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MASS SPECTROMETRIC STUDIES OF INORGANIC VAPORS

David Hoover Feather
(Ph.D. Thesis)

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MASS SPECTROMETRIC STUDIES OF INORGANIC VAPORS

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ABSTRACT

Knudsen cell mass spectrometry was employed in separate studies of the vapors in equilibrium with two inorganic halide solids-sodium chloride and gallium trifluoride.

Simultaneous measurements of the ion intensities attributable to NaCl(g) and Na_3Cl_3(g) as functions of temperature yielded vaporization data for the monomer that are in good agreement with the average of eight previous investigations. These monomer data were used for purposes of pressure calibration and the resulting enthalpy and entropy of sublimation for the trimer at 937°K are 62.2 ± 3 kcal/mole and 30.5 ± 3 eu/mole, respectively. The measured enthalpy for the trimer agrees well with the prediction made by applying a normalization factor to the ionic model calculations of Milne and Cubicciotti. In addition to the trimer, ions attributable to Na_4Cl_4(g) were observed for the first time. Since their low relative concentration prevented measurements of the partial vapor pressure of the tetramer as a function of temperature, the ionic model was extended to this molecule to calculate an enthalpy of sublimation at 1000°K of 70.9 kcal/mole. Combining this calculated enthalpy with a single partial vapor pressure measurement for the tetramer gives an entropy of sublimation of 29.5 eu/mole.

Two molecules were observed in the vapor in equilibrium with solid gallium trifluoride-$GaF_3(g)$ and $Ga_2F_6(g)$. The relative partial vapor pressures as functions of temperature were measured using a mass spectrometer and pressure calibration was achieved by using the torsion-effusion method. The enthalpy and entropy of sublimation of the monomer at 298°K are 58.8 ± 3 kcal/mole and 44.6 ± 3 eu/mole. The enthalpy and entropy of sublimation of the dimer at 914°K are 71.0 ± 4 kcal/mole and 42.8 ± 4 eu/mole, respectively.

GENERAL INTRODUCTION

The accumulation of thermodynamic data for gaseous monomers and polymers in equilibrium with their condensed phases is important for both practical and theoretical reasons. The practical importance of these data is that they can be used to predict the minimum life expectancies of objects fabricated from these condensed phases at high temperatures by using the Hertz-Knudsen* equation:

$$J_{max}\,(\text{moles/cm}^2\text{-sec}) = 44.33 \sum_{i=1}^{n} \frac{X_i\, e^{-\frac{\Delta F_T^{o}i}{RT}}}{(M_i T)^{1/2}}$$

where J_{max} is the total flux assessed as monomers leaving the surface of the object, X_i is the degree of polymerization of the ith specie, $\Delta F_T^{o}i$ is the free energy of sublimation of the ith specie, M_i $(\frac{\text{grams}}{\text{mole}})$ is the molecular weight of the ith specie, R is the gas constant and T is the absolute temperature.

These data are theoretically important since the measured enthalpies of polymerization can be used to test the validity of various bonding models and schemes which purport to describe gas phase equilibria. The verification of the applicability of these models provides a basis for predicting the gas phase properties of heretofore unstudied systems, thereby reducing or even eliminating the need for investigating these systems experimentally.

*J. L. Margrave, Ed., The Characterization of High Temperature Vapors, (John Wiley and Sons, Inc., New York, N.Y., 1967) p.33.

The mass spectrometric technique is well suited to investigations of complex vapors since it permits measurements of the relative partial vapor pressure of each gaseous specie as a function of temperature. The mass spectrometer used in this laboratory is a flow through device and the measured ion currents are related to the partial vapor pressures through the equation**:

$$P_i = K_i \, I_i^+ T$$

where P_i is the partial vapor pressure of the ith specie, K_i is a proportionality constant for the ith specie, I_i^+ is the measured ion current of the ith specie and T is the absolute temperature. Hence, if an observed ion can be shown to be the product of electron impact of a particular neutral molecule, then a plot of $\ln I^+T$ vs. $1/T$ yields and nearly straight line ($\Delta Cp \simeq 0$) whose slope is the enthalpy of sublimation of the molecule. Additional experiments and/or data are required to obtain the proportionality constant, K_i, which is needed to obtain the accompanying entropy of sublimation for the molecule.

The following report presents the results of applying the mass spectrometric technique to two different inorganic compounds. Part I of the report is devoted to the study of the trimer and tetramer in equilibrium with solid sodium chloride. Part II is devoted the study of the gaseous species in equilibrium with solid gallium trifluoride.

** J. L. Margrave, Ed., The Characterization of High Temperature Vapors, (John Wiley and Sons, Inc., New York, N.Y., 1967), Chap. 8.

PART I.

THE STABILITIES OF GASEOUS SODIUM CHLORIDE TRIMERS AND TETRAMERS

I. INTRODUCTION

Good thermochemical data are available for gaseous alkali halide monomers and dimers in equilibrium with their condensed phases,[1,2] while data for trimers and higher polymers are scant. It is of interest, therefore, to obtain as accurate data as possible for these higher polymers, not only for their intrinsic value, but to allow comparison with ionic models[3-7] which work well for predicting the stabilities of gaseous alkali halide monomers and dimers.

We have used a mass spectrometer to measure the enthalpy and entropy for the reaction $3NaCl(s) = Na_3Cl_3(g)$ and have obtained the first intensity measurement for the $Na_4Cl_4(g)$ molecule. The value of the enthalpy of dissociation of the trimer to a monomer and a dimer calculated by Milne and Cubicciotti[4] from an ionic model is compared to the experimental data and their model is extended to tetrameric molecules to permit the calculation of thermodynamic data for Na_4Cl_4 from the measured concentration.

II. EXPERIMENTAL

This study was carried out with a 60° sector, 24 cm radius, Atlas mass spectrometer. The apparatus is a magnetic deflection device and is equipped with a 16-stage, Cu-Be, electron multiplier for use as an ion current detector. Reagent grade sodium chloride was purchased from the J. T. Baker Chemical Co. The only spectroscopically detectable impurities were .001% Ca and .0005% Mg.

All effusion experiments were carried out in copper Knudsen cells. Temperatures were measured with a chromel-alumel thermocouple which had been previously calibrated at the freezing point of aluminum. The thermocouple was securely clamped inside a hole drilled in the bottom of the cell. The cell was heated by radiation from a tungsten filament which was inside copper-clad tantalum heat shields.

Experiments were performed using copper cell lids with two different orifice sizes in order to be sure that equilibrium had been achieved. Orifice diameters were .034 cm and .100 cm while channel lengths were .017 cm and .100 cm, respectively.

Preliminary experiments indicated that ion intensities associated with the trimer decreased below the equilibrium values when the mean free path to diameter ratio (λ/D), as calculated by the hard sphere approximation,[8] fell below ~ 1.7. It is interesting to note that, over the same temperature range, the ion intensities associated with the monomer were unaffected. Similar behavior has since been observed in a mass spectrometric study of cerium trifluoride vaporization.[9] More recently, Meschi[10] has examined this effect theoretically and has shown that it is a consequence of monomer-polymer collisions within the

molecular beam at high pressures. In order to minimize errors resulting from these intra-beam collisions, all subsequent trimer data were taken with $\lambda/D > 1.7$ to insure that molecular flow conditions prevailed.

Ion intensities corresponding to Na^+, $NaCl^+$, Na_2Cl^+, $Na_3Cl_2^+$, and $Na_4Cl_3^+$ were observed and identified by means of the background spectra and their isotopic abundances. A fragmentation pattern at 968°K with 70 eV ionizing electrons is reported in Table 1 where the ion intensities relative to Na^+ have been corrected for isotopic abundances. No ions attributable to products of reaction with the cell were observed.

Na^+, Na_2Cl^+, and $Na_3Cl_2^+$ are the principal ion fragments arising from electron impact with NaCl(g), Na_2Cl_2(g), and Na_3Cl_3(g), respectively.[11-13] $Na_4Cl_3^+$ is the expected principal product of Na_4Cl_4(g) ionization. It has been suggested by Milne and Klein[13] that $NaCl^+$ may originate partly from a polymer in addition to the monomer. Higher polymers than the dimer are improbable sources of a significant fraction of the observed $NaCl^+$ ion intensities because the higher polymers are present at low concentrations. If $NaCl^+$ were the product of dissociative ionization of Na_2Cl_2(g), the $Na^+/NaCl^+$ ratio would decrease by ~ 35% in going from 870°K to 1020°K. The results of two consecutive measurements of the temperature dependence of the $Na^+/NaCl^+$ ratio (Fig. 1), however, indicate that the intensity ratio is constant between 870°K and 1020°K. We conclude, as Berkowitz, Tasman, and Chupka[14] did for the LiCl, LiBr, and LiI systems, that simple ionization of NaCl(g) is the major source of the observed $NaCl^+$ ion intensities.

It should be pointed out that the relative proportion of Na^+ to $NaCl^+$ ion was observed to vary, depending on which mass peak we chose to maximize our ion intensities. This effect is apparent when the

data in Table 1 are compared to the intensity ratio data in Fig. 1. The data in Fig. 1 are particularly significant since they are the results of consecutive runs in which only the beam focusing voltages were altered. Unusual M^+ vs. MX^+ ion intensity ratio variations have been noted by Berkowitz et al.[14] for the LiF system. They attributed the behavior to the formation of Li^+ fragments with excess kinetic energy.

The intensities of the Na^+ and $Na_3Cl_2^+$ ions were followed as functions of temperature using 70 eV ionizing electrons. Temperatures were varied upwards and then downwards to minimize temperature dependent errors and approximately 20 minutes were allowed between datum points to insure that equilibrium had been achieved.

