# Tungsten Chloride Pentafluoride

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ALTHOUGH monomeric volatile chloride fluorides of the characteristic elements are well known, knowledge of halide fluorides of the transition elements is restricted to difficultly volatile compounds, *viz.* $TiCl_2F_2$,[1] $TiClF_3$,[2] $UClF_3$,[3] $VClF_3$,[4] $V_2Cl_4F_5$,[4] $NbCl_4F$,[5] $TaCl_4F$,[6] and $OsIF_4$.[7]

We report the formation of volatile tungsten chloride pentafluoride, $WClF_5$, by the exchange reaction between tungsten hexafluoride and titanium tetrachloride. Preliminary experiments suggest that this kind of exchange reaction is of general applicability in the field.

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When titanium tetrachloride is added drop by drop to an excess of liquid tungsten hexafluoride at 5°, a red solid, which contains chloride fluorides of tungsten (probably $WCl_5F$ and $WCl_4F_2$), is formed. The liquid residue, which is largely unreacted tungsten hexafluoride, contains a little of a less volatile component which can be separated by vacuum-sublimation. From the modified Podbielniak column,[8] the tungsten hexafluoride appears at $-95°$; the less volatile component, which chemical analysis and vapour-density determinations show to be tungsten chloride pentafluoride, appears at $-65°$.

Tungsten chloride pentafluoride is a yellow solid melting at $-33{\cdot}7°$ to a yellow liquid. The monomeric vapour is colourless. At 25° the liquid disproportionates slowly to tungsten hexafluoride and solid tungsten chloride fluorides, and a boiling point has not been determined. The vapour appears to be more stable than the liquid. At about 3 mm. pressure, the infrared spectrum of the vapour, measured on a Perkin-Elmer Model 337 Spectrophotometer, shows three triplet absorptions, with principal maxima at 744, 700, and 655 cm.$^{-1}$, presumably due to W–F stretching modes ($\nu_3$ for $WF_6$ lies[9] at 712 cm.$^{-1}$). The $^{19}F$ nuclear magnetic resonance spectrum, measured on a carbon tetrachloride solution (Varian HR 100 instrument), shows two peaks in the correct intensity ratio of 1 : 4, at 126·5 and 182 p.p.m. respectively downfield from $CCl_3F$ as external standard. There is no indication of fine structure even under high resolution, but it would be expected that a quintuplet, associated with the axial fluorine, should lie under the less intense peak, and a doublet, associated with the equatorial fluorine atoms, under the more intense peak. The difference in chemical shift between the two absorptions is near that in $SClF_5$,[10] and is in the same direction, which suggests that $\pi$-bonding is not an important element in the structure.[11]

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