

MASS SPECTROMETRIC AND THERMOCHEMICAL STUDIES OF THE MANGANESE FLUORIDES

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SUMMARY

Mass spectrometric, calorimetric, thermal analysis and X-ray diffraction studies have been performed on MnF_2 , MnF_3 and MnF_4 . The heat capacity of MnF_2 has been measured from 330°K to 770°K. $D(\text{MnF}-\text{F})$, $D(\text{MnF}_2-\text{F})$ and $D(\text{MnF}_3-\text{F})$ have been determined to be 126 ± 7 , 79 ± 6 and 62.3 ± 2.4 kcal mole⁻¹, respectively. The uncorrected electron impact ionization potentials of MnF , MnF_2 , MnF_3 and MnF_4 are 8.41, 11.18, 12.25 and 13.15 eV, all ± 0.1 eV, respectively. Evidence for the phase $\text{Mn}_2\text{F}_5(\text{c})$ has been found. MnF_3 is far more volatile and stable than previously believed. The vapor pressure of MnF_3 (769–930°K) is given by

$$R \ln P_{\text{atm.}} = \frac{-(67.66 \pm 0.5)10^3}{T} - 4 \ln T + 78.54 \pm 0.7$$

MnF_4 exerts about 10^{-9} atm of fluorine pressure at room temperature and about 10^{-6} atm of sublimation pressure at 600°K. $\text{MnF}_4(\text{c})$ is 10.5 ± 2 kcal mole⁻¹ more stable than $\text{MnF}_3(\text{c})$ at 298°K. Formation and atomization enthalpies for MnF , MnF_2 , MnF_3 and MnF_4 have been derived from these new data and a critical review of existing data. No evidence was found for MnF_5 , MnF_6 or MnF_7 .

A simple method of removing much of the ambiguity from electron impact threshold measurements is reported.

INTRODUCTION

The thermochemistry of the manganese–fluorine system is incomplete from several points of view. Although the large number of valence states exhibited by manganese offers the opportunity to observe the trends in the Mn–F bond dissociation energy (D), the formation enthalpies of MnF , MnF_2 , MnF_3 and MnF_4 are, practically speaking, unknown. The fluorides of Mn^{V} , Mn^{VI} , and Mn^{VII}

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have not been reported. This paper presents the results of mass spectrometric and thermochemical studies of the Mn-F system, including a search for MnF_5 , MnF_6 and MnF_7 and a set of $D(\text{MnF}_x\text{-F})$ values ($x = 0,1,2,3$). In the course of these experiments some new insight into the technique of ionization threshold measurement was gained and a quick but apparently accurate method was developed. Since these points are of practical and theoretical interest they are discussed in detail.

EXPERIMENTAL

For this work several modifications were made to the mass spectrometer-molecular beam apparatus described earlier¹. The tantalum foil radiation shields were replaced by 99.5% nickel foil shields because of the much lower reactivity of nickel toward fluorine and fluorides. A second, resistance-heated, tungsten filament was added to the molecular beam oven directly below the effusion cell. Power to this filament was adjusted to minimize axial temperature gradients which are frequently the greatest error source in mass spectrometric measurements of vapor pressures. As before, cell temperatures were measured with Chromel-Alumel thermocouples, two in the cell wall at the top and two in the cell base wall. One was selected to operate the beam source temperature control, the others were monitored potentiometrically. By using Teflon seals² to bring the wires into the vacuum envelope it was possible to eliminate lead junctions other than those measured and the 273°K reference junctions. Internal consistency between the indicated temperatures was generally within 2 degrees once the axial temperature gradient had been removed. When the thermocouples were checked at the melting point of lead prior to installation, no deviation from the tabulated e.m.f. values could be detected. Cylindrical effusion cells of 99.5% nickel were used. In several experiments the cell top was replaced by one which was bored out to the full inside diameter of the cell so that smaller cells fabricated from alumina, sintered CaF_2 , or platinum foil could be inserted. For the Ni cells the sample-area-to-orifice-area ratios were approximately 1000 while the orifice diameters were 0.050 cm. For the alumina and CaF_2 cells the area ratios were nearer to 50, largely because of the difficulty in producing small orifices in these materials. In the experiments requiring the introduction of fluorine a second molecular beam assembly was used in which fluorine from an external supply at 1 atm was leaked into a nickel effusion cell through a Monel needle valve and a 3 mm diameter nickel tube connected to the cell base with a swaging fitting. To aid in establishing equilibrium between the gas and sample the cell base was filled with sample to a depth of 8 mm. This apparatus was used for *in situ* preparation of $\text{MnF}(\text{g})$ via the high-temperature reduction of MnF_2 with Mn, and of MnF_3 and MnF_4 via direct fluorination of commercial, high-purity MnF_2 (Analysis: F⁻, 100.9% of theoretical value; Mn²⁺, 100.6% of theoretical value) at $\leq 870^\circ\text{K}$ and $\leq 750^\circ\text{K}$, respectively.

For sublimation studies, MnF_3 was prepared by passing fluorine at 1 atm over MnF_2 in a Ni boat at 600–750°K. The boat and its container, a Al_2O_3 tube of purity > 99%, were previously fluorinated at 900°K. Following a 2–3 h fluorination the sample was allowed to cool in the fluorine stream which was then replaced with dry N_2 . The reaction vessel tube was enclosed in a plastic bag and transferred to an inert atmosphere box. Subsequent manipulations were performed *in vacuo* or in H_2O - and O_2 -free N_2 and using Ni or Teflon implements.

The vapor pressure of MnF_3 was measured by an internal, absolute calibration technique described elsewhere³.

The P, T data were subjected to least-squares analysis for the best fit to an equation of the form

$$R \ln P - \Delta C_p \ln T = \frac{\Delta H_1}{T} + B \quad (1)$$

If ΔC_p could not be reliably estimated or if the temperature range was small it was taken as zero so that $\Delta H_1 = \Delta H$, the enthalpy change. The least-squares program used, described by Williamson⁴ and modified by Prof. D. M. Schrader of Marquette University, utilizes estimated uncertainties in each T and P value to calculate the standard deviations of the slope and intercept. This is believed to be more realistic than the usual assumption that T values are exact for purposes of calculating standard deviations.

Chemical analyses for total Mn were performed colorimetrically by converting to MnO_4^- . Mn^{3+} was determined iodimetrically and F^- was found by thorium nitrate titration after decomposition by steam distillation.

Debye–Scherer powder patterns were obtained with 2–4 h exposure to unfiltered Fe radiation.

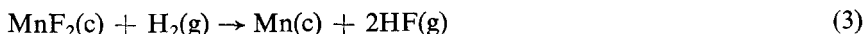
Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were performed on MnF_3 with a Mettler ThermAnalyser operated under vacuum and using Pt cells.

Heat capacity measurements were made with a Perkin–Elmer differential scanning calorimeter (DSC) using a technique described previously⁵. Sample pans and covers were 99.9% Ni foil previously fluorinated at 750°K. Samples were weighed to $\pm 20 \mu\text{g}$ before and after each run. After loading the sample, the DSC was evacuated and then back-filled with nitrogen which had been deoxygenated with BTS catalyst⁶ and dehydrated with Linde 3X molecular sieve. Sapphire was used as the reference material⁷. At least three measurements were made at each temperature on each of three samples. The temperature scale was calibrated to within $\pm 2^\circ$ using high purity Ga, In, Sn, Pb and Zn as standards.