The electron multiplier gain of $Na_3Cl_2^+$ ion was assumed to be equal to that for Na^+ ion.[15,16] The additivity rule of Otvos and Stevenson[17] was used to estimate an ionization cross section of 3.0 for the trimer relative to the total cross section of the monomer. It was assumed the total cross section of NaCl(g) remains constant relative to the polymer species while the $Na^+/NaCl^+$ ratio can vary. Since Na^+ comprises ~ 66% of the total number of Na^+ and $NaCl^+$ ions produced by electron impact of neutral NaCl(g) (Table 1), we estimate the ionization cross section of the trimer for $Na_3Cl_2^+$ production relative to that of the monomer for Na^+ production to be 4.5. The appearance potential of $Na_3Cl_2^+$, measured by the method of extrapolated differences[18] from Hg^+, is 9.9 ± .5 eV.

III. RESULTS AND DISCUSSION

Nine series of measurements for the monomer and eight for the trimer were performed to measure the temperature dependences of the respective ion intensities. The data presented in Fig. 2 are the results of the best two mass spectrometer measurement series. The arithmetic average of the calculated enthalpies from all monomer and trimer data agree to within .05 kcal with the enthalpies calculated from the data in Fig. 2.

The ln I^+T vs. 1/T plots for Na^+ ion from cells with .034 cm and .1 cm orifices were made to coincide at 937°K, the midpoint of the experimental temperature range. All Na^+ data were then normalized to agree with the pressure accepted in the JANAF[1] tables for the monomer at 937°K.

An arithmetic average of the least square analyses of all nine monomer measurement series gives a second law enthalpy of sublimation at 937°K of 51.5 ± .8 kcal/mole where the reported error is the average deviation from the mean. The value accepted by JANAF at the same temperature is 52.0 kcal/mole. The good agreement between the experimental and accepted values indicates that temperature dependent errors were small during the experiments.

The enthalpy and entropy of sublimation for $Na_3Cl_3(g)$ at 937°K were calculated from the average of the least square fits of the data to be 62.2 ± 2.3 kcal/mole of trimer and 30.5 ± 2.3 eu/mole of trimer, respectively. The value for the enthalpy of sublimation for the trimer is only in fair agreement with the second law value of 71.3 kcal/mole at 1002°K reported by Akishin, Gorokhov, and Sidorov.[19]

Combining the enthalpy and entropy of sublimation for the trimer with the corresponding JANAF data for the monomer at 937°K, we calculate the enthalpy and entropy of trimerization to be -93.8 ± 2.3 kcal/mole and -67.7 ± 2.3 eu/mole, respectively. This entropy is consistent with the entropies reported by JANAF at 937°K for the corresponding gaseous reactions in the LiF(g) and LiCl(g) systems-- -70.5 eu and -69.2 eu, respectively.

It is of interest to compare the experimental enthalpy of sublimation for $Na_3Cl_3(g)$ with the enthalpy predicted from the ionic model calculations of Milne and Cubicciotti.[3,4] Table 2 presents their calculated enthalpies at 0°K for the reaction $M_2X_2(g) = 2MX(g)$ where their estimated differences in zero point energies have been neglected. Table 3 lists the results of Milne and Cubicciotti's[4] calculations for dissociation of a trimer into a monomer and dimer. A comparison of the ΔH_0° (calc.)/ΔH_0° (exp.) ratios for the same alkali halide in Tables 2 and 3 indicates that they are the same within the implicit experimental errors. Following this approach, we have divided the calculated enthalpy for the reaction $Na_3Cl_3(g) = NaCl(g) + Na_2Cl_2(g)$ by 1.10 to give a predicted enthalpy at 0°K of 45.5 kcal/mole of trimer. Neglecting the small difference in $\Delta H^\circ_{1000}-\Delta H_0^\circ$ (Table 3) and combining this result with the JANAF enthalpies of formation at 1000°K for the monomer, dimer and condensed NaCl, we calculate a predicted enthalpy of sublimation for the trimer of 62.0 kcal/mole. This result is in good agreement with the value of 62.2 ± 2.3 kcal/mole obtained experimentally.

Our measured $Na_4Cl_3^+$ ion intensities were too low to permit experimental determination of the enthalpy of sublimation, but the data were used to calculate thermodynamic data by extending the ionic model of Milne and Cubicciotti to the tetramer. The customary procedure in obtaining thermodynamic values from a single vapor pressure determination is to estimate the entropy of sublimation and then use the third law method to calculate the enthalpy. Because of the difficulty in estimating the entropies of complex polymers and of the success of the ionic model correlations in predicting the enthalpies of the lower alkali halide polymers, we suggest that the better procedure for Na_4Cl_4 may be to estimate the enthalpy from the ionic model and calculate the entropy from the single vapor pressure determination.

Our ionic model calculations for the tetramer incorporated the same assumptions as did Milne and Cubicciotti's[3,4] for monomers, dimers, and trimers. We employed a computerized, iterative technique which involved fixing the Cl-Cl distances and allowing the Na-Na distances to vary in .05 Å increments (See Appendix A). This process was repeated until a minimum energy was achieved with respect to the gaseous ions at infinite separation.

Calculations were performed for two different molecular structures--a planar ring and a dodecahedron. Figure 3 illustrates these structures with their minimum energy configurations. The minimum enthalpies of formation for the planar ring and dodecahedral structures relative to the gaseous ions at infinite separation are -645.9 kcal/mole and -649.8 kcal/mole, respectively. The difference in these calculated values is too small relative to uncertainties in the model to permit

us to conclude that the dodecahedral structure can be definitely assigned to the tetramer, but we can use its calculated stability to estimate the heat of sublimation of the tetramer.

Combining this value with the calculated stability for $Na_2Cl_2(g)$ of Milne and Cubicciotti,[3] we calculate an enthalpy of 45 kcal for the reaction:

$$Na_4Cl_4(g) = 2Na_2Cl_2(g)$$

Dividing this result by 1.10, as was done previously for the trimer, and estimating $\Delta H^\circ_{1000}-\Delta^\circ_0$ for the reaction to be ~ 0 we calculate the enthalpy of the reaction to be 40.9 kcal at 1000°K. Combining this value with the JANAF data for the enthalpy of sublimation of the dimer at 1000°K yields a predicted enthalpy of sublimation for $Na_4Cl_4(g)$ of 70.9 kcal/mole.

Estimating an ionization cross section of 6.0 for the tetramer relative to Na^+ and assuming the electron multiplier gains of the ions to be equal, we calculate the pressure of Na_4Cl_4 to be 4.3×10^{-10} atmospheres at 968°K. This pressure, combined with the estimated enthalpy of sublimation and the JANAF data for the monomer, gives an entropy of -99.8 eu for the reaction:

$$4NaCl(g) = Na_4Cl_4(g)$$

This value is in satisfactory agreement with the value of -110.4 ± 20 eu which we calculated for the analogous reaction in the TlF system from the data reported at 595°K by Cubicciotti.[20]

It will be interesting to examine the validity of this technique and of this extension of the ionic model to tetrameric alkali halide molecules when experimental data become available to compare with the calculated results. The data of Berkowitz and Chupka[11] indicate that significant concentrations of tetrameric molecules are produced by the vaporization of the lithium halides and sodium fluoride and this makes them suitable for such a study.

REFERENCES

1. "JANAF Thermochemical Data," Dow Chemical Co., Midland, Michigan, (1965).

