69. *Lattice Energies and Heats of Formation of First-row Transition-metal Fluorides: Stabilities of the Vanadium Fluorides.*

By R. G. CAVELL and H. C. CLARK.

The lattice energies of some transition-metal fluorides have been calculated from one of the Kapustinskii formulae. These values have been used to estimate the heats of formation of the fluorides, the resultant values comparing favourably with experimental values. The results have been used to evaluate the relative stabilities of the vanadium fluorides, which are compared with those of the vanadium chlorides.

OUR recent determination [1] of the heats of formation of vanadium tetrafluoride and pentafluoride, from the heats of hydrolysis of these compounds, provides two of the three heats of formation necessary for the estimation of the heat of the recently verified spontaneous disproportionation of vanadium tetrafluoride [2,3] into the pentafluoride and trifluoride. Unfortunately, the extremely slow hydrolysis of vanadium trifluoride prevents the application of the method used for the tetra- and penta-fluorides to the determination of the heat of formation of the trifluoride. In order to complete the series, an attempt was made to estimate the heat of formation of the trifluoride. The method used, based on estimation of the lattice energy, has recently been applied by Barber, Linnett, and Taylor,[4] successfully for chlorides but less so for fluorides.

RESULTS AND DISCUSSION

Estimation of Heats of Formation of Fluorides.—The Born–Haber cycle [5] gives the following expression for the heat of formation:

$$\Delta H_f^\circ(\mathrm{MF}_n) = \sum_1^n I_i + L - n(E - D/2) - U \qquad (1)$$

where $\sum_1^n I_i$ represents the sum of the successive n ionization potentials of the metal M, E is the electron affinity of fluorine, D the enthalpy of dissociation of fluorine, L the enthalpy of sublimation of the metal, and U the lattice energy of the fluoride MF_n. Since most of the quantities except the lattice energy are readily available, the problem of estimating the heat of formation becomes one of evaluating the lattice energy. Although exact lattice-energy calculations are lengthy and involved, reasonably good values can be obtained from simple relations such as those given by Kapustinskii.[5,6] We have employed the second Kapustinskii formula: [6]

$$U = \frac{287{\cdot}2\, v\, Z_A Z_C}{r_A + r_C}\left[1 - \frac{0{\cdot}345}{r_A + r_C}\right] \qquad (2)$$

where U is the lattice energy, Z_A and Z_C are the formal ionic charges on the anion and cation, respectively, r_A and r_C are the ionic radii, and v is the number of ions in a formula unit of the compound.

The formula was used to calculate the lattice energies of di-, tri-, and tetra-fluorides of some first- and second-row transition metals, and the resultant lattice energies, shown in Table 2, were combined with the thermochemical data, given in Table 1, to calculate the heats of formation according to eqn. 1. The results are given in Table 2. The ionic

---

[1] Cavell and Clark, *Trans. Faraday Soc.*, 1963, **59**, 2706.
[2] Ruff and Lickfett, *Ber.*, 1911, **44**, 2539.
[3] Cavell and Clark, *J.*, 1962, 2692.
[4] Barber, Linnett, and Taylor, *J.*, 1961, 3323.
[5] Waddington, " Advances in Inorganic Chemistry and Radiochemistry," Academic Press, New York, 1959, Vol. 1, p. 157.
[6] Kapustinskii, *Quart. Rev.*, 1956, **10**, 283.

TABLE 1.

Heats of sublimation (L) [7] and successive ionization potentials (I) [8] of transition metals (in kcal./mole).

	L	I_1	I_2	I_3	I_4	I_5
Ti	112	147	314	649	997	—
V	122	155	327	685	1106	—
Cr	94	156	380	713	1143	—
Mn	68	171	360	777	1199	—
Fe	99	182	373	706	1153	—
Co	102	182	392	772	(1153) *	—
Zr	125	160	323	572	783	—
Nb	185	156	323	648	883	1143

* Estimated value.

TABLE 2.

Calculated lattice energies and heats of formation of transition-metal fluorides.

Metal	r_c^{+n} (Å)	U (MF_n) (kcal./mole)	$-\Delta H_f^\circ$ (MF_n) (kcal./mole) Calc.	Exptl.	(Ref.)
	Difluorides				
Ti	0·81—0·90	668—646	227—205	198	(9)
V	0·74—0·88	686—651	241—179	—	
Cr	0·68—0·84	702—655	204—158	181	(9)
Mn	0·80	646	179	189	(9)
Fe	0·75	683	161	—	
Co	0·74	686	142	159	(9)
Ni	0·72	691	127	159	(9)
	Trifluorides				
Ti	0·73	1376	345	—	
V	0·67	1409	319	—	
Cr	0·64	1426	281	265	(10)
Mn	0·62	1438	261	—	
Fe	0·60	1449	288	—	
Co	0·63	1432	183	187	(9)
	Tetrafluorides				
Ti	0·68	2339	385	394	(11)
V	0·65	2413	315	321	(1)
Cr	0·56	2454	233	287	(10)
Mn	0·54—0·60	2474—2415	165—105	—	—
Fe	0·52—0·60	2494—2414	246—167	—	
Co	0·50—0·60	2516—2414	180—79	—	—
Zr	0·80	2234	536	457	(12)
	Pentafluoride				
Nb	0·70	3482	466	432	(13)