The DSC was also used in attempts to measure ΔH for



and for



The method used to measure IP and AP values was a variation of the "semi-log" (SL) method⁸ in which the partial pressure of the unknown material is adjusted to give the same, arbitrary 50 eV (or 70 eV) ion current I as the calibrant, then I is measured at regular decrements of the electron accelerating voltage V down to a value as close as possible to the threshold. The data, when plotted as $\log [I(V)/I(50)]$ vs. V , are usually found to be parallel curves which become linear close to the threshold. Curve separations at a given value of $\log [I(V)/I(50)]$ are equal to the differences in the IP or AP values within 0.1 eV in general⁹. It has been pointed out that the above normalization is unnecessary and, in fact, undesirable because of all the processes contributing to the 50 eV current only simple or dissociative ionization, as the case might be, remains as the threshold is approached⁹. Another SL method has been described which avoids normalization by measuring curve separations as the voltages at which the slopes equal $2kT/3$ ¹⁰ or $kT/2$ ^{11,12}. If auto-ionization, internal energy or Franck-Condon factors do not grossly affect the threshold behavior, it is possible to derive an expression showing that by adjusting certain operating conditions, e.g. sample partial pressure, detector gain or ion transmission efficiency, so as to make the $\log [I(V)]$ vs. V curve for the unknown parallel to that of the calibrant, the curves will be separated by the differences in the IP or AP values for the two processes. The 50 eV normalization procedure should thus be regarded as merely a convenient means of approximating these operating conditions. The derivation is as follows: the rate of ion formation at V , $N_i(V)$, due to the thermal spread is given by

$$N_i(V) = \int_{U=0}^{U=\infty} P(E) dN_e(U) \quad (4)$$

where $P(E)$, the probability of ionization, is proportional to the total electron energy E in excess of the threshold value V_{c_i} . That is,

$$\begin{aligned} P(E) &= \alpha_i(E - V_{c_i}) && \text{if } E \geq V_{c_i} \\ P(E) &= 0 && \text{if } E \leq V_{c_i} \end{aligned}$$

α_i being a sample-dependent constant and $dN_e(U)$ the Maxwell-Boltzmann distribution function, i.e. the number of electrons with thermal energies between U and $U + dU$ emitted from the filament per unit time,

$$dN_e(U) = \alpha_1 U \exp\left(\frac{-U}{kT}\right) dU \quad (5)$$

where α_1 is a sample-independent constant. Integrating equation (5) at a constant temperature gives

$$N_i(V) = \alpha_2 \alpha_i (V - V_{c_i}) + 2kT \quad \text{if } V \geq V_{c_i} \quad (6)$$

$$N_i(V) = \alpha_2 \alpha_i (V_{c_i} - V + 2kT) \exp\left(-\frac{V_{c_i} - V}{kT}\right) \quad \text{if } V \leq V_{c_i} \quad (7)$$

The region of interest here is that represented by equation (7). To equate $N_i(V)$ to what one actually measures, the detector output, $T_i(V)$, requires accounting for non-unity precursor density in the ion source, source collection losses and analyzer and detector discrimination:

$$I_i(V) = G_i \tau_i n_i \alpha_s N_i(V) \quad (8)$$

where G_i is the detector gain, τ_i , the analyzer transmission efficiency¹³, n_i , the number density of precursor molecules and α_s the source collection efficiency. Using equation (8) to eliminate $N_i(V)$, equation (7) becomes

$$I_i(V) = \alpha_3 \alpha'_i (V_{c_i} - V + 2kT) \exp\left(-\frac{V_{c_i} - V}{kT}\right) \quad (9)$$

where α_3 combines all sample-independent constants and α'_i combines all sample-dependent constants given in equation (8) with α_i . Equation (9) shows that if one experimentally or mathematically adjusts the value of α'_i for the unknown so that it equals that of the reference sample, i.e. $\alpha'_i = \alpha'_j$, then the I vs. V curves will be identical for corresponding values of $V_{c_i} - V$. This is the basis for the extrapolated voltage difference method¹⁴. To avoid the asymptotic approach to $I = 0$, one may plot the data as

$$\ln [I_i(V)] = \ln \alpha_3 + \ln \alpha'_i + \ln (V_{c_i} - V + 2kT) - \frac{V_{c_i} - V}{kT} \quad (10)$$

Again, when α'_i is set equal to α'_j the plots of $\ln [I_i(V)]$ and $\ln [I_j(V)]$ will be parallel and separated, at a given value of $\ln [I]$, by $V_{c_i} - V_{c_j}$. This is the basis for the method used here and is an alternative to Honig's approach. Since the plot of $\ln [I_i(V)]$ vs. V in this region has a slowly varying slope and since differing values of the sample-dependent constant merely shift the curve in the $\ln [I_i]$ direction, it is clear that the "normalization" required, experimentally or mathematically, assures that the $V_{c_i} - V_{c_j}$ separation is measured between corresponding portions of the reference and unknown curves. Although no expression has been developed which describes the current-voltage relation from threshold to 50 eV or higher, this analysis suggests that the normalization procedure amounts to equating the reference and unknown sample constants. Preliminary work here indicates that inclusion of a filament voltage-drop effect in the equations will not alter the conclusions drawn above.

For IP and AP studies the electron energy supply was altered to permit automatic scanning at the rate of 2 V min⁻¹ and the scanned voltage used to drive the x-axis deflection of an X-Y recorder (Bolt, Beranek, and Newman model 715). By using the zero-offset capability of the recorder it was possible to record data with a calibrated $1.00 \pm 0.1\%$ V in⁻¹ sensitivity over any 10 volt range, e.g. 8-18 V. The electron energy was simultaneously monitored with a calibrated digital voltmeter. The output of the mass spectrometer's secondary electron multiplier was fed into a Keithley 416 picoammeter modified to provide a logarithmic

response to input currents by replacing one of the input resistors with a 2N930 transistor connected base-to-input, emitter-to-output, and collector open. Using a picoampere supply the response of this configuration was found to be logarithmic from 1×10^{-6} A to about 1×10^{-12} A. Below 10^{-12} A non-logarithmic behavior became noticeable but not troublesome. The picoammeter output provided the recorder's y -axis signal, so scanning the electron energy while focused on the ion of interest produced a continuous plot of $\ln [I(V)]$ vs. V . The general procedure for determining an unknown IP or AP value was as follows. Vapors of a calibrant were admitted to the mass spectrometer through a leak valve until the 50 eV signal was approximately 10^{-7} A. The focus and ion energy potentials, the only adjustable ion source potentials, were optimized and locked. The electron energy was then reduced to below the threshold. Several trial scans were made while adjusting the recorder's y -axis gain so as to give full-scale y -axis deflection within 2 eV above the onset of ionization. In effect, this meant that recorded currents were between 0.2 and 2.0% of the 50 eV values, a range quite comparable to those encountered in the VC and SL method¹². After recording \log (ion current) vs. V for the first calibrant, another was introduced and its partial pressure adjusted until its curve paralleled the first, and so on until up to six calibrant curves had been plotted on the same graph. Reproducibility of the relative curve positions was better than 0.1 eV. The IP or AP value of the unknown was determined by generating the necessary parent species in the molecular beam source at an intensity such that the curve for the unknown paralleled those of the calibrants. Reading directly from the chart the distance between the curve for the unknown and those of the calibrants, at the 1% level and below, thus became the differences between the IP and AP values. Following this, one or more calibrants were re-introduced into the mass spectrometer and their curves re-drawn. If displaced by more than 0.1 eV from the previous position the unknown was re-run.