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

3. T. A. Milne and D. Cubicciotti, J. Chem. Phys. 29, 846 (1958).

4. T. A. Milne and D. Cubicciotti, J. Chem. Phys. 30, 1625 (1959).

5. L. Pauling, Proc. Natl. Acad. Sci. (India) 25, Sec. A, Part I, (1956).

6. E. S. Rittner, J. Chem. Phys. 19, 1030 (1951).

7. C. T. O'Konski and W. I. Higuchi, J. Chem. Phys. 23, 1174 (1955).

8. S. Dushman, Scientific Foundations of Vacuum Technique, (Wiley, New York, N.Y., 1962) p. 28.

9. J. Roberts and A. W. Searcy, High Temp. Science (in press).

10. D. Meschi, J. Phys. Chem. (in press).

11. J. Berkowitz and W. A. Chupka, J. Chem. Phys. 29, 653 (1958).

12. R. Porter and R. Schoonmaker, J. Chem. Phys. 29, 1070 (1958).

13. T. A. Milne and H. M. Klein, J. Chem. Phys. 33, 1628 (1960).

14. J. Berkowitz, H. A. Tasman, and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962).

15. H. B. Skinner, (Ph.D. thesis), UCRL-19645, 1970.

16. C. A. Washburn, (Ph.D. thesis), UCRL-18685, 1969.

17. J. W. Otvos and D. P. Stevenson, J. Am. Chem. Soc. 78, 546 (1956).

18. C. A. McDowell, Ed., Mass Spectrometry, (McGraw-Hill, New York, N.Y., 1963) p. 513.

19. P. A. Akishin, L. N. Gorokhov, and L. N. Sidorov, Zh. Fiz. Khim. 33, 2822 (1959) (English Trans.).

20. D. Cubicciotti, High Temp. Sci. 2, 65 (1970).

```
      PROGRAM PLANE(INPUT,OUTPUT,PUNCH)
      DIMENSION B(200),E(200)
      DIMENSION WORD(12)
 9    READ 1,A
 1    FORMAT (F10.6)
      IF (A .GT. 0) GO TO 2
      IF (A .LE. 0) GO TO 4130
 2    PRINT 3,A
 3    FORMAT(1H1,22HANION-ANION SPACING = ,F10.4)
      READ 4, (WORD(I),I=1,12)
 4    FORMAT (12A6)
      PRINT 5, (WORD(I), I=1,12)
 5    FORMAT (12A6)
      READ 6,N,RM,RX,TM,TX
 6    FORMAT (I10,4F10.6)
      X = TM + TX
      Y = X-1.
      BO = .291/X
C     A = ANION,ANION SPACING
C     B = CATION-CATION SPACING WHICH IS BEING VARIED
C     TM AND TX ARE PAULING-S NM AND NX
      DO 10 I = 1,N
      B(I) = 6.-.05*FLOAT(I)
      C = .7071*A-(B(I)/2.)
      D = SQRT(((B(I)/2.)**2.)+C**2)
      F = SQRT(((B(I)/2.)**2.)+(B(I)+C)**2)
      E1 = 8.*(-1./D+(BO*((RM+RX)**Y))/(D**X))
      E2 = 8.*(-1./F+(BO*((RM+RX)**Y))/(F**X))
      E3 = 4.*(1./A+(.75*BO*((2.*RX)**Y))/(A**X))
      E4 = 4.*(1./B(I)+(1.25*BO*((2.*RM)**Y))/(B(I)**X))
      E5 = 2.*(1./(1.4142*B(I))+(1.25*BO*((2.*RM)**Y))/((1.4142*B(
     *I))**X))
      E6 = 2.*(1./(1.4142*A)+(.75*BO*((2.*RX)**Y))/((1.4142*A)**X))
      E(I) = 3.3189E+2*(E1+E2+E3+E4+E5+E6)
 10   CONTINUE
      PRINT 7
 7    FORMAT(///*   DIMENSION       BOND ENERGY*)
      PRINT 8, (B(I),E(I), I = 1,N)
 8    FORMAT (F10.3,E20.6)
      GO TO 9
 4130 STOP
      END
```

APPENDIX A (cont'd)

2. Dodecahedron Structure

```
      PROGRAM CUBIC(INPUT,OUTPUT,PUNCH)
      DIMENSION B(200),E(200)
      DIMENSION WORD(12)
 9    READ 1,A
 1    FORMAT (F10.6)
      IF (A .GT. 0) GO TO 2
      IF (A .LE. 0) GO TO 4130
 2    PRINT 3,A
 3    FORMAT(1H1,22HANION-ANION SPACING = ,F10.4)
      READ 4, (WORD(I),I=1,12)
 4    FORMAT (12A6)
      PRINT 5, (WORD(I), I=1,12)
 5    FORMAT (12A6)
      READ 6,N,RM,RX,TM,TX
 6    FORMAT (I10,4F10.6)
      X = TM + TX
      Y = X-1.
      BO = .291/X
C     A = ANION,ANION SPACING
C     B = CATION-CATION SPACING WHICH IS BEING VARIED
C     TM AND TX ARE PAULING-S NM AND NX
      DO 10 I = 1,N
      B(I) = 6.-.05*FLOAT(I)
      C = .612355*B(I) - .20416*A
      D = SQRT(((.577352*A)**2)+C**2)
      F = .612355*(A+B(I))
      E1 = 12.*(-1./D+(BO*((RM+RX)**Y))/(D**X))
      E2 = 4.*(-1./F+(BO*((RM+RX)**Y))/(F**X))
      E3 = 6.*(1./A+(.75*BO*((2.*RX)**Y))/(A**X))
      E4 = 6.*(1./B(I)+(1.25*BO*((2.*RM)**Y))/(B(I)**X))
      E(I) = 3.3189E+2*(E1+E2+E3+E4)
 10   CONTINUE
      PRINT 7
 7    FORMAT(///*   DIMENSION       BOND ENERGY*)
      PRINT 8, (B(I),E(I), I = 1,N)
 8    FORMAT (F10.3,E20.6)
      GO TO 9
 4130 STOP
      END
```

Table 1. Relative Ion Intensities at 968°K.

Ion	Relative Intensity
Na^+	1.00
$NaCl^+$	.49
Na_2Cl^+	.88
$Na_3Cl_2^+$	.0068
$Na_4Cl_3^+$	.00010

Table 2. Comparison of Calculated and Experimental Enthalpies for the Reaction $M_2X_2(g) = 2MX(g)$

System	ΔH_0° (calc.)[3] kcal	ΔH_0° (exp.)[1] kcal	$\frac{\Delta H_0^\circ \text{ (calc.)}}{\Delta H_0^\circ \text{ (exp.)}}$
LiF	57.6	61.8	.93
LiCl	54.7	48.9	1.12
LiBr	52.3	45.7	1.14
LiI	48.9	42.7	1.15
NaF	55.9	56.0	1.00
NaCl	53.0	48.4	1.10
NaBr	51.6	47.4	1.09
NaI	48.2		
KF	48.2	49.5	.97
KCl	47.4	45.1	1.05
KBr	46.8	43.3	1.08
KI	44.4	39.3	1.13

Table 3. Comparison of Calculated and Experimental Enthalpies for the Reaction: $M_3X_3(g) = MX(g) + M_2X_2(g)$

System	ΔH_0^o (calc.)[3,4] kcal	ΔH_0^o (exp.)[1] kcal	$\frac{\Delta H_0^o \text{ (calc.)}}{\Delta H_0^o \text{ (exp.)}}$	$\Delta H_{1000}^o - \Delta H_0^o$
LiF	65	59.5	1.09	-1.091
LiCl	56	49.3	1.14	- .003
NaCl	50			

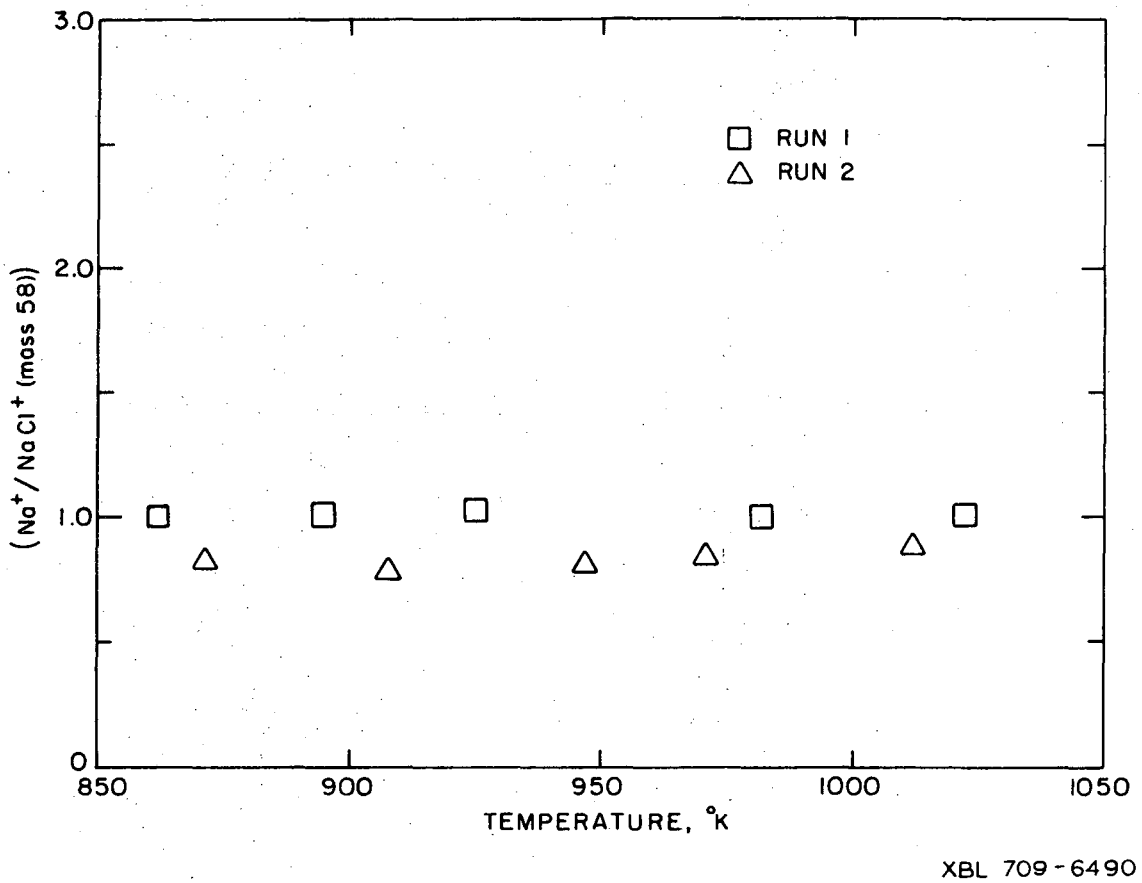


Fig. 1. The monomer fragmentation ratio ($Na^+/NaCl^+$) as a function of temperature.

