

Received: March 24, 1986; accepted: May 18, 1986

COMMENTS ON THE ENTHALPY OF FORMATION OF ReF₄O

A.A. WOOLF

Department of Science, Bristol Polytechnic, Bristol, BS16 1QY, (U.K.)

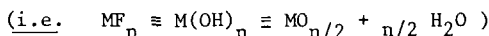
SUMMARY

Heats of formation of Mo, Re and W oxo-tetrafluorides are compared with those of the corresponding hexafluorides by the isoelectronic heat method. The enthalpy of tungsten oxo-tetrafluoride is out of line. Some disproportionation and exchange reactions of oxo-tetrafluorides should be nearly athermal and unlikely to be of preparative use.

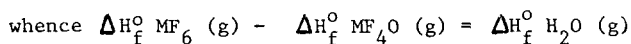
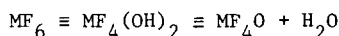
DISCUSSION

Burgess, Fawcett and Peacock have compared the heats of formation of hexafluorides of Mo, W and Re with those of the corresponding oxo-tetrafluorides and considered the possibility of disproportionation and exchange reactions. [1]

The estimation of heats of formation of fluorides by using the heats of iso-electronic hydroxo-compounds [2,3,4] can be applied to check these results. It seems that one fluorine can be replaced by a hydroxy group without appreciable thermal effect. Furthermore, when more than one fluorine is replaced the enthalpy of the resulting hydroxo-compound is approximately the sum of the enthalpies of the dehydration products.



Applying these approximations, the following enthalpy equivalences should hold

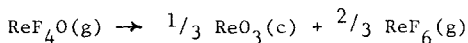


For M = Mo, W and Re the enthalpy differences are 229, 280 and 234 kJ mol⁻¹ respectively, compared with a value for $\Delta H_f^\circ H_2O(g)$ of 241.8 kJ mol⁻¹.

The figures given in Table 1 have been corrected with the newer CODATA (1977) value for $\Delta H_f^\circ \text{F}^-(\text{aq})$ and estimates for heats of sublimation of oxytetrafluorides at 25°C. The difference between a fluoride and oxyfluoride of the corresponding Group VI sub-group element, sulphur, is included for comparison. The difference is near the expected twice $\Delta H_f^\circ \text{H}_2\text{O}(\text{g})$.

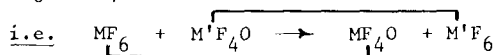
The agreement is as close as can be expected for Mo and Re compounds, but the difference for the W compounds is out of line. Concordant values for WF_6 have been found in three independent fluorine-bomb combustions of tungsten [5,6,7] and it may be that the WF_4O value is in error. A value close to $-1480 \text{ kJ mol}^{-1}$ would bring it in line.

It is of course possible to estimate the stability of ReF_4O to isoivalent disproportionation without knowing the enthalpy of ReO_3 because the enthalpy equivalence $3\text{ReF}_4\text{O} \equiv \text{ReO}_3 + 2\text{ReF}_6$ implies a nearly athermal process. However, a reasonable value for $\Delta H_f^\circ \text{ReO}_3(\text{c})$ of -611 kJ mol^{-1} is available [8] from oxygen-bomb calorimetry and hence the reaction heat for



can be calculated as 7.7 kJ mol^{-1} . The Gibb's free energy would be more positive because the number of gaseous molecules, and hence entropy, decrease.

It also follows from isoelectronic heats that reactions between $\text{MF}_6 - \text{MF}_4\text{O}$ couples would also be athermal



Thus the suggested preparation of ReF_4O from ReF_6 and WF_4O is unlikely to be feasible unless one of the products could be differentially removed. The predicted small value of the equilibrium constant could be tested in the liquid mixture by F^{19} n.m.r. measurements or in the gas phase by Raman spectroscopy.

The partitioning of dissociation energies into separate bond energies is arbitrary since it assumes transferable bond energies. This may be a fair approximation in regular homologous series of organic compounds, but would be unreliable for oxyfluoride systems with metals in different valency states where both the M-O and M-F bond energies vary from compound to compound.

TABLE 1

Comparison of formation enthalpies of fluorides and oxyfluorides
(kJ mol⁻¹)

				Difference
MoF ₆ (g)	- 1,558	MoF ₄ O (g)	- 1,329 ^{a,b}	- 229
	- 1,721.7			
WF ₆ (g)	- 1,722.6	WF ₄ O (g)	- 1,422 ^{a,c}	- 280
	- 1,721.5			
	- 1,722			
ReF ₆ (g)	- 1,349 ^a	ReF ₄ O (g)	- 1,115 ^a	- 234
SF ₆ (g)	- 1,221	SF ₂ O ₂ (g)	- 770	2 x (- 226)

^a corrected using $\Delta H_f^{\circ} F^{-}(aq) - 335.35 \text{ kJ mol}^{-1}$

^b estimated sublimation heat 62 kJ mol⁻¹ at 298 K.

^c " " " 69 kJ mol⁻¹ " " .

REFERENCES

- 1 J. Burgess, J. Fawcett and R.D. Peacock, J. Fluorine Chem., 31 (1986) 25.
- 2 A.A. Woolf, J. Fluorine Chem., 11 (1978) 307.
- 3 A.A. Woolf, J. Fluorine Chem., 15 (1980) 533.
- 4 A.A. Woolf, J. Fluorine Chem., 20 (1980) 627.
- 5 P.A.G. O'Hare and W.N. Hubbard, J. Phys. Chem., 70 (1966) 3353.
- 6 J. Schroeder and F.J. Sieben, Ber., 103 (1970) 76.
- 7 V. Ya. Leonidov, Dokl. Akad. Nauk. S.S.S.R. 205 (1972) 349.
- 8 G.E. Boyd, J.W. Cobble and W.J. Smith, J. Am. Chem. Soc., 75 (1953) 5783.