The ion source was typically operated at an ion energy of 15 eV and a focus potential of 50 eV, both referenced to ground. The trap current was regulated at 20 μ A so the trap electrode was only 0.2 V from the rest of the ion source due the drop in the 10 k Ω sensing resistor in the regulation circuit. With the large trap electrode area and the large ionization region, this trap current represents a lower charge density than that expected in the ion source of, say, a magnetic deflection mass spectrometer operating at a few microamperes of trap current, so space charge effects should be negligible⁹. In practice the only serious difficulty encountered was non-linearity in the energy scale which appeared when the regulation circuit caused the current through, and the voltage drop across, the emitting filament to change as the electron accelerating voltage was scanned. With a clean, annealed filament a 20 μ A beam could be maintained from 7 eV to over 20 eV with no perceptible change in filament current as measured with an 0-5 A meter in series with the filament.

RESULTS

Figure 1 shows the electron impact results on five calibrants obtained at room temperature along with MnF_2^+ and MnF^+ obtained from a MnF_2 beam originating in the Ni cell at 1100°K . Comparison of the average separations between calibrant curves in the lower half of Figure 1 with IP differences from the literature¹⁵ gave 0.08 eV as the average deviation, *i. e.* $\sum_i [(V_{c_i})_{\text{lit.}} - (V_{c_i})_{\text{obs.}}] / 5$. The results obtained for $\text{IP}(\text{MnF}_2)$ and $\text{AP}(\text{MnF}^+/\text{MnF}_2)$ in the first run are summarized in Table 1. The entire process was then repeated. The average of the two runs were $\text{IP}(\text{MnF}_2) = 11.18$ eV and $\text{AP}(\text{MnF}^+/\text{MnF}_2) = 13.29$ eV. Typically, the average deviation found for a particular value of IP or AP was 0.07 eV in a given run.

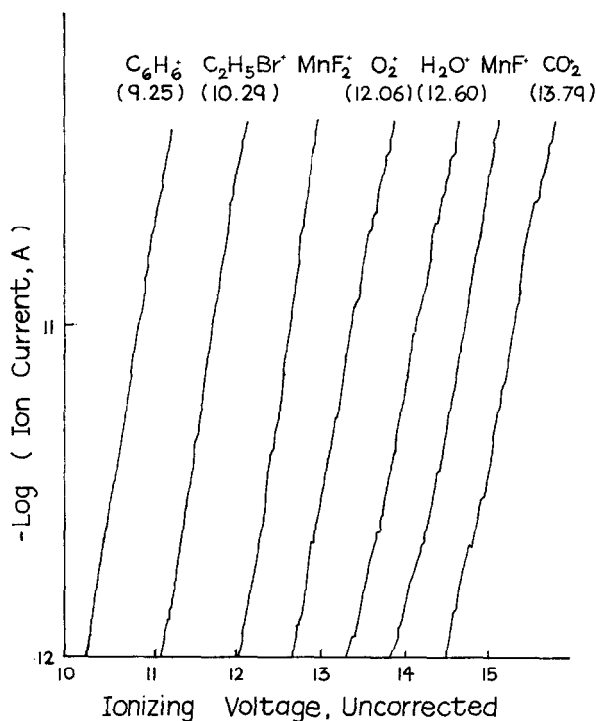


Fig. 1. SL plot determination of $\text{IP}(\text{MnF}_2)$ and $\text{AP}(\text{MnF}^+/\text{MnF}_2)$.

The electron impact fragmentation pattern for MnF_2 is given in Table 2. To avoid the strong dependence of ion transmission efficiency on ion mass known to exist in the quadrupole mass filter these patterns were obtained with the resolution reduced sufficiently to allow practically total transmission of the ionic species. This method gives essentially the same pattern as that obtained when the data obtained in the conventional mode of operation are corrected using experimentally

TABLE 1

TYPICAL IONIZATION THRESHOLD RESULTS FOR Mn FLUORIDES^a

	Calibrant (Calibrant IP)	C ₆ H ₆ (9.25)	C ₂ H ₅ Br (10.29)	O ₂ (12.06)	H ₂ O (12.60)	CO ₂ (13.79)	F ₂ ⁺ (15.69)	Average
From MnF ₂ at 1100°K	MnF ₂ ⁺ (IP)	+1.83	+0.92	-0.69	-1.40	-2.60		(11.21)
		(11.08)	(11.21)	(11.37)	(11.21)	(11.19)		
	MnF ₂ ⁺ (AP)	+4.17	+2.90	+1.33	+0.60	-0.62		(13.27)
		(13.42)	(13.19)	(13.39)	(13.21)	(13.17)		
From MnF ₃ at 870°K	MnF ₃ ⁺ (IP)		+2.00	+0.13	-0.29		-3.38	(12.27)
			(12.29)	(12.19)	(12.30)		(12.31)	
	MnF ₂ ⁺ (AP)		+4.20	+2.40	+1.88		-1.10	(14.50)
			(14.49)	(14.46)	(14.49)		(14.58)	
From MnF ₄ at 700°K	MnF ₄ ⁺ (IP)		+2.86	+0.95	+0.56	-0.63	-2.55	(13.13)
			(13.15)	(13.01)	(13.17)	(13.16)	(13.14)	
	MnF ₃ ⁺ (AP)		+4.82	+2.95	+2.55	+1.37	-0.55	(15.11)
			(15.11)	(15.01)	(15.15)	(15.16)	(15.14)	

^a Data given in eV above (+) or below (-) the calibrant. The IP or AP is shown in parenthesis.

determined ion transmission efficiencies¹³. Since the background was very low within the 3 a.m.u. "window" existing under these conditions the spectra should be comparable to those found with non-discriminating mass spectrometers.

TABLE 2

ELECTRON IMPACT FRAGMENTATION PATTERNS FOR MnF₂, MnF₃ AND MnF₄

Precursor Ion	MnF ₂	MnF ₃		MnF ₄	
	70 eV	70 eV	50 eV	50 eV ^a	70 eV
Mn ⁺	36	28	23	20.2	37
MnF ⁺	100	29	30	100.0	23
MnF ₂ ⁺	38	100	100	35.3	49
MnF ₃ ⁺	—	33	35	3.2	100
MnF ₄ ⁺	—	—	—	—	28

^a Ref. 16.