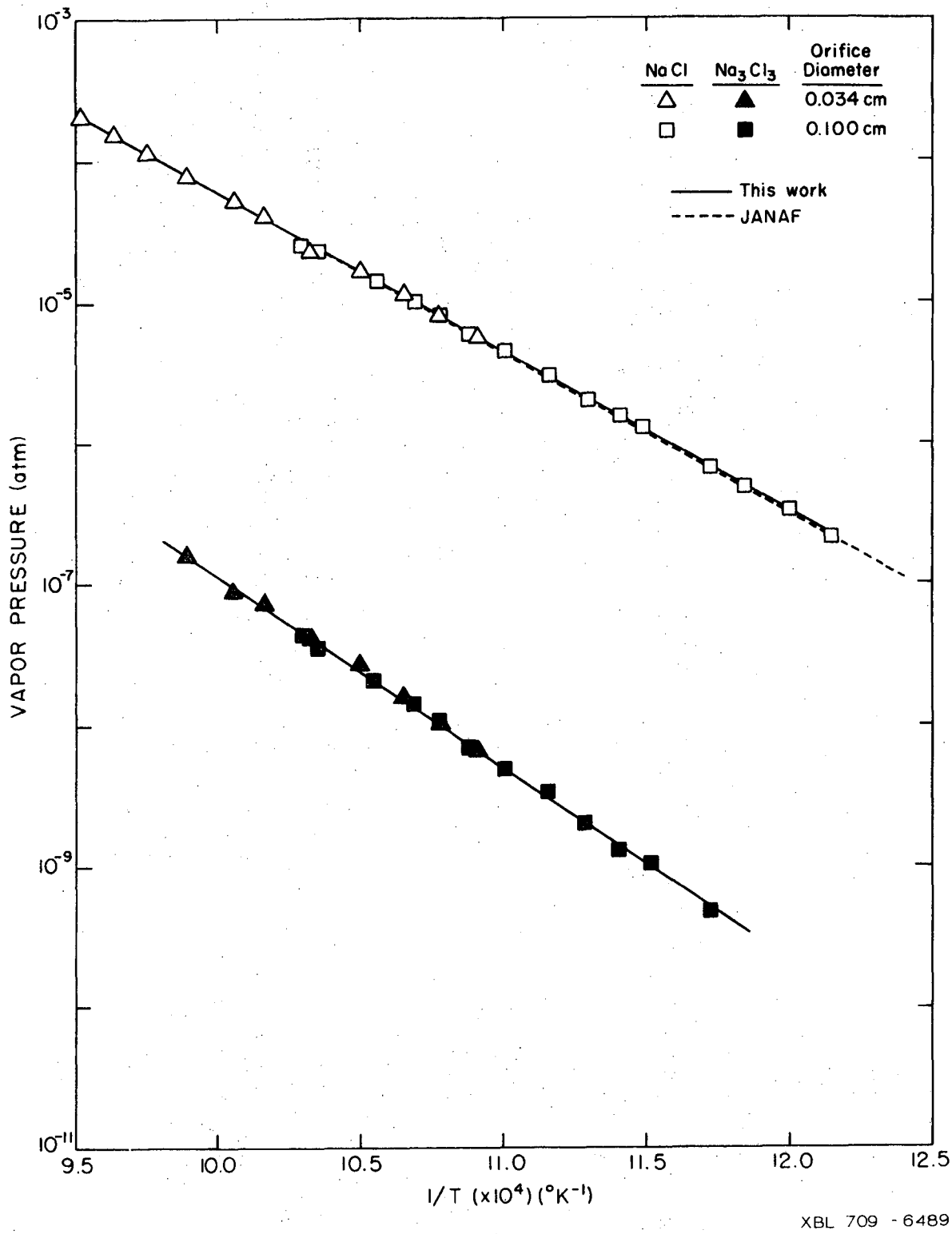
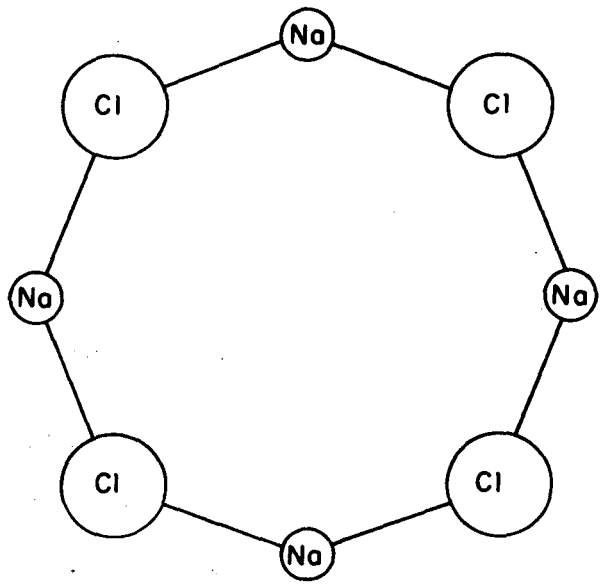


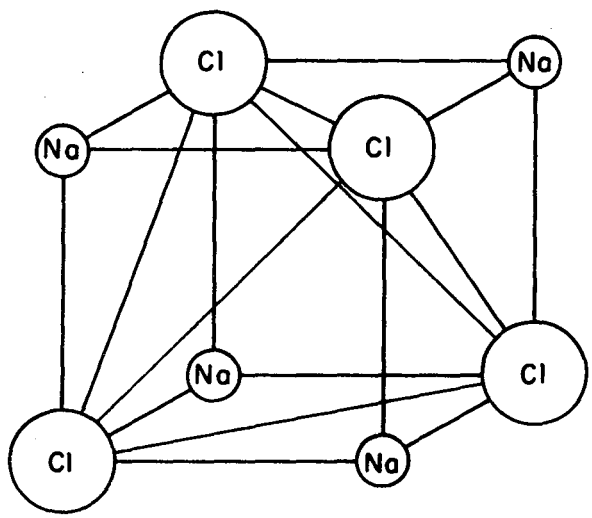
Fig. 2. Vaporization data for sodium chloride.



PLANAR RING

INTERATOMIC DISTANCE

Na - Na	4.55 Å
Cl - Cl	4.60 Å
Na - Cl	2.47 Å



DODECAHEDRON

INTERATOMIC DISTANCE

Na - Na	3.65 Å
Cl - Cl	3.80 Å
Na - Cl	2.63 Å

XBL 709-6491

Fig. 3. Sodium chloride tetramer structures.

PART II.

THE VAPOR PRESSURES OF GALLIUM TRIFLUORIDE MONOMER AND DIMER

I. INTRODUCTION

Limited data[1-3] exist to describe the gas phase compositions and vapor pressures over gallium trichloride, gallium tribromide, and gallium triiodide but apparently no measurements of the vapor pressure of gallium trifluoride as a function of temperature have been reported. This paper reports measurements made with a mass spectrometer. Calibration of the mass spectrometric intensity data was achieved by using the torsion-effusion method to measure the absolute vapor pressure of the monomer.

The partial vapor pressure of the monomer is reported for the temperature range from 714°K - 1015°K and the enthalpy of sublimation at 298°K is given as calculated by the second and third law methods.[4] A small amount of dimer was shown to exist in the equilibrium vapor and its partial vapor pressure is reported for the temperature range from 824°K - 1003°K.

II. EXPERIMENTAL

Gallium trifluoride was purchased from Research Organic/Inorganic Chemical Company. A spectroscopic analysis showed 0.05% mooybdenum and 0.002% iron to be the principal metallic impurities.

A. Mass Spectrometer Studies

The mass spectrometer used throughout the investigation has been described in Part I of this report. Samples were contained in Knudsen cells fabricated from either nickel or graphite. Orifice diameters employed with the nickel cell were 0.034 cm and 0.100 cm while 0.034 cm, 0.051 cm, and 0.100 cm diameter orifices were used with the graphite cell. Each orifice channel length was less than the channel diameter and, to insure molecular flow, data were only collected in pressure ranges for which the vapor mean free path to diameter ratios, as calculated by the hard sphere approximation,[5] were greater than unity.

The Knudsen cells were heated by radiation from a tungsten filament that encircled the cells. Heat shields fabricated from copper surrounded the cell and filament assembly. Temperatures were measured by means of a chromel-alumel thermocouple which was securely clamped inside a hole drilled in the bottom of the cell. The thermocouple had been calibrated at the freezing point of aluminum.

Two calibration measurement series were made in the graphite cell using lead as a standard. The first series of 14 measurements in the temperature range from 813°K to 1013°K gave a linear least squares enthalpy of vaporization of 43.02 ± 0.59 kcal/mole from measurement

of the slope of the $\ln I^{+}T$ vs. 1/T plot, where the reported error is the standard deviation from the mean. The second series of eight measurements in the temperature range from 845°K to 995°K yielded 44.29 ± 0.72 kcal/mole. Hultgren et al.[6] report 44.26 kcal/mole for the enthalpy of vaporization of lead at 914°K, the approximate mean temperature for each run.

Experiments performed with gallium trifluoride yielded ion intensities corresponding to GaF_2^+, GaF^+, Ga^+ and small amounts of $Ga_2F_5^+$ ($I^{235}Ga_2F_5^+/I^{107}GaF_2^+ \simeq 0.0021$ at 885°K). In each case the ion identity was verified by means of the background spectrum and the isotopic abundances. At low temperatures, a large peak of mass 20, attributable to HF^+, was observed which decreased in intensity with time. No other species were observed to effuse from the cell region when the spectrum was scanned to mass 500. By analogy with the mass spectra of $AlF_3(g)$,[7,8] $Al_2F_6(g)$[8] and $BF_3(g)$[9,10] GaF_2^+, GaF^+, and Ga^+ are the expected fragments of dissociative ionization of $GaF_3(g)$ by electron impact fragment of dissociative ionization of the dimer - $Ga_2F_6(g)$.

Fragmentation patterns for $GaF_3(g)$ produced by 70 ev ionizing electrons were measured at a variety of temperatures (Table 1). The intensities of GaF^+ and Ga^+ ions relative to GaF_2^+ ion varied in a non-systematic manner with temperature. The variation could result because a) changes in the ion source focussing potentials or the source location[11] altered the ionization efficiency for the various species

from experiment to experiment or b) small amounts of GaF(g) and Ga(g) are present in the system as a result of the reduction of $GaF_3(g)$ by the cell assembly. Appearance potential measurements support the second explanation.

