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Sublimation Pressures of Refractory Fluorides

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ABSTRACT

Studies of the sublimation of refractory fluorides by Knudsen and/or Langmuir measurements utilizing a semi-microbalance and a mass spectrometer have provided the identities of the vapor species, absolute vapor pressures and heats of sublimation for MgF_2, CaF_2, SrF_2, BaF_2, ScF_3, VF_2, VF_3, CrF_2, MnF_2, FeF_2, CoF_2, NiF_2, CuF_2, YF_3, CdF_2, LaF_3, CeF_3, DyF_3, HoF_3, and ErF_3. Atomization energies and average bond energies have been calculated. Reduced systems, in which subfluorides are generated, have also been studied.

The reviews by Brewer, et. al.[1,2] in 1950 and still in 1963 showed that vapor pressure data on fluorides were relatively incomplete and, in fact, that there were many di- and trifluorides for which vaporization and/or sublimation pressures are not known. In addition, the stabilities of the mono-fluorides of the elements were poorly known except for the alkali fluorides and a few others scattered through the periodic table.[3,4] An extensive effort is now underway to produce a comprehensive set of reliable data on the high temperature behavior of a variety of mono-, di- and trifluorides and, from these, to establish

orders of magnitude and trends in energetic relationships for fluorides throughout the periodic table. This paper mainly summarizes work from the High Temperature Laboratory at the Rice University, but includes other related contributions which provide supporting or supplementary data.

Currently, there are published mass spectrometric and/or microbalance studies of the vapors over ScF_3[5], CrF_2[6], MnF_2[7], FeF_2[8], CoF_2[9], NiF_2[10], CuF_2[11], YF_3[5], ZrF_2[12], CdF_2[13], LaF_3[5], and CeF_3[14]. The dissociation energies of CrF[6] and MnF[7] have been established mass spectrometrically and there are limited spectral data on ScF[15,16], YF[16], MnF[17], CuF[18], ZrF[19], CdF[20], and HgF[21].

NEW RESULTS

Sublimation Pressures of VF_2 and VF_3

VF_2 and VF_3 samples were generously provided by Professor J. W. Stout of the University of Chicago and were used without further purification. The solids were heated in tantalum, nickel and/or carbon Knudsen cells in the high temperature mass spectrometer described previously.[5,6]

At low electron energies and temperatures the VF_2 yielded only VF_2^+ ions. The appearance potentials of the various ionic species were 11.5 ± 0.3 e.v. (VF_2^+/VF_2); 17.1 ± 0.3 e.v. (VF^+/VF_2); and 23.0 ± 0.3 e.v. (V^+/VF_2). From the temperature dependence of the ion current data (VF_2^+) one finds $\Delta H^{\circ}_{sub,298^{\circ}K.} = 100 \pm 10$ kcal. mole.$^{-1}$ where the large uncertainty arises because of apparent disproportionation of

$VF_2(g)$ to yield $V(s) + VF_3(g)$ in the temperature range 1000-1300°K.

When the VF_3 sample was heated in the tantalum cell, large amounts of VOF_3^+, VOF_2^+ and VOF^+, as well as TaF_4^+, were observed at ~485°C. By varying the electron voltage the appearance potential of VOF_3^+ was established as 15.4 ± 0.3 e.v. and of VOF_2^+ as 16.3 ± 0.3 e.v. With further heating to ~860°C, all VOF_x species disappeared, and, finally, VF_3^+, VF_2^+, VF^+ and V^+ were studied at 868°C. where the appearance potentials were 10.8 ± 0.3 e.v. (VF_3^+/VF_3); 11.5 ± 0.3 e.v. (VF_2^+/VF_2) and 15.5 e.v. (VF_2^+/VF_3); 13.6 ± 0.3 e.v. ($VF^+/VF?$); 17 e.v. (VF^+/VF_2) and 20.5 e.v. (VF^+/VF_3); 25.2 ± 0.3 e.v. (V^+/VF_3).

From the temperature dependence data for the VF_3^+ peak over the range 1044-1230°K. one finds,

$$\Delta H^o_{sub,1162^oK} = 80.8 \pm 0.7 \text{ kcal. mole.}^{-1}$$

Sublimation Pressures of Rare Earth Trifluorides

Lim and Searcy[14] studied CeF_3 sublimation by a torque-effusion technique. Work at Rice University has established the vapor species over NdF_3, DyF_3, HoF_3, and ErF_3 as the gaseous trifluoride monomers and appearance potentials and temperature dependence studies are summarized in Table I.

CONCLUSIONS

By making use of the extensive data now available, one can extrapolate and interpolate to get properties of many transition-element fluorides. Table II presents measured and estimated vapor pressure data for difluorides and Table III summarizes data for trifluorides.

Table I.