For the electron impact studies on MnF₃, benzene was replaced by fluorine because the former was found to alter the emission of the ionization filament thereby causing a small shift in the filament voltage drop. MnF₃ was formed by passing F₂ over MnF₂ at 870°K at which temperature the vaporization of MnF₂ is negligible. Preliminary results indicated IP(MnF₃) = 12.2 ± 0.2 eV and AP(MnF₂⁺/MnF₃) = 14.4 ± 0.2 eV. The data summarized in Table 1 were then taken. As a final check the O₂⁺, MnF₃⁺, MnF₂⁺ and F₂⁺ curves were repeated giving IP(MnF₃) = 12.24 and AP(MnF₂⁺/MnF₃) = 14.44 eV. The best values

have therefore been taken to be 12.25 and 14.47 eV, respectively. The mass spectrum of MnF_3 , Table 2, shows both MnF_2^+ and MnF_3^+ to be far more abundant, relative to MnF^+ , than found by Zmbov and Margrave¹⁶. It should be noted that MnF_4^+ was not found under our operating conditions and that the same spectrum resulted without a fluorine flow if the prior fluorination was done below 700°K so as to retain the MnF_3 as it formed. Interestingly, the spectrum of commercial MnF_3 , in addition to revealing large amounts of SiF_4 , HF, H_2O , Cl_2 , HCl and O_2 impurities, diminished in intensity at a constant temperature, implying that the MnF_3 activity decreased. Chemical and X-ray analysis verified that these samples were roughly 50 mole %, MnF_2 after baking *in vacuo*. The likely causes of activity variation would be fluorine loss on heating or formation of a MnF_3 - MnF_2 solid solution. No evidence of fluorine evolution from MnF_3 in CaF_2 , Al_2O_3 or Ni cells could be found; however under these high temperature-low pressure conditions it would have been thoroughly dissociated and difficult to detect in the presence of our high F^+ background*. Since weight losses occurred only when MnF_3 sublimation was proceeding measurably, one can conclude that decomposition is not an important process.

The threshold potentials for MnF_4 were found to be $\text{IP}(\text{MnF}_4) = 13.13$ and $\text{AP}(\text{MnF}_3^+/\text{MnF}_4) = 15.11$ eV as shown in Table 1. Other trials gave 13.17 and values of 15.22, 15.15 and 15.28 eV, so the best values are taken to be 13.15 and 15.19 eV for $\text{IP}(\text{MnF}_4)$ and $\text{AP}(\text{MnF}_3^+/\text{MnF}_4)$, respectively. The fragmentation pattern for MnF_4 is presented in Table 2.

Repeated efforts at producing still higher fluorides in the effusion cell were unsuccessful even with as much as 10^{-4} atm of fluorine in the cell and temperatures from 330 to 750°K. It is still quite conceivable, however, that more extreme conditions could yield higher binary fluorides of manganese. The possibility that MnF_4^+ was itself a fragment of some higher fluoride was excluded by studies of its dependence on the fluorine pressure and bond energy arguments as discussed below.

When elemental Mn was heated to 1300°K in the thoroughly fluorinated Ni cell, the MnF^+ threshold was found to lie 0.98 eV above that for Mn. Since $\text{IP}(\text{Mn}) = 7.43$ eV the provisional value for $\text{IP}(\text{MnF})$ is 8.41 eV.

Although the activity variation in the MnF_2 - MnF_3 system was believed due to the formation of a solid solution, X-ray diffraction patterns obtained at room temperature from numerous residues of mass spectrometric experiments consistently showed the presence of two phases, one not identifiable with any reported compound and the other either MnF_2 ¹⁷ or MnF_3 ¹⁸. Only MnF_2 remained in samples deliberately depleted of MnF_3 by heating *in vacuo* until the effusion

* Although this high F^+ background seems to be common to mass spectrometers used to study fluorides, no explanation has been given. The ionization threshold suggests the parent is atomic fluorine.

of MnF_3 was no longer detectable mass spectrometrically. MnF_3 -rich residues exhibited the diffraction patterns of MnF_3 and the unknown phase while 50% MnF_2 -50% MnF_3 mixtures gave very intense patterns of the unknown phase. Although the MnF_2 - MnF_3 system has not been studied, it is known that $\text{CrF}_2(\text{c})$ and $\text{CrF}_3(\text{c})$ form a solid solution at elevated temperatures, which gives the compound Cr_2F_5 on cooling^{19,20}, and that the phase Fe_2F_5 exists²¹, so it seems reasonable to believe the unknown phase is Mn_2F_5 . Table 3 summarizes the average d spacings for the strongest lines of " Mn_2F_5 " found in six residues. It

TABLE 3
PARTIAL X-RAY DIFFRACTION PATTERN OF Mn_2F_5^a

Interplanar spacings (± 0.01 Å)	Intensity ^b
3.71	40
3.27	100
3.07	30
1.99	4
1.97	4
1.93	50

^a Fe radiation, 40 kV, no filter, 4 h.

^b Visual estimates.

should be noted that the melting point of MnF_3 is unknown but can be estimated as 1700°K from the fact that the respective melting points of MnF_2 , CrF_2 and CrF_3 are 1203°K²², 1160°K and 1677°K¹⁹. The sample of MnF_3 (Analysis: F⁻ = 94% of theoretical value; Mn³⁺ = 94% of theoretical value) prepared from MnF_2 gave time-independent mass spectra and an X-ray diffraction pattern in excellent agreement with that of MnF_3 ¹⁸. Averaging the sublimation pressure data for MnF_3 obtained in four separate experiments gave the relationship

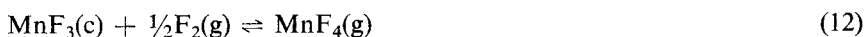
$$R \ln P_{\text{atm.}} = \frac{-(67.66 \pm 0.5)10^3}{T} - 4 \ln T + 78.54 \pm 0.7 \quad (11)$$

over the temperature range 769-930°K, where ΔC_p has been estimated as 4 cal deg⁻¹ mole⁻¹. At 850°K, the median temperature, $\Delta H_{\text{subl.}}^\circ = 64.30 \pm 0.5$ kcal mole⁻¹ while $P(\text{MnF}_3) = 7 \times 10^{-7}$ atm, three orders of magnitude greater than reported previously¹⁶. When a Pt-lined cell was used, as in the previous work, PtF_4 was formed at about 3% of $P(\text{MnF}_3)$. While the PtF_4 weight loss was negligible, this process undoubtedly contributed to the conversion of MnF_2 to MnF_3 . In a final check on $\Delta H_{\text{subl.}}^\circ$, made on MnF_3 generated *in situ*, nine points between 738 and 943°K gave $\Delta H_{\text{subl.}}^\circ = 64.31 \pm 0.3$ kcal mole⁻¹. Therefore, $\Delta H_{\text{subl.}, 850^\circ\text{K}}^\circ = 64.3 \pm 0.5$ kcal mole⁻¹ is taken as the best value. The $P = kIT$ equation²³ was used to relate $I_{\text{MnF}_3^+}$ to $P(\text{MnF}_3)$ using the internal calibration technique described elsewhere³.

DTA/TGA analysis of our sample of MnF_3 showed no transitions between room temperature and 1080°K other than the continuous sublimation endotherm beginning at 710°K . Thus equation (11) accurately represents the sublimation pressure over the stated interval.

The mass spectrum of MnF_4 subliming at $570\text{--}650^\circ\text{K}$ after *in situ* preparation was identical to that attributed to MnF_4 in the electron impact studies. The temperature dependence of MnF_4^+ in this range was found to correspond to $\Delta H^\circ_{\text{subl.}} = 31 \text{ kcal mole}^{-1}$. A duplicate determination made using $\text{MnF}_2^+/\text{MnF}_4$ as a measure of $P(\text{MnF}_4)$ from 557 to 641°K gave $34 \pm 3 \text{ kcal mole}^{-1}$. Therefore $\Delta H^\circ_{\text{subl.}}(\text{MnF}_4) = 32 \pm 4 \text{ kcal mole}^{-1}$ at 600°K , assuming that the melting point of MnF_4 is above 600°K . Even at room temperature the mass spectrum clearly showed that F_2 is evolved by MnF_4 , since the F_2^+ peak disappeared sharply and completely when the molecular beam was blocked with the shutter. Although $P(\text{F}_2)$ could not be measured, the known instrumental sensitivity gave $P(\text{F}_2) \approx 10^{-9} \text{ atm}$ at room temperature as the decomposition pressure of MnF_4 , presumably forming MnF_3 . Similarly, $P(\text{MnF}_4)$ at 600°K could be estimated as 10^{-6} atm . The decomposition of MnF_4 at temperatures much above 600°K is rapid.