The appearance potentials of GaF_2^+, GaF^+, and Ga^+ ions were measured by the method of extrapolated differences[12] using H_2O^+ as the standard. Three measurements for GaF_2^+ ion gave an appearance potential of 15.1 ± 0.5 ev, compared to 16.4 ev for BF_2^+ and 15.2 ev for AlF_2^+ from the neutral $MF_3(g)$ molecules.[13] The appearance potential measured for GaF^+ ion, 10.7 ± 0.6 ev, is close to the value of 10.6 ± 0.4 ev reported by Murad et al.[14] for GaF^+ produced by simple ionization of GaF(g). The measured appearance potential for Ga^+ ion was approximately 9.0 ev. Since this value is less than that for GaF^+ ion, it is reasonable to associate this ion with Ga(g). The 3.0 ev discrepancy between the measured appearance potential and the reported ionization potential[15] could result because only a small amount of Ga(g) was present in the system and since the majority of the Ga^+ ions observed are produced from dissociative ionization of $GaF_3(g)$.

The intensity of $^{107}GaF_2^+$ ion was measured as a function of temperature using three different orifice sizes with the nickel and carbon cells. Temperatures were raised and lowered with approximately 20 minutes allowed between datum points to be sure that equilibrium has been achieved. The results of linear least squares treatments of the data from each measurement series with errors listed as the standard deviations from the means are summarized in Table 2. A composite curve was formed

by making the least squares lines from each measurement series coincide at 865°K, the mid-temperature for all measurements (See final column, Table 2).

Dimer data are summarized in Table 3. Using the value ΔC_p = -11 cal/degree for sublimation of a mole of dimer, as estimated by Skinner and Searcy[16] for $La_2F_6(g)$, and the 60°K temperature difference between the mi-points of the high and low temperature data, we calculate that the change in the enthalpy of sublimation due to the temperature difference between the two sets of data amounts to 0.66 kcal/mole of dimer. Consideration of this result and the combined error limits on the two sets of data indicates that they are in satisfactory agreement. Accordingly, the dimer measurements were fitted together at 914°K, the midpoint of the temperature range for the 22 datum points (See final column, Table 3).

The ion intensities attributable to the dimer were fixed relative to those associated with the monomer by using measurements of the concentrations of both species at a single temperature. The electron multiplier gains of the two ions were assumed to be equal and the additivity rule of Otvos and Stevenson[17] was used to estimate a relative ionization cross section of 2.0 for the dimer as compared to the monomer. The appearance potential of $Ga_2F_5^+$ ion, measured by the method of extrapolated differences[12] with Hg^+ used as the reference, is 15.6 ± 0.5 eV.

B. Torsion-Effusion Studies

Torsion-effusion measurements were made to obtain the absolute pressure of $GaF_3(g)$ for calibration of the mass spectrometer intensity measurements. The techniques used in this laboratory have been described previously.[18-20]

The tungsten fiber used to suspend the torsion cell measured 3.8×10^{-3} cm in diameter and approximately 45 cm in length. The torsion constant of the fiber, determined by measuring the periods of rotational oscillation of two suspended weights with different moments of inertia, was 0.8233 dyne-cm/radian.

The torsion cell used in the experiments was made of National Carbon ZT101 grade graphite. The cell measured 4.1 cm in length by 1.9 cm in height and width. The two cell orifices measured 0.0998 cm and 0.0997 cm in diameter with channel lengths of 0.1574 cm.

Temperatures were measured with a chromel-alumel thermocouple mounted directly below the suspended torsion cell. The cell temperature was correlated with the fixed thermocouple temperature by installing another thermocouple fitted with a dummy cell in the same position as the torsion cell and measuring the difference in temperature between the two thermocouples. Both thermocouples were previously calibrated at the freezing point of zinc.

In order to check the accuracy of measurement with the experimental arrangement, the vapor pressure of lead was measured over the temperature range from 976°K to 1083°K. A least squares fit of the five datum points gave second law values for the enthalpy and entropy of

vaporization at 1029°K of 44.9 ± 0.33 kcal/mole and 22.1 ± 0.03 eu/mole, respectively, where the reported errors are the standard deviations from the means. The values accepted by Hultgren[6] at this temperature for the heat and entropy are 44.02 kcal/mole and 22.07 eu/mole, respectively. The absolute pressures measured at the midpoint of the experimental temperature range exceed the pressure accepted by Hultgren[6] by approximately 19%.

A gallium trifluoride sample that was first degassed at 420°K and then heated to approximately 1000°K over a two day period interrupted by overnight storage in vacuum at room temperature showed an initial pressure that was anomolously high and never leveled off to a constant value. X-ray analysis of the sample remaining in the cell after heating showed β-Ga_2O_3. Since the mass spectrometer studies showed that HF(g) effuses from the cell at low temperatures, hydrolysis of GaF_3(s) is almost certainly responsible for this observed behavior. Sample deterioration occurred more rapidly in the torsion apparatus than in the mass spectrometer because the background pressure in the torsion apparatus ($\sim 10^{-5}$ torr.) is approximately 2 orders of magnitude higher than that in the mass spectrometer.

To minimize interference from hydrolysis a second series of measurements was taken during which the sample was not allowed to cool to room temperature after low temperature degassing. Datum points 1 through 4 indicated that a gradual decrease in pressure occurred with time. Points 5 through 10 fell on a straight line when plotted as ln P vs. 1/T and points 11-16 described a line at about 1/2 the total pressure of

the line described by points 5 through 10. The decrease in pressure observed during the measurement of points 1 through 4 is ascribed to high temperature degassing of residual H_2O and HF, while the decrease observed in points 11 through 16 indicated the depletion of one of the Knudsen cells. Points 7 through 9 were accepted as being accurate measurements of the absolute vapor pressure. These points were corrected by a factor of 19%, due to the discrepancy in the lead data, and appear in Fig. 1.

III. RESULTS AND DISCUSSION

Linear least squares fits of the monomer and dimer data gave slopes of 55.36 ± 0.24 kcal/mole and 70.98 ± .88 kcal/mole, respectively, where the errors are the standard deviations from the means. Mass spectrometer values of ln I^+T were multiplied by a factor that made the least squares plots of the monomer mass spectrometer data coincide with the absolute pressures measured at 953°K, the midpoint of the temperature range of the torsion-effusion measurements. The resulting absolute pressures for the monomer and dimer are plotted in Fig. 1 and tabulated in Tables 4 and 5, respectively.

Linear least squares fits of these absolute pressure data yield the equations:

$$(714°K\text{-}1015°K)\ \mathrm{Log}_{10}P_{monomer} = -\frac{(1.210 \pm 0.005) \times 10^4}{T} + 8.36 \pm 0.06$$

$$(824°K\text{-}1003°K)\ \mathrm{Log}_{10}P_{dimer} = -\frac{(1.551 \pm 0.019) \times 10^4}{T} + 9.35 \pm 0.21$$

where, again, the reported errors are the standard deviations from the means.

The enthalpy of sublimation at 298°K for $GaF_3(g)$ was calculated by both the second and third law methods.[4] The second law calculations require heat capacity data and the third law calculations require knowledge of the free energy functions.

We have accepted Glassner's[21] estimate of $C_p = 18.8 + 10.4 \times 10^{-3}T$ for the heat capacity of solid GaF_3. Our independent estimate of the heat capacity, using Kelley's[22] method and our extrapolated value of

1448°K for the sublimation point of GaF_3 yields a value for C_p at 1000°K which differs from Glassner's estimate by only 1.9 cal/degree-mole.

Brewer,[3] Glassner,[21] and Kelley and King[23] have estimated the entropy of solid GaF_3 at 298.15°K to be 26 eu/mole, 28 eu/mole, and 20.0 ± 0.5 eu/mole, respectively. We made an independent estimate by means of a modification of Latimer's rule[24] which states, S^o_{298} (eu/g - atom) = 3/2 Rln(at.wt.)-0.94, where the constant was deduced empirically from available data for metal chlorides. We recalculated the value of the constant as being equal to 3.38 using the known entropy data for YF_3[25] and CeF_3.[26,27] Application of the modified equation to GaF_3 gave S^o_{298} = 25.5 eu/mole, leading us to accept Brewer's estimate.

In order to calculate the heat capacity and free energy functions for $GaF_3(g)$ by the methods of statistical mechanics, it was necessary to estimate molecular constants. The Ga-F stretch force constant for $GaF_3(g)$ was estimated by first calculating values for the ratio of force constants for the M-F bond in the diatomic molecule and the M-F bond in the corresponding trihalide. For the B-F and Al-F systems[14,28] these ratios are 0.910 and 0.918, respectively. The mean of these ratios was applied to the force constant reported by Murad et al.[14] for GaF(g) to give 3.71×10^5d cm^{-1} for the estimated stretch force constant, k_1, in $GaF_3(g)$.

Before proceeding further, it is of interest to compare the result of this calculation with that found by applying the empirical

equation formulated by Herschbach and Laurie[29] which has been shown to give reasonable values for the stretch force constants of rare earth trihalides. Akishin et al.[2] report a length of 1.88 ± 0.02Å for the Ga-F bond in gaseous GaF_3 molecule as measured by electron diffraction techniques. Using this value in the Herschbach and Laurie equation gives a value for k_1 of 2.82×10^5 d cm^{-1} which is quite different from the value we estimate by using the normalizing factor. In an attempt to understand the reason for the discrepancy, values for the M-X bond lengths in the monohalides and trihalides were tabulated (Table 6). Inspection of these data indicate that, to a good approximation, the M-X bond length in the trihalide is equal to that measured in MX(g). With this relationship in mind the reported value for the length in GaF_3(g) appears to be somewhat high and when it is reduced to 1.775Å, the Herschbach and Laurie equation gives k_1 as being equal to 4.13×10^5d cm^{-1} which is in better agreement with our estimate. In light of this analysis, we suggest that Akishin's data may be in error but have accepted his value for our thermodynamic calculations since the question remains to be resolved experimentally.