Vaporization and Appearance Potential Data for

NdF_3, DyF_3, HoF_3, and ErF_3

(a) Vaporization Data

Compound	Temp. Range (°K)	A*	B*	ΔH^o Kcal mole^{-1}
NdF_3	1383-1520	1.873 ± 0.025	8.028 ± 0.11	$\Delta H_{1448} = 93.7 \pm 1.1$
DyF_3	1426-1622	1.842 ± 0.032	7.54 ± 0.32	$\Delta H_{1443.1} = 92.3 \pm 1.4$
HoF_3	1300-1413	2.296 ± 0.2	10.6 ± 0.5	$\Delta H_{1367} = 107 \pm 2$
ErF_3	1374-1521	1.907 ± 0.025	7.62 ± 0.12	$\Delta H_{1443} = 95.3 \pm 0.8$

*For the equation $\log P_{atm} = B - \frac{A \times 10^4}{T}$

(b) Appearance Potentials (Electron Volts)

Ion	M = Nd	Dy	Ho	Er
MF_2^+	12.8 ± 0.3	--	14.5 ± 0.3	13.7 ± 0.3
MF^+	19.8 ± 0.4	19.6 ± 0.4	21.0 ± 0.4	20.5 ± 0.4
M^+	25.5 ± 0.5	25.0 ± 0.5	27.2 ± 0.5	26.5 ± 0.5

Table II

(a) Vapor Pressure Data for Alkaline Earth Difluorides

Compound	A*	B*	Log P (Atmospheres) 1000°K	1500°K	ΔH°_{298} Kcal mole^{-1}	Reference
MgF_2	1.93	8.53	-10.8	-4.4	88±3	29
CaF_2	2.08	8.14	-12.7	-5.7	103±3	28
SrF_2	2.17	8.72	-13.0	-5.8	104±5	29,30
BaF_2	1.86	7.66	-10.9	-4.7	92±4	29,30

(b) Vapor Pressure Data for Transition Metal Difluorides

ScF_2	1.65	9.0	-7.5	-2.0	(100±15)	estimated
TiF_2	± 0.15	± 0.5			(100±15)	estimated
VF_2					100±10	This work
CrF_2	1.882	9.14	-9.08	-3.01	106.4±3	6
MnF_2	1.596	8.70	-7.26	-1.94	76.1±2	7
FeF_2	1.582	9.42	-6.40	-1.13	75.6±1	8
CoF_2	1.532	8.54	-6.78	-1.67	78±3	9
NiF_2	1.690	10.17	-6.73	-1.097	79.4±1	10
CuF_2	1.300	8.58	-4.42	-0.09	63.9±1	11
CdF_2	1.409	7.391	-6.70	-2.00	72.0±3	13
ZnF_2			-4.3	-1.0	61	26
HgF_2			(BP = 920°K)		33	27

Values in parentheses are estimated

* For the equation $\log P_{atm} = B - \frac{A \times 10^4}{T}$

Table III

Vapor Pressure Data for Transition Metal Trifluorides[a]

Compound	A*	B*	Log P (Atmospheres) 1000°K	1500°K	ΔH^{o}_{298}	Reference
ScF_3	1.938	9.43	-9.95	-3.49	101±5	5
TiF_3	(1.57)	(9.6)	(-5.35)	(-0.36)	(59.3)[c]	32
VF_3	(1.80)	(9.0)	(-9.0)	(-3.0)	(92±5)[b]	This work
FeF_3	(1.4)	(11.1)	(-2.8)	(+1.92)	(65.5)[c]	32
YF_3	2.185	9.77	-12.08	-4.80	115±5	5
ZrF_3	(1.683)	(12.25)	(-4.58)	(+1.03)	(77)[c,d]	32
LaF_3	2.02	8.20	-12.00	-5.27	108±5	5
CeF_3	1.983	8.816	-11.01	-4.40	99.5±3	14
NdF_3	1.873	8.028	-10.70	-4.46	94±3	25
DyF_3	1.842	7.54	-10.88	-4.74	92±3	25
HoF_3	2.296	10.6	-12.36	-4.70	107±3	25
ErF_3	1.907	7.62	-11.45	-5.09	95.3±3	25

* For the equation $\log P_{atm} = B - \frac{A \times 10^4}{T}$

a Values in parentheses are estimated.

b $\Delta H^{\circ}_{s}(1162°K) = 82\pm3$ Kcal mole^{-1} from mass spectrometric data

c These estimates from the JANAF Table appear to be too low.

d Hildenbrand gives $\Delta H^{\circ}_{f}[ZrF_3(g)] = -264\pm5$ kcal mole^{-1} and one predicts $\Delta H^{\circ}_{f}[ZrF_3(g)] = -375\pm15$ kcal mole^{-1}, in contrast with -330 ± 25 kcal mole^{-1} from the JANAF Tables.

Table IV presents bond energies for the monofluorides derived from these various data.