The equilibrium



was studied by measuring $I_{\text{MnF}_4^+}$ while adjusting the fluorine flow into the effusion cell to keep $I_{\text{F}_2^+}$ constant. Under these conditions $P(\text{F}_2)$ is constant so $\Delta H(\text{eq. (12)})$ was found from the slope of $-R \ln (I_{\text{MnF}_4^+}/T^{1/2})$ vs. $1/T$. From the data, Table 4, and with $\Delta C_p = 0$, $\Delta H_{680^\circ\text{K}} = 23.1 \pm 0.5 \text{ kcal mole}^{-1}$ for the equilibrium depicted in equation (12). To check on the mechanism of MnF_4 formation the dependence of $I_{\text{MnF}_4^+}$ on $I_{\text{F}_2^+}$ was determined at 750°K . The slope of $\log (I_{\text{MnF}_4^+})$ vs. $\log (I_{\text{F}_2^+})$ was found to be unity for a 50 fold change in $I_{\text{F}_2^+}$. Thus, the process is $\text{MnF}_3(\text{c}) + \text{F}(\text{g}) \rightarrow \text{MnF}_4(\text{g})$ since both $P(\text{F})$ and $P(\text{MnF}_4)$ vary as the square of $P(\text{F}_2)$.

TABLE 4

MASS SPECTRAL DATA FOR THE REACTION^a $\text{MnF}_3(\text{c}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{MnF}_4(\text{g})$

T (°K)	ΔT (°K)	$I_{\text{MnF}_4^+} \times 10^{11}$ (A)	$(\Delta I/I) \times 100$
735.3	1	7.30	4
723.8	2	5.90	4
704.1	3	4.30	8
692.1	1	3.35	3
669.1	3	1.47	8
654.1	1	1.07	4
644.1	1	0.83	3
604.1	3	0.47	5

^a $\Delta H_{680^\circ\text{K}} = 23.1 \pm 0.5 \text{ kcal mole}^{-1}$.

No transitions could be detected in MnF_2 between room temperature and 773°K using the DSC. The heat capacity data, summarized in Table 5, were fitted to an equation of the form $C_p = a + bT + cT^2$ for $T = 330^\circ\text{K}$ to $T = 770^\circ\text{K}$. For this purpose each point was given a statistical weight proportional

TABLE 5

THE HEAT CAPACITY OF $\text{MnF}_2(\text{c})$

T (°K)	C_p (cal deg ⁻¹ mole ⁻¹)	ΔC_p (cal deg ⁻¹ mole ⁻¹)
330.0	16.4	0.2
340.0	16.6	0.2
350.0	16.7	0.2
400.0	17.2	0.0
410.0	16.9	0.3
420.0	17.3	0.5
430.0	17.5	0.6
440.0	17.6	0.4
450.0	17.8	0.4
500.0	18.0	0.3
550.0	17.9	0.6
600.0	18.4	0.5
650.0	18.6	0.7
700.0	19.4	0.2
750.0	19.5	0.6
770.0	19.9	0.4

to $(1/\Delta C_p)^2$ where the ΔC_p values shown are our average deviations. The appreciable scatter in our data appears to be caused by roughly 2% variations in the amplitude measurements. Since this is essentially a random effect, each value shown, being the average of up to nine determinations, should be uncertain by less than 2%. The smoothed C_p values obtained from the "best fit" of our data:

$$C_p = 13.103 + 1.14 \times 10^{-2}T - 3.55 \times 10^{-6}T^2 \quad (330\text{--}770^\circ\text{K}, \pm 2\%) \quad (13)$$

are listed in Table 6 along with the derived thermal functions. While these data should be regarded as approximations they can be used without significant loss in accuracy for purposes of determining the various reaction enthalpies. It should be noted that temperature uncertainties are quite negligible for such slowly varying C_p data. Equation (13) gives C_p values at 300, 310 and 320°K , respectively of 16.2, 16.3 and 16.4 cal deg⁻¹ mole⁻¹ compared to literature values²⁴ of 16.27, 16.44 and 16.60 cal deg⁻¹ mole⁻¹.

Attempts at measuring $C_p(\text{MnF}_3(\text{c}))$ were abandoned because of a lack of reproducibility exhibited by the data. MnF_4 was not studied owing to its instability.

Although equation (3), the reduction of MnF_2 , is thermodynamically permitted in the temperature range accessible to the DSC (773°K max.) if the product

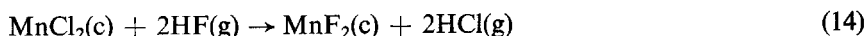
HF is swept away as it forms, no indication of the reaction was found using flowing 10% H₂ in Ar at 1 atm as the atmosphere. Under the same conditions MnF₃ was reduced to MnF₂ between 650 and 750°K. The reproducibility of the weight loss and ΔH (equation (2)) values was poor, however. ΔH (equation (2)) appeared to be 20 ± 10 kcal mole⁻¹ at 700°K.

TABLE 6
SOME THERMAL FUNCTIONS FOR MnF₂(c)

<i>T</i> (°K)	<i>S_T</i> — <i>S₂₉₈</i> (cal deg ⁻¹ mole ⁻¹)	<i>H_T</i> — <i>H₂₉₈</i> (cal mole ⁻¹)	<i>C_p</i> (cal deg ⁻¹ mole ⁻¹)
300	0.10	30	16.2
400	4.89	1700	17.1
500	8.80	3450	17.9
600	12.13	5280	18.7
700	15.06	7180	19.4
800	17.69	9150	20.0
900	20.07	11 200	20.5
1000	22.26	13 300	21.0
1100	24.28	15 400	21.4
1200	26.15	17 500	21.7

CONCLUSIONS

Obviously, an accurate value for $\Delta H_f(\text{MnF}_2(\text{c}))$ is essential in defining the thermochemistry of the manganese fluorides. Jellinek and Rudat²⁵ obtained the equilibrium constant for equation (3) at 873, 973 and 1073°K but because of the low HF yields only estimated ΔH_f as -190 kcal mole⁻¹ by the third law. Using the thermal functions for H₂ and HF²⁶, Mn²⁷ and MnF₂ (Table 6) these data give $\Delta H_f(\text{MnF}_2(\text{c})) = -182$ to -186 kcal mole⁻¹ at 298°K. A second-law analysis of their data gives $\Delta H_f = -150$ kcal mole⁻¹. On the other hand, from a study²⁸ of the reaction