Semilogarithmic plots of the out-of-plane bend force constants $k\Delta/\ell^2$ and of the in-plane bend force constants, $k\delta/\ell^2$, where ℓ is the cation-anion distance, versus k_1 for D_{3h} point group species show straight line relationships.[30] $k\Delta/\ell^2$ and $k\delta/\ell^2$ for GaF_3(g) were assumed to fall on this line and were accordingly estimated to be 2.93×10^4d cm^{-1} and 1.33×10^4d cm^{-1}, respectively. Using the three force constants and the valence force model,[31] the vibrational frequencies

for $GaF_3(g)$ were calculated to be 575 cm^{-1}, 218 cm^{-1}, 686 (2) cm^{-1}, and 213 (2) cm^{-1}.

The electronic contribution to the heat capacity was assumed to be the same as that for Ga^{+3} ion.[32] Brewer et al.[33] have shown that this assumption yields good agreement with known data for the transition metal dihalides. Heat capacities for gaseous GaF_3 were calculated at 100° intervals from 300°K to 1800°K as shown in Table 7 and the equation $C_p = 19.361 + 2.886 \times 10^{-4}T - \frac{2.983 \times 10^5}{T^2}$ was fitted to these values.

The free energy functions for solid and gaseous GaF_3 were calculated from the estimated heat capacities and entropies at 298°K. These results are given in Table 8 at 100° intervals over the temperature range from 300°K to 1800°K. The free energy functions when combined with the absolute pressure datum points using the relationship:

$$\Delta H^\circ_{298} = - RT \ln P_T - T \left(\frac{\Delta F^\circ_T - \Delta H^\circ_{298}}{T}\right)$$

gave 58.27 ± .17 kcal/mole as a third law value for the enthalpy of sublimation at 298°K where the reported error is the standard deviation from the mean of the heats given in Table 4.

A second law treatment of the monomer data by the sigma plot method[4] gave the equation

$$\Sigma = \frac{58.16 \pm 0.26}{T} + 42.32 \pm 0.31$$

where the errors are the standard deviations from the means. The values of Σ are plotted in Fig. 2 and appear in Table 9. Combining this result with the appropriate equations gave second law values for the enthalpy and entropy of sublimation at 298°K of 58.83 ± 0.26 kcal/mole and 44.58 ± 0.31 eu/mole, respectively.

Since the lead calibration data showed systematic errors in temperatures and temperature dependence of the mass spectrometer measurements to be low, greater confidence is placed in the second law calculations than in the third law values which are more strongly dependent on the estimated data. These considerations lead to values for the enthalpy and entropy of sublimation at 298°K of 58.8 ± 3 kcal/mole and 44.6 ± 3 eu/mole, respectively.

A linear least squares fit of the 22 data points for $Ga_2F_6(g)$ molecule yields values for the enthalpy and entropy of sublimation at 914°K, the midpoint of the experimental temperature range, of 70.98 ± 0.88 kcal/mole and 42.76 ± 0.98 eu/mole, respectively. Combining these results with the second law values for the enthalpy and entropy of sublimation of the monomer corrected to the same temperature gives an enthalpy and entropy of dimerization at 914°K of -38.48 kcal/mole of dimer and -32.20 eu/mole of dimer, respectively. This value for the entropy is in good agreement with the reported[28] entropies of dimerization at 900°K for the AlF_3, $AlCl_3$, $AlBr_3$, AlI_3, and $FeCl_3$ systems which are -36.3, -32.4, -34.2, -29.4, and -31.6 eu/mole of dimer, respectively. The estimated error limit on the enthalpy of sublimation of the dimer for which 90% confidence can be assigned is ± 4 kcal/mole. This limit

leads to final values for the enthalpy and entropy of sublimation of the dimer at 914°K of 71.0 ± 4 kcal/mole and 42.8 ± 4 eu/mole, respectively.

Our equation for the vapor pressure of $GaF_3(g)$ in equilibrium with $GaF_3(s)$ yields 1448°K for the extrapolated sublimation point. The dimer partial pressure at this temperature is 4.4×10^{-2} atmospheres. This result differs markedly from the approximate value of 1225°K ± 50°K reported by Hannebohn and Klemm.[34] Since our mass spectrometrically determined enthalpies of sublimation were reproducible from run to run, we feel that the only possible source of a large error in our data is in our absolute pressure measurements. An increase in our pressures by a factor of about 30 would be necessary to give an extrapolated sublimation point in agreement with that reported by Hannebohn and Klemm.

To provide an independent check on the accuracy of the absolute pressures determined by the torsion-effusion technique, a series of three consecutive experiments was performed with the mass spectrometer. In the first experiment, a sample of lead was vaporized from a graphite cell and the $^{208}Pb^+$ ion intensity was measured as a function of temperature over the range from 845°K to 995°K. The secondary electron multiplier gain for Pb^+ ion was found to be 3.71×10^5. Lead was replaced with gallium trifluoride and the $^{107}GaF_2^+$ ion intensity was measured as a function of temperature over the overlapping temperature range from 766°K to 914°K. The secondary electron multiplier gain for this species was found to be 8.73×10^5. Finally, the lead sample was returned to the apparatus and the resulting ion intensity data was

found to agree to within 25% of the ion intensities obtained during the first run, indicating that the machine constant throughout all three experiments remained approximately the same.

Using relative ionization cross sections as given by Otvos and Stevenson,[17] the known vapor pressure of lead,[6] the measured gains for the two species, and correcting the data for isotopic abundances yields 8.2×10^{-6} atmospheres for the vapor pressure of the monomer at 900°K. This result differs by only 3% from the value measured in the torsion-effusion experiments at the same temperature.

Gallium trihalides are easily reduced to the gaseous monohalides.[35] It appears possible that the approximate sublimation point reported by Hannebohn and Klemm is in error because of a reaction to yield GaF(g). An additional or alternative possibility for error is pointed out by Brewer, Garton and Goodgame[36] who were unable to synthesize stoichiometric samples of $GaF_3(s)$ by the technique employed by Hannebohn and Klemm. The samples of Brewer et al. sublimed in the same temperature range as those of Hannebohn and Klemm but did not analyse chemically as $GaF_3(s)$ or show the x-ray pattern of a known form of that solid.

It is interesting to examine the results of this and other similar studies of metal trihalide vapors in light of Brewer's discussion of the factors that influence the stabilities of the condensed phases relative to the vapor and of the dimers relative to the monomers. Among Brewer's comments are the following:[37]

1) "The size [of the ions] is important in two respects. The M-X distance or the distance between the cation and anion is

important in that the strength of an electrostatic bond increases as the M-X distance is decreased. The cation-anion radius ratio is an important measure of the contribution of cation-cation repulsion or anion-anion repulsion toward decreasing the stability of the condensed phase. Because coordination numbers are higher in the condensed phase than in the gaseous molecules, crowding of cation or anion has an important effect upon stability of the solid phase."

2) ". . . with compounds of very low cation to anion ratio, dimerization does not occur because the dimer would be very unstable owing to the large anion repulsion, which prevents any increase of coordination number above the stoichiometric ratio. Thus BCl_3 does not form dimers because ΔH_D for B_2Cl_6 would be too small owing to the difficulty of putting a fourth Cl atom around the B atom."

In his original discussion Brewer next presented his very important arguments which show that minor species of an equilibrium vapor become more important with increasing temperature. The quotations already given, however, are sufficient for our present purposes. They lead to the expectation that the stabilities of both the metal trihalide solids and dimers relative to the monomers, while must importantly influenced by the interionic distance, will also depend upon the cation to anion radius ratio. Given in Table 10 are the radius ratios, heats of dimerization and heats of sublimation to monomers for the various trihalides for which data are available . In general the heats of

dimerization and sublimation decrease with decreasing radius ratio describing a trend which is consistent with Brewer's discussion.

A low radius ratio will usually have a more adverse effect on the stability of the solid relative to the monomer than on that of the dimer. Consequently, the seemingly paradoxical situation arises that those dimers with the highest heats of dissociation to monomers are found in the vapor at low concentration relative to the monomers while dimers with low dissociation enthalpies are major species.

REFERENCES

1. I. R. Beattie and J. R. Horder, J. Chem. Soc. (London), Sec. A 17, 2655 (1969).
2. P. A. Akishin, V. A. Naumov, and V. M. Tatevskii, Kristallografiya 4, 194 (1959).
3. L. L. Quill, Ed. The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, (McGraw-Hill, New York, N. Y., 1950).
4. L. Brewer and K. S. Pitzer, Thermodynamics (McGraw-Hill, New York, N. Y., 1961) Chap. 15.
5. S. Dushman, Scientific Foundations of Vacuum Technique, (Wiley, New York, N. Y., 1962) p. 28.
6. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys (Wiley, New York, N. Y., 1963).
7. R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960).
8. A. Büehler, E. P. Marram, and J. L. Stauffer, J. Phys. Chem. 71, 4139 (1967).
9. R. F. Porter, D. R. Bidinosti, and K. F. Watterson, J. Chem. Phys. 36, 2104 (1962).
10. J. Marriott and J. D. Craggs, J. Elect. and Cont. 3, 194 (1957).
11. D. H. Feather and A. W. Searcy, High Temp. Sci. 3, 155 (1971).
12. C. A. McDowell, Ed., Mass Spectrometry, (McGraw-Hill, New York, N. Y., 1963) p. 513.
13. J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions, (NSRDS-NBS 26, June 1969).

