Kirk-Othmer Encyclopedia of Chemical Technology.

TUNGSTEN COMPOUNDS

1. Tungsten

Tungsten is a Group VIB transition element with atomic number of 74. It has the valence state of 0, +2, +3, +4, +5 or +6 in compounds. However, tungsten alone has not been observed as a cation. Its most stable, and therefore most common, valence state is +6. Tungsten complexes vary widely in stereochemistry and oxidation states. Complex formation is exemplified by the large number of polytungstates. Simple tungsten compounds, such as the halides, are also known.

The chemical uses of tungsten have increased substantially in more recent years. Catalysis of photochemical reactions and newer types of soluble organometallic complexes for industrially important organic reactions are among the areas of new applications (See also Catalysis).

2. Tungsten Hexacarbonyl

Tungsten hexacarbonyl [14040-11-0], $W(CO)_6$, may be prepared in yields >90% by the aluminum reduction of tungsten hexachloride [1283-01-7] in anhydrous ether under a pressure of 0.1 MPa (∼ 1 atm) of carbon monoxide at 70°C. It is purified by sublimation or steam distillation. A colorless to white solid, tungsten hexacarbonyl decomposes without melting at ∼ 150°C, although it sublimes *in vacuo*. It is a zero-valence monomeric compound, with a relatively low vapor pressure of 13.3 Pa (0.1 mm Hg) at 20°C and 160 Pa (1.20 mm Hg) at 67°C, and is fairly stable in air, water, or acid, but is decomposed by strong bases and attacked by halogens. Tungsten carbonyl is slightly soluble in organic solvents but insoluble in water (see Carbonyls).

Various applications such as lubricant additives, dyes, pigments, and catalysts are under investigation. Tungsten can be deposited from tungsten hexacarbonyl, but carbide formation and gas-phase nucleation present serious problems (1, 2). As a result, tungsten halides are the preferred starting material.

3. Tungsten Halides and Oxyhalides

Tungsten forms binary halides for all oxidation states between +2 and +6; oxyhalides are only known for oxidation states +5 and +6. In general, tungsten halogen compounds are reactive toward water and oxygen in air and must therefore be handled in an inert atmosphere. These are all solid-colored compounds at room temperature, except the fluorides, and many decompose on heating before melting. The hexachloride and hexafluoride [7783-82-6] are commercially available and are particularly suitable starting materials for the chemical vapor deposition of tungsten, which is an important process technique for coatings and free-standing parts such as thin-walled tubing. The resulting structure is generally columnar, but a method has been described for obtaining a fine-grained, noncolumnar tungsten structure (3).

3.1. Fluorides

Tungsten hexafluoride [7783-82-6],WF_6, is a colorless gas at room temperature, sp gr (specific gravity) 12.9 with respect to air. At 17.5°C, it condenses into a pale-yellow liquid, and at 2.5°C a white solid is formed. It may be prepared by treating hydrogen fluoride, arsenic trifluoride, or antimony pentafluoride with tungsten hexachloride or by direct fluoridation of tungsten:

$$\begin{aligned} WCl_6 + 6\ HF &\longrightarrow WF_6 + 6\ HCl \\ WCl_6 + 2\ AsF_3 &\longrightarrow WF_6 + 2\ AsCl_3 \\ WCl_6 + 3\ SbF_5 &\longrightarrow WF_6 + 3\ SbF_3Cl_2 \\ W + 3\ F_2 &\longrightarrow WF_6 \end{aligned}$$

Direct fluoridation of pure tungsten in a flow system at atmospheric pressure at 350–400°C is the most convenient procedure (4). Tungsten hexafluoride is extremely unstable in the presence of moisture and hydrolyzes completely to tungstic acid [7783-03-1]:

$$WF_6 + 4\ H_2O \longrightarrow H_2WO_4 + 6\ HF$$

Tungsten hexafluoride dissolves in benzene or cyclohexane to give a bright red color, in dioxane a pale red, and in ether a violet-brown.