$\Delta H_{673^\circ\text{K}}$ (equation (14)) = 6122 cal mole⁻¹, leading to $\Delta H_{f, 298^\circ\text{K}}(\text{MnF}_2(\text{c})) = -206$ kcal mole⁻¹ by the second law using literature data on HCl, HF and MnCl₂^{29, 30, 31, 32}. The same data give $\Delta H_{f, 298^\circ\text{K}}(\text{MnF}_2(\text{c})) = -202$ kcal mole⁻¹ via the third law. Jellinek and Koop²⁸ also repeated the study of equation (3). Their data give $\Delta H_{f, 298^\circ\text{K}}(\text{MnF}_2(\text{c})) = -189$ to -193 kcal mole⁻¹ (second law) and -175 kcal mole⁻¹ (third law). From solubility and related data $\Delta H_{f, 298^\circ\text{K}} = -204.6$ kcal mole⁻¹³³. Excluding the inherently more difficult equation (3) studies, a value of -203 ± 5 kcal mole⁻¹ for $\Delta H_f(\text{MnF}_2(\text{c}))$ at 298°K is indicated, compared to the previously accepted values of -189.5 kcal mole⁻¹ by Mah³⁴ and -190

± 5 kcal mole⁻¹ by Brewer *et. al.*³⁵ which relied heavily on the Jellinek-Rudat data. Clearly, additional efforts should be made towards determining $\Delta H_f(\text{MnF}_2)$. The sublimation of MnF_2 has been studied with microbalance³⁶ and mass spectrometric³⁷ effusion techniques. For third-law analyses of the data, the thermal functions for $\text{MnF}_2(\text{g})$ were calculated for a linear model with $r(\text{Mn-F}) = 1.93 \text{ \AA}$, ${}^6\Sigma$ ground state and with $\omega_1 = 569 \text{ cm}^{-1}$, $\omega_2 = 132 \text{ cm}^{-1}$ and $\omega_3 = 740 \text{ cm}^{-1}$. The radius was estimated from the Mn-F distances in crystalline MnF_2 and MnF_3 , the degeneracy is that of Mn^{2+} , ω_2 and ω_3 are gas-phase values derived from matrix isolation spectra^{38,39} and ω_1 was calculated from ω_3 using Herzbergs's valence force field equations⁴⁰. The major difference between these results (Table 7) and the previous estimates⁴¹ arises almost entirely from the larger ω_2 value.

TABLE 7

SOME THERMAL FUNCTIONS FOR $\text{MnF}_2(\text{g})$

T (°K)	C_p (cal deg ⁻¹ mole ⁻¹)	S	$(G-H_{298^\circ\text{K}})/T$	$H_T-H_{298^\circ\text{K}}$ (cal mole ⁻¹)
0.0	0.0	0.0	Infinite	-3094
100.0	9.965	52.876	-75.525	-2265
200.0	11.495	60.277	-66.219	-1188
298.0	12.650	65.096	-65.096	0
300.0	12.668	65.174	-65.096	23
400.0	13.409	68.929	-65.603	1330
500.0	13.858	71.973	-66.582	2696
600.0	14.140	74.526	-67.699	4096
700.0	14.324	76.721	-68.835	5520
800.0	14.451	78.642	-69.943	6959
900.0	14.540	80.350	-71.006	8409
1000.0	14.606	81.885	-72.018	9867
1100.0	14.656	83.280	-72.980	11 330
1200.0	14.694	84.557	-73.892	12 797

With the thermal functions from Table 6 and 7 the second-law result obtained mass spectrometrically was corrected to 298°K, giving $\Delta H_{\text{subl}}^\circ = 77.1 \pm 1.5$ kcal mole⁻¹ compared to 76.5 ± 1.0 and 74.4 ± 1.0 kcal mole⁻¹ from second- and third-law analyses of the microbalance-effusion work. While it is tempting to discount the third-law result as due to errors in the model, it should be noted that both second-law values are based on data spanning less than 100°K. Therefore, the preferred value for $\Delta H_{f, 298^\circ\text{K}}(\text{MnF}_2(\text{g})) = -127 \pm 7$ kcal mole⁻¹.

By a second-law analysis, the equilibrium constant data³⁷ for



give $\Delta H_{1100^\circ\text{K}}$ (equation (15)) = -14.3 ± 7 kcal mole⁻¹ which becomes -15.8 kcal mole⁻¹ at 298°K, using the thermal functions for MnF ³⁴ and Mn ³². Similarly,

third-law analysis gives $\Delta H_{298^\circ\text{K}}$ (equation (15)) = -20.7 ± 0.2 kcal mole⁻¹. Owing to uncertainties in the free energy functions and the absolute values of the equilibrium constants this quantity is probably uncertain by ± 3 kcal mole⁻¹. Thus, from the third-law value for ΔH (equation (15)) and $\Delta H_f(\text{Mn(g)})^{42}$ one obtains $\Delta H_{f, 298^\circ\text{K}}^\circ(\text{MnF(g)}) = -20 \pm 5$ kcal mole⁻¹, $D^\circ(\text{Mn-F}) = 105 \pm 4$ kcal mole⁻¹ and $D^\circ_{298^\circ\text{K}}(\text{MnF-F}) = 126 \pm 7$ kcal mole⁻¹. This analysis shows MnF and MnF₂ to be more stable than previously believed^{37,42}. It should be noted that while the electronic degeneracy and ω_e for the MnF(g) ground state are well known, an equilibrium radius and the absence of low-lying electronic states were assumed in calculating the thermal functions.

The electron impact data provide a means of approximating $D(\text{MnF}_x\text{-F})$ since

$$D(\text{MnF}_x\text{-F}) \approx \text{AP}(\text{MnF}^+_{x-1}/\text{MnF}_{x-1}) - \text{IP}(\text{MnF}_x) \quad (16)$$

The quality of this approximation improves with instrumental sensitivity, within limits, because as the ionization voltage required to produce detectable numbers of ions is reduced the kinetic and excitation energy deposited in the products is reduced. The sensitivity of the instrument used here should be sufficient to reduce these effects to insignificant levels. Unfortunately, the means of accounting exactly for effects of thermal internal energy (E_{int}) on the IP and AP values is not clear. While there is evidence that E_{int} is fully effective in lowering thresholds in some cases, it is not certain that vibration-rotation interaction is sufficiently effective in simple molecules⁴³. Fortunately, the corrections are not large and are in part self-cancelling. Assuming that E_{int} is fully effective, the IP and AP values have been corrected to 298°K with $E_T - E_{298^\circ\text{K}}$ data. Thus IP(MnF₂) and AP(MnF⁺/MnF₂) at 1100°K (11.18 and 13.29 eV) become 11.38 and 13.60 eV, respectively. Previous investigations^{37,44} gave 11.5 and 11.7 eV for IP(MnF₂) and 14.5 eV for AP(MnF⁺/MnF₂), all ± 0.3 eV and uncorrected for E_{int} effects. IP(MnF₃) and AP(MnF₂⁺/MnF₃) at 870°K (12.25 and 14.47 eV) become 12.57 and 14.79 eV, respectively, using $E_T - E_{298^\circ\text{K}}$ data for FeF₃(g)²⁶. For these processes Zmbov and Margrave reported 12 ± 0.8 eV and 13.7 ± 0.3 eV respectively, again uncorrected for thermal effects.