14. E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem. Phys. 45, 263 (1966).

15. C. E. Moore, Atomic Energy Levels, NBS No. 467, 1949.

16. H. B. Skinner and A. W. Searcy, J. Phys. Chem. 75, 108 (1971).

17. J. W. Otvos, and D. P. Stevenson, J. Am. Chem. Soc. 78, 546 (1956).

18. M. J. Lim and A. W. Searcy, J. Phys. Chem. 70, 1762 (1966).

19. R. W. Mar and Searcy, J. Phys. Chem. 71, 888 (1967).

20. P. E. Hart, Lawrence Berkeley Laboratory Report, UCRL-11124, January, 1964.

21. A. Glassner, Argonne National Laboratory Report, ANL-5750, 1958.

22. K. K. Kelley, U. S. Bur. Mines Bull. No. 371, 1934.

23. K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. No. 592, 1961.

24. W. M. Latimer, Oxidation Potentials (Prentice Hall, 1952), App. III.

25. E. Rudzitis, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. 69, 2305 (1965).

26. E. F. Westrum Jr. and A. F. Beale Jr., J. Phys. Chem. 65, 353 (1961).

27. E. G. King and A. L. Christensen, U. S. Bur. Mines Bull. No. 5510, 1959.

28. JANAF Thermochemical Data, Dow Chemical Co., Midland, Michigan, 1963.

29. D. R. Herschbach and V. W. Laurie, J. Chem. Phys. 35, 458 (1961).

30. M.Lim and A. W. Searcy, J. Phys. Chem. 70, 1762 (1966).

31. G. Herzberg, Molecular Spectra and Molecular Structure. Infrared and Raman Spectra of Polyatomic Molecules, (D. Van Nostrand Co., Inc., New York, N. Y. 1959).

32. C. E. Moore, Atomic Energy Levels, NBS No. 467, 1952.

33. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Rev. 63, 111 (1963).

34. V. O. Hannebohn and W. Klemm, Z. Anorg. Chem. 229, 342 (1936).

35. A. W. Searcy, Progress in Inorganic Chemistry, Vol. III, Edited by F. A. Cotton, (Wiley, New York, N. Y., 1962) p. 103.

36. F. M. Brewer, G. Garton, and D. M. L. Goodgame, J. Inorg. Nucl. Chem. 9, 56 (1959).

37. See Ref. 3, pp. 258-262.

38. R. F. Barrow, P. G. Dodsworth, P. B. Zeeman, Proc. Phys. Soc. (London) A70, 34 (1957).

39. J. Roberts and A. W. Searcy, (submitted to High Temp. Science).

40. R. W. Mar and A. W. Searcy, J. Phys. Chem. 71, 888 (1967).

Table 1. Fragmentation Patterns Relative to $^{107}GaF_2^+$ ion using 70 eV Ionizing Electrons

Temp(°K)	Cell	$^{107}GaF_2^+$	$^{88}GaF^+$	$^{69}Ga^+$
901	Ni	100.00	8.29	8.62
948	Ni	100.00	9.25	7.55
813	C	100.00	6.28	6.32
881	C	100.00	5.02	4.39
881	C	100.00	3.06	4.20
901	C	100.00	3.52	5.42
908	C	100.00	3.62	5.72
918	C	100.00	2.66	4.36
953	C	100.00	2.73	4.17
954	C	100.00	8.44	6.68
960	C	100.00	2.94	3.07
973	C	100.00	3.88	7.23
1020	C	100.00	4.70	2.84

Table 2. Mass Spectrometer Runs on $^{107}GaF_2^+$ Using 70 eV Ionizing Electrons

Run	1	2	3	4	Composite
Cell	Ni	Ni	C	C	-
Orifice diameter (cm)	0.034	0.100	0.051	0.051	-
Temperature Range (°K)	808-1015	756-926	771-955	714-826	714-1015
No. of datum points	15	14	12	10	51
ΔH°_{sub} at mean temperature (kcal/mole)	55.99 ± .55	55.20 ± .81	55.60 ± .49	54.89 ± .96	55.36 ± .24

Table 3. Mass Spectrometer Runs on $^{235}Ga_2F_5^+$

Using 70 eV Ionizing Electrons

Run	1	2	Composite
Cell	C	C	-
Orifice diameter (cm)	0.034	0.100	-
Temperature Range (°K)	875-1003	824-934	824-1003
No. of datum points	10	12	22
ΔH°_{sub} at mean temperature (kcal/mole)	69.52 ± 1.61	72.14 ± 1.37	70.98 ± .88

Table 4. Temperatures, Pressures, and the Third Law Heats of Sublimation of $GaF_3(g)$ in Equilibrium with $GaF_3(s)$

Temperature (°K)	Pressure (atm)	$\Delta H^\circ_{298.15}$ (kcal/mole)
0.034 cm diameter orifice		
867	2.827×10^{-6}	58.129
942	3.457×10^{-5}	58.134
916	1.386×10^{-5}	58.312
972	8.086×10^{-5}	58.172
899	7.708×10^{-6}	58.340
854	1.394×10^{-6}	58.529
829	5.040×10^{-7}	58.595
955	5.217×10^{-5}	58.094
931	2.444×10^{-5}	58.134
995	1.710×10^{-4}	57.941
1015	2.918×10^{-4}	57.968
883	5.094×10^{-6}	58.068
842	1.021×10^{-6}	58.230
808	2.567×10^{-7}	58.262
947	3.977×10^{-5}	58.156
0.100 cm diameter orifice		
855	1.210×10^{-6}	58.818
926	1.987×10^{-5}	58.241
904	1.014×10^{-5}	58.149
814	3.522×10^{-7}	58.159
864	2.600×10^{-6}	58.100
777	6.830×10^{-8}	58.191
846	1.063×10^{-6}	58.437
831	5.921×10^{-7}	58.413
891	6.056×10^{-6}	58.283
756	2.378×10^{-8}	58.283
794	1.326×10^{-7}	58.350
769	4.049×10^{-8}	58.436
804	2.120×10^{-7}	58.282
876	3.832×10^{-6}	58.148

Table 4. (continued)

Temperature (°K)	Pressure (atm)	$\Delta H^{\circ}_{298.15}$ (kcal/mole)
0.051 cm diameter orifice		
900	7.671×10^{-6}	58.424
940	3.175×10^{-5}	58.179
890	5.726×10^{-6}	58.306
855	1.628×10^{-6}	58.314
798	1.599×10^{-7}	58.297
880	3.706×10^{-6}	58.440
837	7.616×10^{-7}	58.398
815	3.123×10^{-7}	58.387
917	1.474×10^{-5}	58.230
771	4.944×10^{-8}	58.260
786	9.165×10^{-8}	58.371
955	5.781×10^{-5}	57.885
0.051 cm diameter orifice		
787	9.842×10^{-8}	58.329
738	1.026×10^{-8}	58.194
765	3.073×10^{-8}	58.509
714	2.679×10^{-9}	58.291
779	6.495×10^{-8}	58.411
752	1.921×10^{-8}	58.289
725	5.428×10^{-9}	58.113
826	5.448×10^{-7}	58.251
802	2.219×10^{-7}	58.051
815	3.117×10^{-7}	58.407

Table 5. Temperatures and Pressures of $Ga_2F_6(g)$ in equilibrium with $GaF_3(s)$

Temperature (°K)	Pressure (atm)
0.034 cm orifice	
944	9.110×10^{-8}
919	3.473×10^{-8}
976	2.702×10^{-7}
902	1.463×10^{-8}
875	3.968×10^{-9}
934	5.802×10^{-8}
906	1.871×10^{-8}
1003	6.233×10^{-7}
966	1.765×10^{-7}
887	6.477×10^{-9}
0.100 cm orifice	
884	7.029×10^{-9}
847	1.206×10^{-9}
896	1.187×10^{-8}
916	2.791×10^{-8}
900	1.351×10^{-8}
934	5.116×10^{-8}
852	1.259×10^{-9}
825	2.938×10^{-10}
863	2.045×10^{-9}
920	2.799×10^{-8}
886	7.222×10^{-9}
920	3.069×10^{-8}

Table 6. M-X Bond Lengths in Monohalides and Trihalides

System	Monohalide (Å)	Ref.	Trihalide (Å)	Ref.
BF	1.265	28	1.307	28
BCl	1.7157	28	1.75	28
BBr	1.887	28	1.87±.02	28
AlF	1.6547	28	1.63±.01	2
AlCl	2.1298	28	2.06	28
AlBr	2.295	28	2.27	28
GaF	1.775	38	1.88±.02	2

Table 7. Calculated Heat Capacities for $GaF_3(g)$

Temperature (°K)	Cp (cal/deg/mole)	Temperature (°K)	Cp (cal/deg/mole)
300	16.230	1100	19.486
400	17.479	1200	19.546
500	18.214	1300	19.593
600	18.667	1400	19.631
700	18.962	1500	19.661
800	19.162	1600	19.686
900	19.304	1700	19.707
1000	19.408	1800	19.725

Table 8. Calculated Free Energy Functions for GaF_3

Temp. (°K)	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_s$ (cal/°)	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_g$ (cal/°)	$-\left(\frac{\Delta F_T^\circ - \Delta H_{298}^\circ}{T}\right)_{sub}$ (cal/°)
300	26.000	70.051	44.051
400	26.873	70.705	43.832
500	28.554	71.976	43.422
600	30.479	73.433	42.954
700	32.453	74.920	42.467
800	34.399	76.375	41.976
900	36.291	77.773	41.482
1000	38.118	79.107	40.989
1100	39.878	80.374	40.496
1200	41.574	81.579	40.005
1300	43.210	82.723	39.513
1400	44.790	83.812	39.022
1500	46.318	84.849	38.531
1600		85.838	
1700		86.783	
1800		87.688	

Table 9. Calculated Values of Sigma Used in the Second Law Analysis of the GaF_3 Data

Temperature (°K)	Sigma	Temperature (°K)	Sigma
867	24.606	769	33.417
942	19.326	804	29.998
916	21.248	876	23.966
972	17.516	900	22.489
899	22.485	940	19.504
854	26.061	890	23.112
829	28.180	855	25.750
955	18.455	798	30.582
931	20.062	880	24.018
995	15.932	837	27.331
1015	14.783	815	29.187
883	23.374	917	21.125
842	26.730	771	33.013
808	29.601	786	31.731
947	19.027	955	18.252
855	26.339	787	31.586
926	20.493	738	36.259
904	21.919	765	33.983
814	28.950	714	39.010
864	24.783	779	32.442
777	32.349	752	34.962
846	26.632	725	37.570
831	27.855	826	28.038
891	22.996	802	29.915
756	34.523	815	29.190
794	30.967		

Table 10. Radius ratios, heats of dimerization, and heats of sublimation to monomers for metal trihalides at 298°K.