radii used were Pauling's crystal radii[14] which are self-consistent and yield fair agreement with available measured interatomic distances in these fluorides. Where such radii were not available (*e.g.*, for Fe, Co, and Ni), empirical crystal radii, also given by Pauling,[14] were used. Where the ionic radii were extremely uncertain (*e.g.*, Ti^{2+} and Mn^{4+}), upper and lower limits were assigned to the radii and hence to the lattice energies and heats of formation, following the practice of Barber *et al.*[4] The ionic radius of the fluoride ion[14] was taken as 1·36 Å. The value 66·3 kcal./mole was taken for the term ($E - D/2$) for fluorine.[4]

---

[7] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 2nd edn, 1958.

[8] National Bureau of Standards, Circular 467, Washington, D.C., 1949.

[9] National Bureau of Standards, Circular 500, Washington, D.C., 1952.

[10] von Wartenberg, *Z. anorg. Chem.*, 1942, **249**, 100.

[11] Greenberg, Settle, and Hubbard, *J. Phys. Chem.*, 1962, **66**, 1345.

[12] Greenberg, Settle, Feder, and Hubbard, *J. Phys. Chem.*, 1961, **65**, 1168.

[13] Meyers and Brady, *J. Phys. Chem.*, 1960, **64**, 591.

[14] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 3rd edn, 1960.

The agreement between the calculated and experimental heats of formation is surprisingly good, considering the approximate nature of the lattice-energy calculations on which the results are based and the fact that the heats of formation represent the difference between two large quantities. This agreement is considerably better than that of Barber *et al.*[4] who used the simplest Kapustinskii lattice-energy formula to estimate the heats of formation of mono-, di-, and tri-halides of the first-row transition elements. They obtained good agreement with experiment only for the chlorides; the differences for the trifluorides were of the order of 100 kcal./mole. The more-elaborate formula employed in the present study gives good agreement for fluorides only; in the case of the chlorides, the calculated lattice energies gave heats of formation which differed from the experimental values to a greater extent than those obtained by Barber *et al.*[4]

This is the first time that lattice-energy estimates have been extended to the usually " less ionic " tetrafluorides. In principle, all solid compounds possess a lattice energy, and it is often reasonable to attempt estimations based on an ionic model. In the rare cases where sufficient data are available, the calculations can be extended to pentafluorides, as shown by the reasonable result calculated for niobium pentafluoride, although vanadium pentafluoride cannot be treated in this manner as it is a liquid at 298°K.

The improvement in the agreement between calculated and experimental heats of formation when Kapustinskii's more elaborate formula is used suggests that the Kapustinskii formulae arbitrarily compensate for a constant amount of covalent character in the metal–halogen bond; thus the formula which is successful for fluorides is not reliable for chlorides, and *vice versa*, because of the greater ionic character of the metal–fluorine bond. Additional factors are, of course, involved; for example, the lattice energies are quite sensitive to small changes in ionic radius, and many of the available values are rather uncertain. The agreement between calculated and experimental heats of formation is thus probably fortuitous, arising from cancellation of errors. This chance agreement need not prevent the employment of the results in illustrating the thermodynamics of the transition-metal fluorides, as it is quite reasonable to assume that this agreement will be maintained throughout a valence series. For example, the value —319 kcal./mole can be used for the unknown heat of formation of vanadium trifluoride, with the reservation that it is probably about 20 kcal./mole too large, as suggested by the deviation of the calculated heat of formation of chromium trifluoride from the experimental value.

The Stability of the Vanadium Fluorides.—Using the calculated heat of formation of vanadium trifluoride, —319 kcal./mole, the heat of the disproportionation of vanadium tetrafluoride into the pentafluoride and the trifluoride:

$$2\,VF_4 \longrightarrow VF_3 + VF_5 \qquad (a)$$

can be estimated. Using the experimental values [1] of —321 and —352 kcal./mole for the heat of formation of the tetrafluoride and pentafluoride, respectively, the heat of the above disproportionation reaction, ΔH_a, is —29 kcal./mole. This exothermic heat of reaction indicates that disproportionation according to reaction (*a*) is more feasible than the other alternative, dissociation into vanadium trifluoride and fluorine:

$$VF_4 \longrightarrow VF_3 + 1/2F_2 \qquad (b)$$

for which ΔH_b is +2 kcal./mole.