IP(MnF₄) and AP(MnF₃⁺/MnF₄) at 700°K (13.15 and 15.19 eV) give 13.46 and 15.50 eV, respectively, using TiF₄ data²⁶ to correct for E_{int} . At 298°K, IP(MnF) becomes 8.51 eV. Until the method used here and the corrections applied are tested, an uncertainty of ± 0.2 eV is assumed for these threshold values. Again, because of error cancelling, the D values obtained with equation (16) should be correct to within 0.2 to 0.3 eV. Thus, the electron impact values at 298°K are $D^\circ(\text{MnF-F}) = 5.09$ eV (117 ± 6 kcal mole⁻¹), $D^\circ(\text{MnF}_2\text{-F}) = 3.41$ eV (79 ± 6 kcal mole⁻¹), and $D^\circ(\text{MnF}_3\text{-F}) = 2.93$ eV (68 ± 6 kcal mole⁻¹).

Corrected to 298°K using FeF₃(c,g) thermal functions²⁶, $\Delta H^\circ_{\text{subl.}}(\text{MnF}_3)$ is 68.1 ± 1 kcal mole⁻¹. The increased uncertainty should account for errors in the

temperature correction. From $\Delta H^\circ_{\text{subl.}}(\text{MnF}_2)$ and $D^\circ(\text{F}_2)$, it is found that $\Delta H^\circ_f(\text{MnF}_3(\text{c})) = -256 \pm 14 \text{ kcal mole}^{-1}$ at 298°K compared to $-249 \pm 15 \text{ kcal mole}^{-1}$ by the DSC experiments. Under the circumstances a reduction in the uncertainties is not warranted.

The $\text{MnF}_2\text{-F}$ bond energy can also be used to estimate the equilibrium $\text{F}(\text{g})$ pressure over MnF_3 since it predicts that the process



is endothermic by $71 \text{ kcal mole}^{-1}$. Assuming ΔH does not vary appreciably with temperature and using the entropy of $\text{FeF}_3(\text{c})$ to approximate that of MnF_3 , $\Delta S_{850^\circ\text{K}}(\text{equation (17)}) = 40 \text{ cal deg}^{-1} \text{ mole}^{-1}$ whence $P(\text{F}) \approx 10^{-10} \text{ atm}$ in comparison with $P(\text{MnF}_3) \approx 7 \times 10^{-7} \text{ atm}$ at 850°K from equation (11). Thus, for MnF_3 sublimation predominates over decomposition up to the sublimation temperature, *i.e.* at 1300°K where $P(\text{MnF}_3) = 1 \text{ atm}$ according to equation (11), in agreement with the prediction by Brewer *et al.*³⁵. That MnF_3 did not change weight at 873°K in flowing fluorine at 0.1 atm was reported by von Wartenberg⁴⁵. It seems likely that the MnF_3 sample used by Zmbov and Margrave¹⁶ was extensively decomposed to MnF_2 , lowering the partial pressure of MnF_3 over its solid solution in MnF_2 and thus giving the apparently low vapor pressure and low abundance of MnF_3^+ (3.2% of MnF^+) in the mass spectrum. One would expect considerable molecular ion abundance since the electron lost is not likely to have much bonding character. Lastly, their $\text{AP}(\text{MnF}^+/\text{MnF}_3)$ value of $14.2 \pm 0.3 \text{ eV}$ is very close to $\text{AP}(\text{MnF}^+/\text{MnF}_2)$. The sublimation pressure they reported is actually quite close to that of MnF_2 , rather than being markedly higher due to increased covalent character which typically accompanies an increase in valence state. Their sublimation heat, determined by monitoring MnF_2^+ , is within probable error of $\Delta H_{\text{subl.}}(\text{MnF}_2)$. The molecular constants of $\text{MnF}_3(\text{g})$ have not been reported.

Using TiF_4 thermal functions to approximate those of MnF_4 gives $\Delta H^\circ_{\text{subl.}}(\text{MnF}_4) = 34 \pm 4 \text{ kcal mole}^{-1}$ from 298°K to $\Delta H^\circ_{\text{subl.}} = 32 \pm 3 \text{ kcal mole}^{-1}$ at 600°K . By a third-law argument, the estimated sublimation pressure of MnF_4 at 600°K , 10^{-6} atm , corresponds to $\Delta H_{\text{subl.}} = 40 \pm 5 \text{ kcal mole}^{-1}$ in agreement with the second-law result. The value $34 \pm 4 \text{ kcal mole}^{-1}$ was taken as $\Delta H^\circ_{\text{subl.}}(\text{MnF}_4)$ at 298°K .

Again, using TiF_3 , TiF_4 thermal functions, $\Delta H^\circ_{298^\circ\text{K}}(\text{equation (12)})$ was found to be $24.7 \pm 1 \text{ kcal mole}^{-1}$. The transport rate data obtained by Hoppe *et al.*⁴⁶ for equation (12) indicate $\log K_p \approx -2.5$ at 823°K which corresponds to $\Delta H_{298^\circ\text{K}}(\text{equation (12)}) \approx 26 \text{ kcal mole}^{-1}$, supporting the result obtained above. Combining $\Delta H(\text{equation (12)})$, $\Delta H_{\text{subl.}}(\text{MnF}_3)$ and $D^\circ(\text{F}_2)$ gives $D^\circ(\text{MnF}_3\text{-F}) = 62.3 \pm 2.4 \text{ kcal mole}^{-1}$ in good agreement with, but more accurate than, the electron impact result. The evolution of fluorine by MnF_4 at room temperature has been noted previously^{46,47}. Our estimate that $P(\text{F}_2) = 10^{-9 \pm 1} \text{ atm}$ near 300°K ,

and the requirement that $P(\text{F}_2) < 10^{-3\pm 1}$ atm near 700°K in order that MnF_4 could be produced in this experiment,



means that $\Delta H_{500^\circ\text{K}}$ (equation (18)) $\leq 7 \pm 3$ kcal mole⁻¹, in good agreement with the value 9 ± 5 kcal mole⁻¹ at 298°K derivable from ΔH (equation (12)) and $\Delta H_{\text{subl.}}(\text{MnF}_4)$. By making the reasonable assumption that $\Delta S_{298^\circ\text{K}}$ (equation (18)) = 15 ± 1.5 cal deg⁻¹ mole⁻¹ based on TiF_3 , TiF_4 data, $P(\text{F}_2) = 10^{-9\pm 1}$ atm corresponds to ΔH (equation (18)) = 10.5 ± 1.5 kcal mole⁻¹ by a third-law analysis. Thus $\Delta H_{298^\circ\text{K}}$ (equation (18)) is taken to be 10.5 ± 2 kcal mole⁻¹, although it is not possible to specify either of the formation enthalpies, summarized in Table 8 along with other results, with satisfactory accuracy.

TABLE 8

SUMMARY OF THERMOCHEMICAL DATA AT 298°K^a

	$\Delta H^\circ_{\text{f}}$ (kcal mole ⁻¹)	$\Delta H^\circ_{\text{atom.}}(\text{g})$ or $\Delta H^\circ_{\text{subl.}}(\text{c})$	$D^\circ(\text{MnF}_x-\text{F})$
$\text{MnF}(\text{g})$	-20 ± 5	105 ± 4	105 ± 4
$\text{MnF}_2(\text{g})$	-127 ± 7	231 ± 11	126 ± 7
$\text{MnF}_2(\text{c})$	-203 ± 5	76 ± 2	
$\text{MnF}_3(\text{g})$	-188 ± 14	310 ± 17	79 ± 6
$\text{MnF}_3(\text{c})$	-256 ± 14	68.1 ± 1	
$\text{MnF}_4(\text{g})$	-231 ± 17	372 ± 19	62.3 ± 2.4
$\text{MnF}_4(\text{c})$	-265 ± 21	34 ± 4	

^a The subscript atom. denotes atomization.