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Table IV
Dissociation Energies of Metal Monofluorides*
(Kcal mole^{-1})

LiF 137±2 (32)	BeF 135+2 (33)											BF 180+3 (33)
NaF 114±2 (32)	MgF 100+2 (31)											AlF 159+2 (33)
KF 117±5 (32)	CaF 125+2 (28)	ScF 145+20 (5)	TiF 145+10 (est)	VF 140+10 (est)	CrF 106+2 (6)	MnF 101+2 (7)	FeF 108+3 (8)	CoF 104+3 (9)	NiF 104+3 (10)	CuF 88+2 (11)	ZnF 88+5 (2,25)	GaF 138+2 (33)
RbF 116±2 (34)	SrF 125+2 (31)	YF 140+10 (5)	ZrF 149+6 (12,22, 23)	NbF 140+10 (est)	MoF 110+10 (est)	TcF 100+10 (est)	RuF 100+10 (est)	RhF 100+10 (est)	PdF 90+10 (est)	AgF 70+10 (24)	CdF 74+5 (13)	IrF 121+2 (33)
CsF 120+2 (34)	BaF 134+2 (31)	LaF 150+20 (5)	HfF 150+20 (est)	TaF 150+20 (est)	WF 120+10 (est)	ReF 100+10 (est)	OsF 100+10 (est)	IrF 100+10 (est)	PtF 90+10 (est)	AuF 60+10 (est)	HgF 40+10 (est)	TlF 101+2 (33)

CeF 150+10 (14,25)	PrF 140+10 (est)	NdF 130.3±3 (25)	PmF	SmF	EuF	GdF	TbF	DyF 140+10 (est)	HoF	ErF	TmF	YbF	LuF

* numbers in parentheses are reference citations: "est" means estimated by consideration of periodic table trends and experimental data on transition metal monoxide

References

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

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

3. Pugh, A. C. P., and Barrow, R. F., Trans. Faraday Soc. 54, 671 (1958)

4. Brewer, L. and Brackett, E., Chem. Revs. 61, 425 (1961).

5. Kent, R. A., Zmbov, K. F., Kana'an, A. S., Besenbruch, G., McDonald, J. D., and Margrave, J. L., to be published, J. Inorg. and Nucl. Chem., (1966).

6. Kent, R. A., and Margrave, J. L., J. Amer. Chem. Soc. 87, 3582 (1965).

7. Kent, R. A., Ehlert, T. C., and Margrave, J. L., J. Amer. Chem. Soc. 86, 5090 (1964).

8. Kent, R. A., and Margrave, J. L., J. Amer. Chem. Soc. 87, 4754 (1965).

9. Kana'an, A. S., Besenbruch, G., and Margrave, J. L., to be published, J. Inorg. and Nucl. Chem. (1966).

10. Ehlert, T. C., Kent, R. A., and Margrave, J. L., J. Amer. Chem. Soc. 86, 5093 (1964).

11. Kent, R. A., McDonald, J. D., and Margrave, J. L., to be published, J. Phys. Chem., (1966).

12. Hildenbrand, D. H., private communication, 1965.

13. Besenbruch, G., Kana'an, A. S., and Margrave, J. L., J. Phys. Chem. 69, 3174 (1965).

14. Lim, M. J. and Searcy, A. W., to be published, J. Phys. Chem., (1966) UCRL-16150, 1965.

15. Gurvich, L., and Shenyavskaya, E., Opt. and Spectros. 14, 161 (1963).

16. (a) Barrow, R. F., Gissane, W.J., Bargy, R., Rose, G., and Ross, P., Proc. Phys. Soc. 83, 889 (1964)
(b) Barrow, R. F. and Gissance, W. J., Proc. Phys. Soc. 84, 615 (1964)

17. Rochester, G. D. and Olsson, E., Z. Physik 114, 495 (1963).

18. (a) Ritschl, R., Z. Physik 42, 172 (1927).
(b) Woods, L. H., Phys. Rev. 64, 259 (1943).

19. Afaf, M., Proc. Phys. Soc. 63A, 544 (1950)

20. Fowler, C. A. Jr. Phys. Rev. 62, 141 (1942).

21. Howell, H. G., Proc. Roy. Soc. (London) 182, 95 (1943).

22. Akishin, et. al., Russ. J. Inorg. Chem., 8, 789 (1963).

23. Greenberg, E., et. al., J. Phys. Chem. 65, 1168 (1961).

24. Feber, R. C., Los Alamos Report, LA-3164, Nov. 1964.

25. Zmbov, K. F., Kent, R., Besenbruch, G., Charlu, T. V., and Margrave, J. L., unpublished work, 1965-1966.

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

27. (a) Niwa, K., J. Fac. Sci. Hokkaido Univ. Ser. III, 3, 17 (1940).
(b) Shibaka, Z., Niwa, K., Ibid. 2, 183 (1938).

28. Blue, G. D., Green, J. W., Bautista, R. G., and Margrave, J. L., J. Phys. Chem. 67, 877 (1963).

29. Green, J. W., Blue, G. D., Ehlert, T. C. and Margrave, J. L., J. Chem. Phys. 41, 2245 (1964).

30. Bautista, R. G., and Margrave, J. L., J. Phys. Chem. 69, 1770 (1965).

31. Ehlert, T. C., Blue, G. D., Green, J. W. and Margrave, J. L., J. Chem. Phys. 41, 2250 (1964).

32. JANAF Interim Thermochemical Tables, Edited by D. R. Stull, Dow Chem. Co, Midland, Michigan.

33. Hildenbrand, D., Murad, E., Potter, N. D., et. al., Progress Reports, Aeronutronic Division, Philco Corporation, Newport Beach, California, 1965-1966.