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COMMENTS ON THE ENTHALPY OF FORMATION OF ReF_4O

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.

(i.e. $MF_n \equiv M(OH)_n \equiv MO_{n/2} + n/2\ H_2O$)

Applying these approximations, the following enthalpy equivalences should hold

$MF_6 \equiv MF_4(OH)_2 \equiv MF_4O + H_2O$

whence $\Delta H_f^o\ MF_6\ (g) - \Delta H_f^o\ MF_4O\ (g) = \Delta H_f^o\ H_2O\ (g)$

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

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The figures given in Table 1 have been corrected with the newer CODATA (1977) value for ΔH_f^o $F^-(aq)$ and estimates for heats of sublimation of oxytetrafluorides at 25^oC. 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 ΔH_f^o H_2O (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 kJ mol^{-1} would bring it in line.

It is of course possible to estimate the stability of ReF_4O to isovalent disproportionation without knowing the enthalpy of ReO_3 because the enthalpy equivalence $3ReF_4O \equiv ReO_3 + 2ReF_6$ implies a nearly athermal process. However, a reasonable value for ΔH_f^o $ReO_3(c)$ of -611 kJ mol^{-1} is available [8] from oxygen-bomb calorimetry and hence the reaction heat for

$ReF_4O(g) \rightarrow {}^1/_3\ ReO_3(c) + {}^2/_3\ ReF_6(g)$

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 MF_6 - MF_4O couples would also be athermal

i.e. $MF_6 + M'F_4O \rightarrow MF_4O + M'F_6$

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	$MoF_4O_{(g)}$	- 1,329 [a,b]	- 229
WF_6 (g)	- 1,721.7 - 1,722.6 - 1,721.5 - 1,722	$WF_4O_{(g)}$	- 1,422 [a,c]	- 280
ReF_6 (g)	- 1,349 [a]	$ReF_4O_{(g)}$	- 1,115 [a]	- 234
SF_6 (g)	- 1,221	SF_2O_2 (g)	- 770	2 x (- 226)

[a] corrected using ΔH_f^o $F^-(aq)$ - 335.35 $kJ\ mol^{-1}$.

[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.