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REFERENCES

- 1 T. C. EHLERT, R. M. HILMER AND E. BEAUCHAMP, *J. Inorg. Nuclear Chem.*, 30 (1968) 3112.
- 2 T. C. EHLERT, *J. Sci. Instr.*, 2 (1969) 760.
- 3 T. C. EHLERT AND M. HSIA, *J. Chem. and Eng. Data*, in press.
- 4 J. H. WILLIAMSON, *Canad. J. Phys.*, 46 (1968) 1845.
- 5 W. P. BRENNAN, B. MILLER AND J. C. WHITWELL, *Ind. and Eng. Chem. (Fundamentals)*, 8 (1969) 314.

- 6 D. F. SHRIVER, *The Manipulation of Air Sensitive Compounds*, McGraw-Hill, New York, 1969, p. 197.
- 7 G. T. FURUKAWA, T. B. DOUGLAS, R. E. MCCOSKEY AND D. C. GINNINGS, *J. Res. Nat. Bur. Stds.*, 57 (1956) 67.
- 8 F. P. LOSSING, A. W. TICKNER AND W. A. BRYCE, *J. Chem. Phys.*, 19 (1951) 1254.
- 9 A. J. C. NICHOLSON, *J. Chem. Phys.*, 29 (1958) 1312.
- 10 R. E. HONIG, *J. Chem. Phys.*, 16 (1948) 105.
- 11 J. E. COLLIN in R. I. REED (ed.), *Mass Spectrometry*, Academic Press, London, 1965, p. 201.
- 12 R. W. KISER, *Introduction to Mass Spectrometry and Its Application*, Prentice-Hall, Englewood Cliffs, N.J. 1965, p. 166.
- 13 T. C. EHLERT, *J. Phys. E.*, 3 (1970) 237.
- 14 J. W. WARREN, *Nature*, 165 (1950) 810.
- 15 J. L. FRANKLIN, J. G. DILLARD, H. M. ROSENSTOCK, J. F. HERRON AND K. DRAXL, Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, *Nat. Stand. Ref. Data Ser.*, NBS, 26, U.S. Government Printing Office, Washington, D.C., 20402, 1969.
- 16 K. M. ZMBOV AND J. L. MARGRAVE, *J. Inorg. Nuclear Chem.*, 29 (1967) 673.
- 17 J. W. STOUT AND S. A. REED, *J. Amer. Chem. Soc.*, 76 (1954) 5279.
- 18 M. A. HEPWORTH AND K. H. JACK, *Acta Cryst.*, 10 (1957) 345.
- 19 B. J. STURM, *Inorg. Chem.*, 1 (1962) 665.
- 20 H. STEINFINK AND J. H. BURNS, *Acta Cryst.*, 17 (1964) 832.
- 21 G. BAUER AND M. EICHNER, *Z. anorg. allgem. Chem.*, 296 (1958) 13.
- 22 M. GRIFFEL AND J. W. STOUT, *J. Amer. Chem. Soc.*, 72 (1950) 4351.
- 23 W. A. CHUPKA AND M. G. INGRAM, *J. Chem. Phys.*, 21 (1953) 371.
- 24 J. W. STOUT AND H. E. ADAMS, *J. Amer. Chem. Soc.*, 64 (1942) 1535.
- 25 K. JELLINEK AND A. RUDAT, *Z. anorg. allgem. Chem.*, 175 (1928) 281.
- 26 *JANAF, Thermochemical Tables*, with revisions through June 1966, The Dow Chemical Co., Midland, Mich.
- 27 D. R. STULL AND G. C. SINKE, Thermodynamic Properties of the Elements, *Adv. Chem. Ser.*, No. 18, 1956.
- 28 K. JELLINEK AND R. KOOP, *Z. physik. Chem.*, A145 (1929) 305.
- 29 D. D. WAGMAN, W. H. EVANS, V. B. PARKER, I. HALOW, S. M. BAILEY AND R. H. SCHUMM, Selected Values of Chemical Thermodynamic Properties, *U.S. Nat. Bur. Std. Tech. Note 270-3*, 1968, U.S. Government Printing Office, Washington, D.C.
- 30 D. D. WAGMAN, W. H. EVANS, V. B. PARKER, I. HALOW, S. M. BAILEY AND R. H. SCHUMM, Selected Values of Chemical Thermodynamic Properties, *U.S. Nat. Bur. Std. Tech. Note 270-4*, 1969, U.S. Government Printing Office, Washington, D.C.
- 31 K. K. KELLEY, Contributions to the Data on Theoretical Metallurgy, XIV. Entropies of the Elements and Inorganic Compounds, *U.S. Dept. of the Interior, Bur. of Mines Bull.* 592, 1961, U.S. Government Printing Office, Washington, D.C.
- 32 K. K. KELLEY, Contributions to the Data on Theoretical Metallurgy, XII. High-Temperature Heat-Contents, Heat Capacity, and Entropy Data for the Elements and Inorganic Compounds, *U.S. Dept. of the Interior, Bur. of Mines Bull.*, 584, 1960, U.S. Government Printing Office, Washington, D.C.
- 33 R. H. SCHUMM, private communication.
- 34 A. D. MAH, *U.S. Dept. of the Interior, Bur. of Mines Report of Investigation 5600*, 1960, U.S. Government Printing Office, Washington, D.C. (1960), p. 10.
- 35 L. BREWER, L. A. BROMLEY, P. W. GILLES AND N. L. LOFGREN in L. L. QUILL (Ed.), *The Chemistry and Metallurgy of Miscellaneous Materials*, McGraw-Hill, 1950, p. 76.
- 36 R. G. BAUTISTA AND J. L. MARGRAVE, *J. Phys. Chem.*, 67 (1963) 1504.
- 37 R. A. KENT, T. C. EHLERT AND J. L. MARGRAVE, *J. Amer. Chem. Soc.*, 86 (1964) 5090.
- 38 J. W. HASTIE, R. H. HAUGE AND J. L. MARGRAVE, *Chem. Commun.*, (1969) 1452.
- 39 S. H. GARNETT, *Ph. D. Thesis*, Princeton University, Princeton, N.J., 1968, p. 81.
- 40 G. HEZBERG, *Molecular Spectra and Molecular Structure, II. Infrared and Raman Structure of Polyatomic Molecules*, Van Nostrand, Princeton, N.J., 1945, p. 168.
- 41 L. BREWER, G. R. SOMAYAJULU AND E. BRACKETT, *Chem. Rev.*, 63 (1963) 111.

- 42 T. C. EHLERT, *J. Inorg. Nuclear Chem.*, 31 (1969) 2705.
- 43 W. A. CHUPKA, *J. Chem. Phys.*, 54 (1971) 1936.
- 44 K. F. ZMBOV AND J. L. MARGRAVE, *J. Phys. Chem.*, 72 (1968) 1099.
- 45 H. VON WARTENBERG, *Z. anorg. allgem. Chem.*, 244 (1940) 337.
- 46 R. HOPPE, W. DAEINE AND W. KLEMM, *Ann. Chem.*, 658 (1962) 1.
- 47 H. W. ROESKY, O. GLEMSER AND K. H. HELLBERG, *Chem. Ber.*, 98 (1965) 2046.