691 | | 1705 | 2101 | 2785 |
| $CaCl_2$ | 6.78 | 6.42 | 1055 | 1073 | 1276 | 1601 | |
| $CaBr_2$ | | | 1033 | 990 | 1180 | 1476 | |
| $CaI_2$ | | | 1013 | (965) | (1140) | | |
| $SrF_2$ | | | 1673 | | 1683 | 2077 | 2768 |
| $SrCl_2$ | (8.0) | (7.0) | 1145 | (1056) | (1252) | | |
| $SrBr_2$ | (6.48) | (7.0) | 926 | 1040 | 1234 | | |
| $SrI_2$ | (4.72) | (6.0) | 788 | (960) | (1129) | | |
| $BaF_2$ | (6.37) | (4.0) | 1593 | | 1512 | 1882 | |
| $BaCl_2$ | (8.65) | (7.0) | 1235 | | 1273 | 1575 | |
| $BaBr_2$ | | | 1120 | 1090 | 1298 | | |
| $BaI_2$ | | | 984 | (975) | (1151) | | |

Table XI

Fusion and vaporization data for metal dihalides [a]

| Compound | $\Delta H^{\circ}_m$ kcal/mole | $\Delta S^{\circ}_m$ cal/deg mole | $T_m$ °K | T°K at pressures of $10^{-6}$ | $10^{-4}$ | $10^{-2}$ | 1 atm. |
|---|---|---|---|---|---|---|---|
| $ZnF_2$ | (6.87) | (6.0) | 1145 | | | 1315 | 1777 |
| $ZnCl_2$ | (5.5) | (9.31) | 591 | 543 | 609 | | |
| $ZnBr_2$ | (4.0) | (6.0) | 667 | 516 | 612 | 715 | 929 |
| $ZnI_2$ | (4.5) | (6.26) | 719 | 492.4 | 588.5 | | |
| $CdF_2$ | | | 1383 | | | 1525 | 2015 |
| $CdCl_2$ | 7.22 | 8.58 | 842 | 653 | 762 | 914 | 1240 |
| $CdBr_2$ | 7.57 | 9.48 | 841 | 585 | 686 | 836 | |
| $CdI_2$ | 4.95 | 7.49 | 661 | | | 739 | 1017 |
| $HgF_2$ | | | 918 | | | | 920 |
| $HgCl_2$ | 4.64 | | 553 | 315 | 369 | 447 | 577 |
| $HgBr_2$ | | | 511 | 316 | 371 | 444 | 592 |
| $HgI_2$ | | | 523 | 333 | 389 | 470 | 627 |
| $SnF_2$ | | | >900 | | | | |
| $SnCl_2$ | | | 500 | | 515.5 | 654.5 | 938 |
| $SnBr_2$ | | | 505 | | 553.5 | 683 | 912 |
| $SnI_2$ | | | 593 | | | 612.5 | 990 |
| $PbF_2$ | 5.54 | 5.04 | 1097 | 823 | 954.5 | 1160 | 1572 |
| $PbCl_2$ | 5.8 | 7.52 | 771 | 653.5 | 749.6 | 908 | 1227 |
| $PbBr_2$ | 4.43 | 6.89 | 643 | 611 | 698.5 | 868.5 | 1189 |
| $PbI_2$ | 6.01 | 8.77 | 685 | 587 | 684 | 817 | 1170 |

Table XI

Fusion and vaporization data for metal dihalides [a]

| Compound | $\Delta H_m^\circ$ kcal/mole | $\Delta S_m^\circ$ cal/deg mole | $T_m$ °K | T°K at pressures of $10^{-6}$ | $10^{-4}$ | $10^{-2}$ | 1 atm. |
|---|---|---|---|---|---|---|---|
| $TiCl_2$ | | | >1200 | 822 | 938 | | |
| $TiBr_2$ | | | >1200 | (805) | (919) | | |
| $TiI_2$ | | | >1200 | 806 | 922 | | |
| $VCl_2$ | | | >1273 | (806) | (917) | (1073) | |
| $VBr_2$ | | | (1100) | (798) | (910) | | |
| $VI_2$ | | | (1050) | (765) | (871) | | |
| $CrF_2$ | | | 1375 | (1179) | (1371) | | |
| $CrCl_2$ | (9.4) | (8.64) | 1088 | 881 | 1013 | 1217 | |
| $CrBr_2$ | | | 1115 | 849.5 | 989 | | |
| $CrI_2$ | (9.0) | (8.0) | 1123 | 827 | 950.5 | 1130 | 1421 |
| $MnF_2$ | (5.5) | (4.87) | 1129 | (1068) | (1249) | (1515) | |
| $MnCl_2$ | 8.97 | 9.72 | 923 | 776 | 901 | 1093 | 1465 |
| $MnBr_2$ | (7.0) | (7.21) | 971 | 737 | 852 | 1016 | |
| $MnI_2$ | (6.5) | (7.14) | 911 | 704 | 822 | 995 | |
| $FeF_2$ | | | 1375 | (1017) | (1175) | | |
| $FeCl_2$ | 10.28 | 10.92 | 950 | 728 | 836 | 987 | 1277 |
| $FeBr_2$ | (10.1) | (10.5) | 962 | 686.5 | 793 | 943 | 1247 |
| $FeI_2$ | (10.0) | (11.62) | 860 | 654 | 755 | 873 | 1202 |

