The Electron Affinity of Tungsten Hexafluoride

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Summary From the measured heat of hydrolysis of KWF_6 in alkaline hypochlorite ($-123{\cdot}6 \pm 2{\cdot}6$ kcal mol^{-1}), the heat of formation of KWF_6, the electron affinity of WF_6, and the fluoride ion affinity of WF_5 are estimated to be -541 ± 3, 120 ± 5, and 145 ± 6 kcal mol^{-1} respectively, at 25°.

FEW electron affinities of compounds have been reported. From the reactions of transition metal hexafluorides with oxidisable molecules such as O_2, NO, and NO_2, Bartlett[1] has made qualitative estimates of the minimum values of the electron affinities of PtF_6 (156), IrF_6 (135), OsF_6 (108) and ReF_6 (90 kcal mol^{-1}), but so far these have not been confirmed quantitatively.

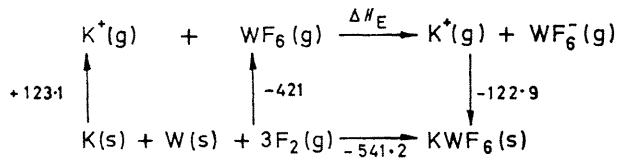
The hydrolysis of $KW^{V}F_6$, by alkaline hypochlorite occurs quantitatively according to equation (1).

$$KWF_6(S) + \tfrac{1}{2}OCl^-(aq) + 7OH^-(aq) \rightarrow K^+(aq) + WO_4^{2-}(aq) + \tfrac{1}{2}Cl^-(aq) + \tfrac{7}{2}H_2O \quad (1)$$

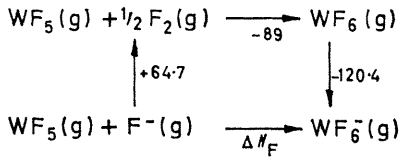
A frangible glass bulb, containing a known mass of the compound, was broken into a solution of sodium hydroxide

(N or 0·01N) and sodium hypochlorite (1·5%) contained in a glass Dewar calorimeter. The temperature change of the contents of the calorimeter was followed using a thermistor whose changing resistance was monitored by a Kipp BD2 recorder incorporated in a Wheatstone bridge. The recorder was calibrated by supplying a known amount of heat into the calorimeter through a constantin wire heater.

Using the measured heat of hydrolysis ($-123{\cdot}6 \pm 2{\cdot}6$ kcal mol^{-1}) and the known standard enthalpies of formation[2,3,4] (in kcal mol^{-1}) of OCl^-(aq) (−26·2), OH^-(aq) (−54·97), K^+(aq) (−60·04), WO_4^{2-}(aq) (−266·6), Cl^-(aq) (−39·95), F^-(aq) (−79·50), and H_2O(aq) (−68·315), the enthalpy or formation of KW^VF_6 is estimated to be -541 ± 3 kcal mol^{-1}. KW^VF_6 has a structure which is a slightly distorted tetragonal variant of the CsCl type;[5] the K–W distance, deducted from the lattice constants, is 4·40 Å, from which a lattice enthalpy of 122·9 kcal mol^{-1} may be calculated (assuming an undistorted CsCl structure) using the Born-Mayer equation. Using a heat of formation of gaseous WF_6 (−421 kcal mol^{-1}) estimated from heat of hydrolysis measurements[6]† the electron affinity ($-\Delta H_E$) of gaseous WF_6 is estimated to be 120 ± 5 kcal mol^{-1} at 25° from the appropriate thermochemical cycle (Scheme 1). From the known heat of oxidation of solid WF_5 to gaseous WF_6 (−65·63)[7] and the heat of sublimation of WF_5 (23·4 kcal mol^{-1}),[8] the fluoride affinity of WF_5 (ΔH_F) is estimated (Scheme 2) to be 145 ± 6 kcal mol.$^{-1}$



SCHEME 1. (*Enthalpies in kcal mol*$^{-1}$)



SCHEME 2. (*Enthalpies in kcal mol*$^{-1}$)

Bartlett's data suggest a minimum value for the electron affinity of WF_6 of 75—80 kcal mol^{-1}, but this can be reconciled with the present estimate if allowance is made for the probable exothermic nature of the gas reactions and for entropy changes in them. The only other estimate of fluoride ion affinity is that for the reaction $BF_3(g) + F^-(g) \rightarrow BF_4^-(g)$ ($-\Delta H_F = 76$ kcal mol^{-1}).[9]

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† There is disagreement between this and the fluorine bomb calorimeter value of 411·7 ± 0·5 kcal mol^{-1}.[7]

[1] N. Bartlett, *Angew. Chem.*, 1968, **7**, 433.
[2] J. E. McDonald, J. P. King, and J. W. Cobble, *J. Phys. Chem.*, 1960, **64**, 1345.
[3] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Circular NBS 1952, 500.
[4] D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, NBS Technical Note 1965, 270—1.
[5] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1957, 4212.
[6] O. E. Myers and A. P. Brady, *J. Phys. Chem.*, 1960, 64, 591.
[7] J. Schröder and F. J. Sieben, *Chem. Ber.*, 1970, **103**, 76.
[8] J. Schröder and F. J. Grewe, *Chem. Ber.*, 1970, **103**, 1536.
T. C. Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 159.