Tungsten pentafluoride [19357-83-6], WF_5, is prepared by the reduction of the hexafluoride on a hot tungsten filament in almost quantitative yield (5).

Tungsten tetrafluoride [13766-47-7], WF_4, is a nonvolatile, hygroscopic, reddish-brown solid. It has been prepared in low yields by the reduction of the hexafluoride with phosphorus trifluoride in the presence of liquid anhydrous hydrogen fluoride at room temperature (6).

Tungsten oxytetrafluoride [13520-79-1], WOF_4, forms colorless plates, mp 110°C, bp 187.5°C,. It is prepared by the action of an oxygen–fluorine mixture on the metal at elevated temperatures (7). The compound is extremely hygroscopic and decomposes to tungstic acid in the presence of water.

Tungsten oxydifluoride [14118-73-1],, WO_2F_2, is a white solid prepared by the hydrolysis of WOF_4 (8). Its chemistry has not been investigated.

3.2. Chlorides

Tungsten hexachloride [1283-01-7], WCl_6, is a blue-black crystalline solid, mp 275°C, bp 346.7°C,. It is prepared by the direct chlorination of pure tungsten in a flow system at atmospheric pressure at 600°C. Solidification usually occurs without incident, but further cooling may result in a violent, explosion-like expansion of the solid mass at 168–170°C. This phenomenon may be associated with an $\alpha_2 \longrightarrow \alpha_1$ transition. However, tungsten hexachloride may be safely cooled if it occupies not more than one-half of the containing vessel. In the presence of moisture or oxygen, some $WOCl_4$ is formed as an impurity. Tungsten hexachloride is very soluble in carbon disulfide but decomposes in water to form tungstic acid. The hexachloride is easily reduced by hydrogen to the lower halides and finally to the metal itself (8).

Tungsten pentachloride [13470-13-8], WCl_5, is a black crystalline deliquescent solid, mp 243°C, bp 275.6°C. It is very slightly soluble in carbon disulfide and decomposes in water to the blue oxide, $W_{20}O_{58}$. Magnetic properties suggest that tungsten pentachloride may contain trinuclear clusters in the solid state, but this structure has not been defined. Tungsten pentachloride may be prepared by the reduction of the hexachloride with red phosphorus (9).

Tungsten tetrachloride [13470-14-9], WCl_4, is obtained as a coarse, crystalline, deliquescent solid that decomposes on heating. It is diamagnetic and may be prepared by the thermal-gradient reduction of WCl_6 with aluminum (10).

Tungsten dichloride [13470-12-7], WCl_2, is an amorphous powder. It is a cluster compound and may be prepared by the reduction of the hexachloride with aluminum in a sodium tetrachloroaluminate melt (11).

Tungsten oxytetrachloride [13520-78-0], $WOCl_4$, is a red crystalline solid, mp of 211°C, bp 327°C. It is soluble in carbon disulfide and benzene and is decomposed to tungstic acid by water. It may be prepared by refluxing sulfurous oxychloride, $SOCl_2$, on tungsten trioxide (12) and purified after evaporation by sublimation.

Tungsten oxydichloride [13520-76-8], WO_2Cl_2, a pale-yellow crystalline solid mp of 266°C, is soluble in cold water and in alkaline solution, although partly decomposed by hot water. It is prepared by the action of carbon tetrachloride on tungsten dioxide at 250°C in a bomb (13).

Tungsten oxytrichloride [14249-98-0], $WOCl_3$, a green solid, is prepared by the aluminum reduction of $WOCl_4$ in a sealed tube at 100–140°C (14).

3.3. Bromides

Tungsten hexabromide [13701-86-5], WBr_6, bluish-black crystals, mp of 232°C, is formed by metathetical exchange reaction of BBr_3 with tungsten hexachloride (15).