Both of these values are subject to a very large uncertainty, of the order of 20 kcal./mole; however, because the uncertainty arises from the same source in each case, *i.e.*, the calculated heat of formation of vanadium trifluoride, any alterations due to errors in this estimated value will change ΔH_a and ΔH_b equally. Thus the relative exothermicities will remain unchanged, *i.e.*, ΔH_a will always be more exothermic than ΔH_b.

The feasibility of chemical change depends, of course, on the free energy, rather than the heat, of reaction. In both reactions (*a*) and (*b*), gaseous products are evolved; hence the entropy change is likely to be positive, favouring the reactions as written. Since reaction (*a*) is considerably more favourable than (*b*), entropy contributions of the same sign will be likely to maintain the relative favourability of (*a*).

The stability of vanadium trifluoride to disproportionation into the difluoride and the tetrafluoride:

$$2VF_3 \longrightarrow VF_2 + VF_4 \tag{c}$$

can be estimated in a similar fashion, assuming a value of —210 kcal./mole (the average of the range of calculated values) for the heat of formation of the unknown difluoride. The heat of disproportionation, ΔH_c, is +107 kcal./mole, and is so definitely endothermic that errors of 30 kcal./mole in both of the calculated values are not likely to have any effect. Entropy changes will probably be small because only condensed phases are involved.

Decomposition of vanadium trifluoride into vanadium difluoride and fluorine:

$$VF_3 \longrightarrow VF_2 + 1/2F_2 \tag{d}$$

is also strongly endothermic ($\Delta H_d = +109$ kcal./mole), and the positive entropy effect is unlikely to be sufficiently large to alter this conclusion. Thus it is hardly likely that vanadium difluoride could be prepared by decomposition of vanadium trifluoride either according to reaction (*c*) or (*d*).

The heat of decomposition of vanadium pentafluoride into vanadium tetrafluoride and fluorine can be calculated from the available experimental heats of formation;[1] thus for

$$VF_5 \longrightarrow VF_4 + 1/2F_2 \tag{e}$$

ΔH_e is endothermic, +31 kcal./mole, and hence (*e*) is not a likely mode of decomposition.

The Stabilities of the Vanadium Chlorides.—It is interesting to compare the above results with the stabilities of the three known chlorides. The necessary heats of formation are given in Table 3.

TABLE 3.

Heats of formation of vanadium chlorides (in kcal./mole).

	VCl_2	VCl_3	VCl_4
$\Delta H_f°$	−108	−143	−136
Ref.	9	15	16

The heat of the disproportionation

$$2VCl_3 \longrightarrow VCl_2 + VCl_4 \tag{f}$$

calculated from the above figures, is +42 kcal./mole. The enthalpy of this reaction has recently been determined experimentally as +38 kcal./mole,[17] and the disproportionation was found to occur at appreciable rates only above 425°.

The above data give a heat of reaction of —7 kcal./mole for the dissociation

$$VCl_4 \longrightarrow VCl_3 + 1/2Cl_2 \tag{g}$$

The heat of the *reverse* reaction has been found to be +13·8 kcal./mole.[18]

The heat of dissociation of vanadium trichloride into the dichloride and chlorine:

$$VCl_3 \longrightarrow VCl_2 + 1/2Cl_2 \tag{h}$$

calculated from the above data, is +35 kcal./mole, of the same order of endothermicity as the disproportionation (*f*). Thus neither decomposition (*f*) nor (*h*) of vanadium trichloride is as likely as is the dissociation of the " middle " fluoride, vanadium tetrafluoride, into the trifluoride and pentafluoride, a dissociation which is probably exothermic. The

---

[15] Shchukarev, Vasil'kova, Perfilova, and Chernykh, *Russ. J. Inorg. Chem.*, 1962, **7**, 779.

[16] Gross and Hayman, *Trans. Faraday Soc.*, 1964, **60**, 45.

[17] Oranskaya, Lebedev, and Perfilova, *Russ. J. Inorg. Chem.*, 1961, **6**, 132.

[18] Simons and Powell, *J. Amer. Chem. Soc.*, 1945, **67**, 75.

other possible mode of decomposition of vanadium tetrafluoride, (*b*), is, as we have seen, endothermic. The highest chloride is also much more likely to dissociate to lower chloride and free chlorine than is the highest fluoride to a lower fluoride and free fluorine; this is a reflection of the lower bond-energy of fluorine relative to chlorine and of the higher bond-energy of fluorides relative to chlorides.

We thank the U.S. Office of Naval Research for financial support, and the National Research Council, Ottawa, for the award of a Studentship (to R. G. C.).

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, BRITISH COLUMBIA, CANADA.

[*Received, April* 14*th*, 1964.]