System	r^{+3}/r^{-1}	$-\Delta H°$ dimerization	$\Delta H°$ sublimation	Ref.
LaF_3	0.85	59.3*	107.0	39, 40
CeF_3	0.82	56.6*	102.2	30, 39
GaF_3	0.46	40.9*	58.8	This work
AlF_3	0.37	51.4	72.0	28
$FeCl_3$	0.35	35.4	35.0	28
$AlCl_3$	0.28	30.2	29.0	28
$AlBr_3$	0.26	29.3	24.9	28
AlI_3	0.23	23.0	24.9	28

* Corrected to 298°K using $\Delta Cp = 4$ cal/deg for the reaction 2 monomer → dimer as estimated by Skinner and Searcy[16] for LaF_3.

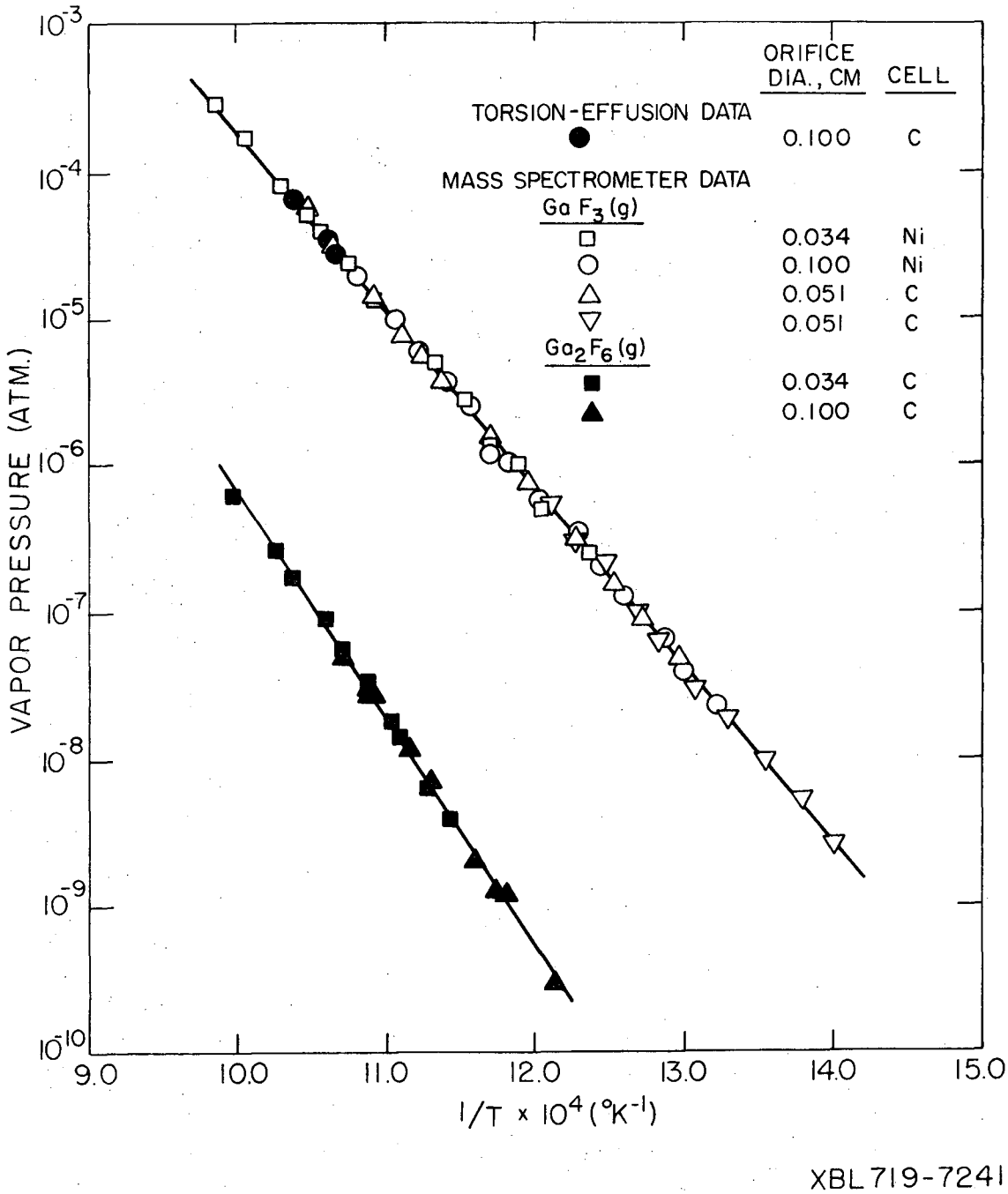


Fig. 1. Vapor pressure of gallium trifluoride.

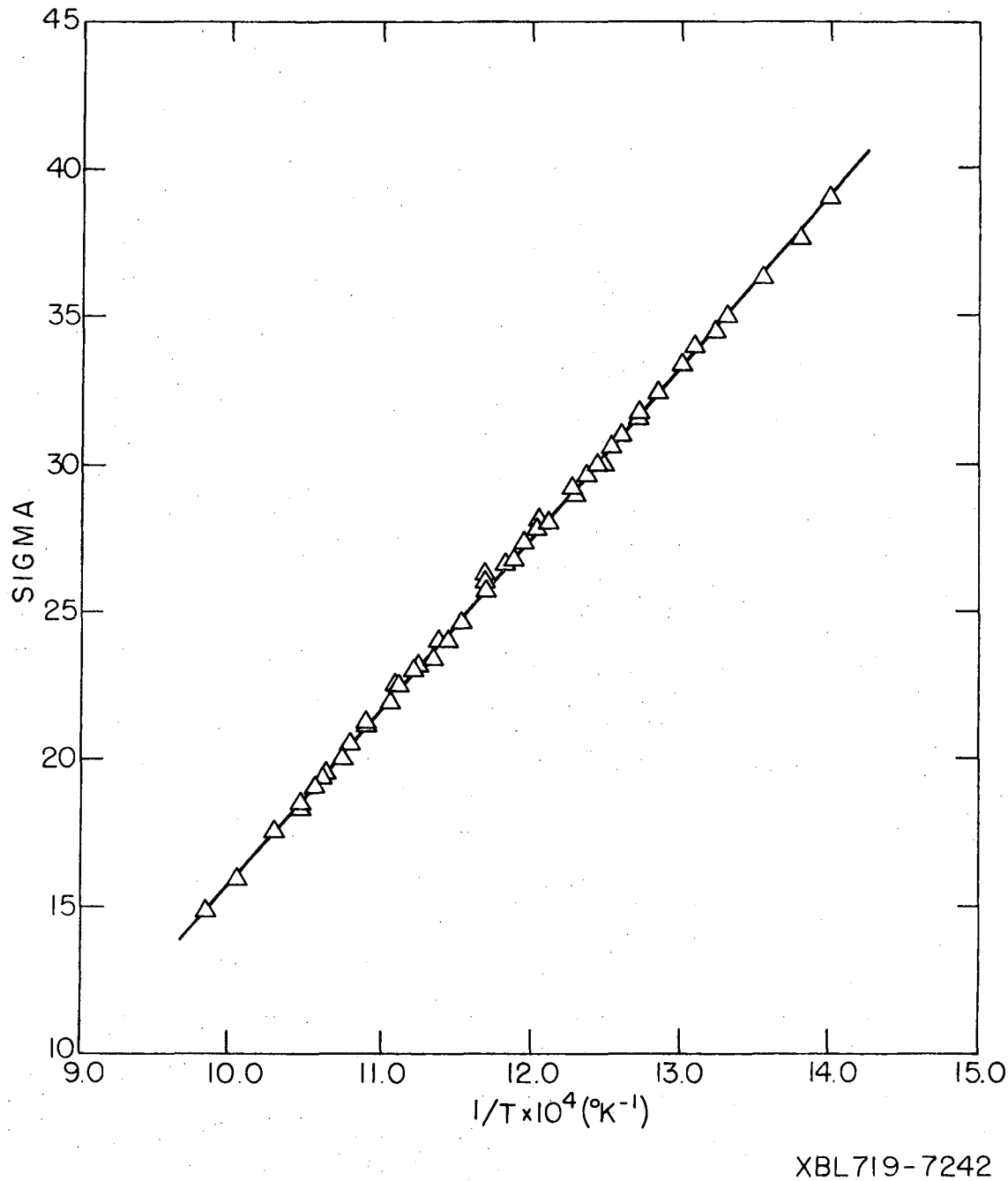


Fig. 2. Sigma Plot.

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