Table XI

Fusion and vaporization data for metal dihalides [a]

| Compound | $\Delta H_m^\circ$ kcal/mole | $\Delta S_m^\circ$ cal/deg mole | $T_m$ °K | T°K at pressures of $10^{-6}$ | $10^{-4}$ | $10^{-2}$ | 1 atm. |
|---|---|---|---|---|---|---|---|
| $CoF_2$ | | | 1475 | (1003) | (1157) | (1370) | |
| $CoCl_2$ | (11.0) | (11.0) | 1000 | 737 | 848 | 1003 | |
| $CoBr_2$ | | | 951 | 727 | 839 | | |
| $CoI_2$ | | | 790 | (675) | (778) | | |
| $NiF_2$ | | | >1365 | 1032 | 1185 | 1400 | |
| $NiCl_2$ | 18.47 | 14.18 | 1303 | 768 | 879 | 1030 | 1247 |
| $NiBr_2$ | | | 1236 | 753 | 856 | 998 | 1192 |
| $NiI_2$ | | | 1070 | 690 | 787 | 919 | |
| $CuCl_2$ | | | d .800 | 639 | 738 | 877 | |

(a) Values in parentheses are assumed.

(b) Pressures given are total pressures including polymers.

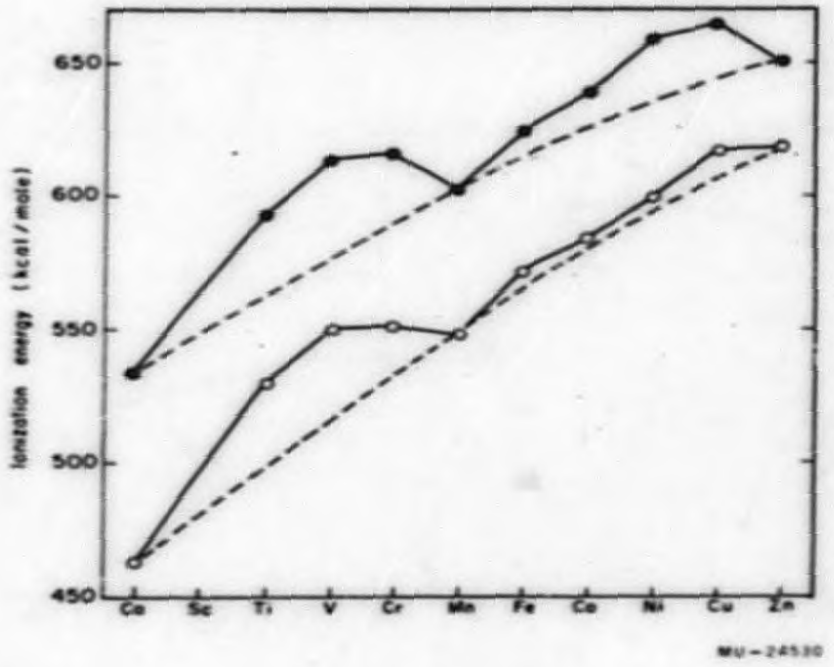


Fig. 1. (●) $\Delta H^{\circ}_{298.15}$ in kcal/mole for $MCl_2(s) = M^{++}(g) + 2Cl^{-}(g)$
(○) $\Delta H^{\circ}_{298.15}$ in kcal/mole for $MCl_2(g) = M^{++}(g) + 2Cl^{-}(g)$.

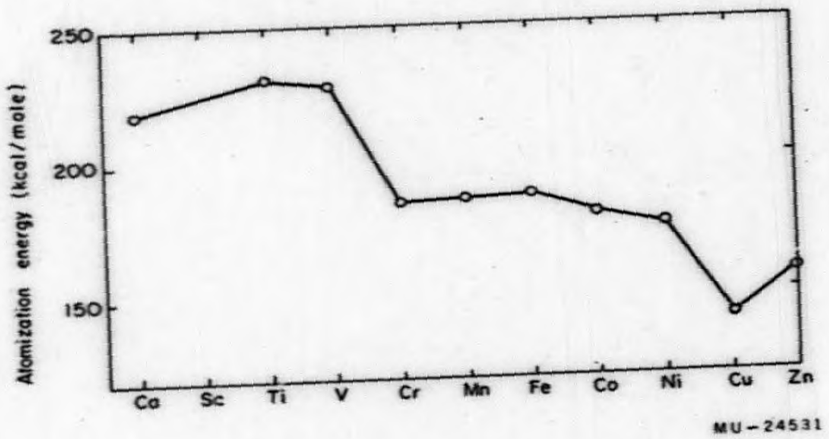


Fig. 2. $\Delta H^{\circ}_{298.15}$ in kcal/mole for $MCl_2(g) = M(g) + 2\ Cl(g)$.

END