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THE VAPOR PRESSURES OF GALLIUM TRIFLUORIDE MONOMER AND DIMER

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ABSTRACT

The partial pressures of $GaF_3(g)$ and $Ga_2F_6(g)$ in equilibrium with solid gallium trifluoride were measured using a mass spectrometer and 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.

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% molybdenum and 0.002% iron to be the principal metallic impurities.

A. Mass Spectrometer Studies

The Atlas CH-4 mass spectrometer used throughout the investigation was a 60° sector, 24 cm radius, magnetic deflection device which was equipped with a 16-stage electron multiplier using Cu-Be dynodes. 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 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 runs were made in the graphite cell using lead as a standard. The first run of 14 points 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, where the reported error is the standard deviation from the mean. The second run of eight points 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 shutterable 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 partially shutterable 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 and $Ga_2F_5^+$ is the expected 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 run to run 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 and ion efficiency 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 had been achieved. The results of linear least squares treatments of the data from each run 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 run 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 midpoints 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 runs 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 runs 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 used 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 to 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. Our 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 overnite storage in the apparatus 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) effused 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 (~ 10^{-5} torr.) is approximately 2 orders of magnitude higher than that in the mass spectrometer.

To minimize interference from hydrolysis a second run was made 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 accumulation 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.

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 illustrated in Fig. 1.

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 $Cp = 18.8 + 10.4 \times 10^{-3}T$ 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 yield a value for Cp 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 $GaF_3(g)$.

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. $k\Delta/\ell^2$ 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,[29] the vibrational frequencies for $GaF_3(g)$ were calculated to be 575.3 cm^{-1}, 217.9 cm^{-1}, 686.2(2) cm^{-1}, and 213.1(2) cm^{-1}.

The electronic contribution to the heat capacity was assumed to be the same as that for Ga^{+3} ion.[30] Brewer et al.[31] 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 and the equation $Cp = 19.361 + 2.886 \times 10^{-4}T - \frac{2.983 \times 10^5}{T^2}$ was fitted to the values.

The free energy functions for solid and gaseous GaF_3 were calculated from the estimated heat capacities and entropies. These results are given in Table 4 at 100° intervals over the temperature range from 300°K to 1800°K. The free energy functions for the gas and the solid when combined with the absolute pressure datum points 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.

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. 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 runs with the mass spectrometer showed systematic errors in temperatures and temperature dependence to be low, greater confidence can be 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 datum 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 ± .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 4.352×10^{-2} atmospheres. This result differs markedly from the approximate value of 1225°K ± 50°K reported by Hannebohn and Klemm.[32] 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 were 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 shown 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.[33] 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[34] 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.[35] Among Brewer's comments are the following:

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 5 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.

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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° 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. Calculated Free Energy Functions for GaF_3

Temp. (°K)	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_s$	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_g$	$-\left(\frac{\Delta F_T^\circ - \Delta H_{298}^\circ}{T}\right)_{sub}$
	(cal/°)	(cal/°)	(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 5. 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	76.4*	107.0	16,37
CeF_3	0.82	65.6*	102.2	36,38
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.

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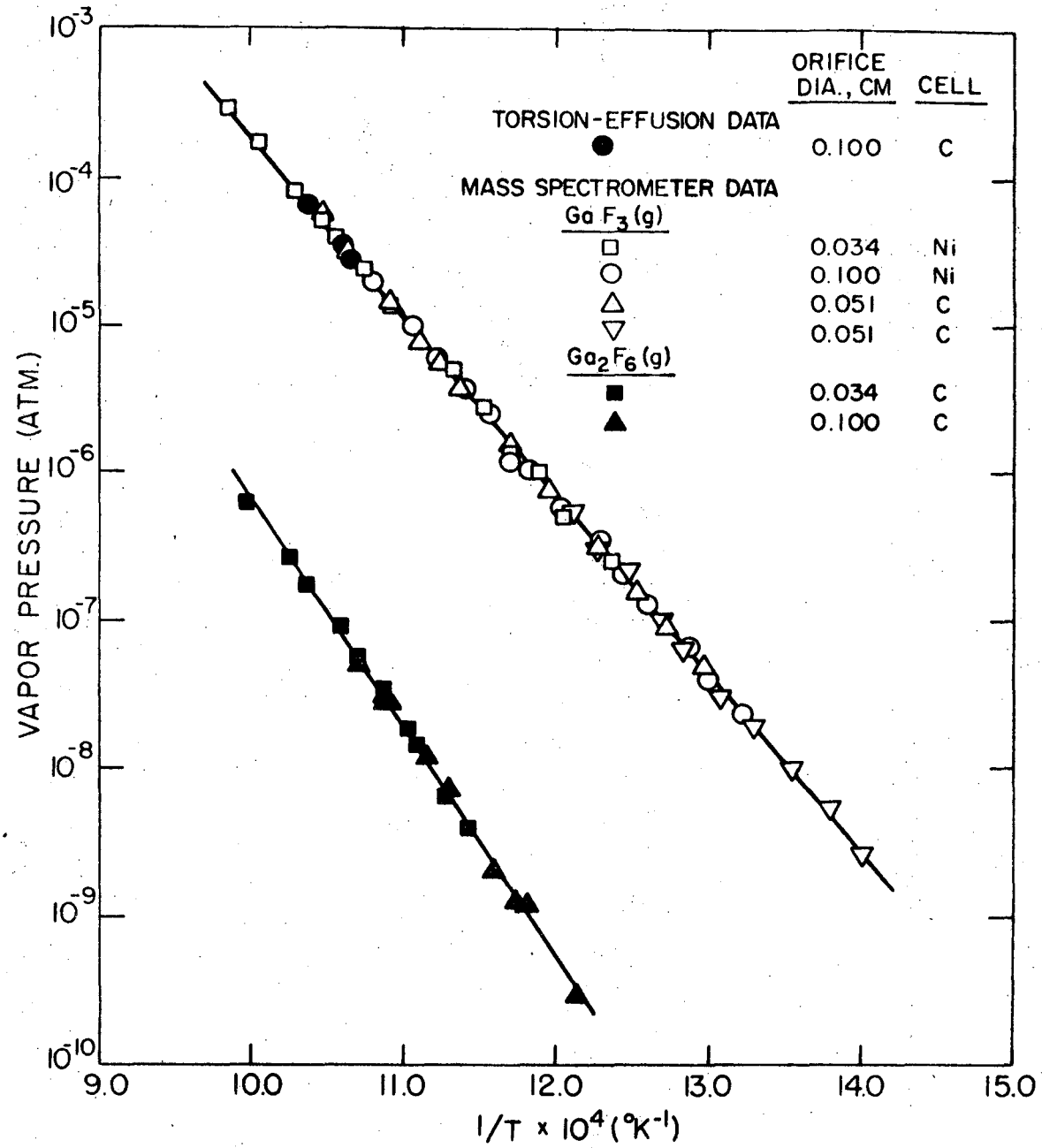

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Fig. 1. Vapor pressure of gallium trifluoride.

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