Tungsten pentabromide [13470-11-6], WBr_5, violet-brown crystals, mp of 276°C, bp 333°C, is extremely sensitive to moisture. It is prepared by the action of bromine vapor on tungsten at 450–500°C (16).

Tungsten tetrabromide [12045-94-2], WBr_4, black orthorhombic crystals, is formed by the thermal-gradient reduction of WBr_5, with aluminum, similar to the reduction of WCl_4 (10).

Tungsten tribromide [15163-24-3], WBr_3, is prepared by the action of bromine on WBr_2, in a sealed tube at 50°C (17). It is a thermally unstable black powder that is insoluble in water.

Tungsten dibromide [13470-10-5], WBr_2, formed by the partial reduction of the pentabromide with hydrogen, is a black powder that decomposes at 400°C.

Tungsten oxytetrabromide [13520-77-9], $WOBr_4$, black, deliquescent needles, mp of 277°C, bp 327°C, is formed by the action of carbon tetrabromide on tungsten dioxide at 250°C (13).

Tungsten oxydibromide [13520-75-7], WO_2Br_2, light-red crystals, is formed by passing a mixture of oxygen and bromine over tungsten at 300°C.

3.4. Iodides

Tungsten tetraiodide [14055-84-6], WI_4, is a black powder that is decomposed by air. It is prepared by the action of concentrated hydriodic acid on tungsten hexachloride at 100°C.

Tungsten triiodide [15513-69-6], WI_3, is prepared by the action of iodine on tungsten hexacarbonyl in a sealed tube at 120°C (18).

Tungsten diiodide [13470-17-2], WI_2, is a brown powder, sp gr 6.79, It is reported to be prepared by the action of anhydrous hydrogen iodide on tungsten hexachloride at 400–500°C (14). Research by other investigators, however, failed to show the existence of the diiodide, but a stable tungsten oxydiiodide, WO_2I_2, is described (20).

Tungsten oxydiiodide [14447-89-3],, is prepared by heating a mixture of tungsten and tungsten trioxide with excess iodine in a 500–700°C temperature gradient for 36 h (21).

3.5. Oxides, Acids, and Salts

Tungsten oxides form a series of well-defined ordered phases to which precise stoichiometric formulas can be assigned (22–29) (see Table 1). The composition of the tungsten oxides may vary over a fixed range without change in crystalline structure. Thus, the homogeneity ranges are represented by $WO_{2.95--3.0}$, $WO_{2.88--2.92}$ [12165-57-0], $WO_{2.664--2.776}$, and $WO_{1.99--2.02}$. Each tungsten atom is octahedrally surrounded by six oxygen atoms. In WO_3, these WO_6 units are joined through sharing of corner oxygen atoms only; but as the

Table 1. Tungsten Oxides

Oxide	CAS Registry no.	Phase	Average Oxygen/tungsten	Theoretical density, g/cm^3	Color
WO_3	[1314-35-8]	α	3.00	7.29	Yellow
$W_{20}O_{58}$	[12037-58-0]	β	2.90	7.16	Blue-violet
$W_{18}O_{49}$	[12037-57-9]	γ	2.72	7.78	Reddish violet
WO_2	[12036-22-5]	δ	2.00	10.82	Brown
W_3O	[39368-90-6]	(β−W)	0.33	14.4	Gray

oxygen-to-tungsten ratio decreases, the units become more intricately joined in combinations of corners, edges, and faces to form chains and slabs. The loss of each oxygen atom from the oxide lattice means that two electrons are added to the conduction band of the lattice, and it is meaningless to speak of pentavalent and tetravalent tungsten atoms in such a lattice.

Tungsten trioxide is a yellow powder. However, the smallest diminution of oxygen brings about a change in color. Tungsten trioxide, which is pseudorhombic at room temperature but tetragonal above 700°C, is usually prepared from tungstic acid or tungstates. It is the most important tungsten oxide and is the starting material for the production of tungsten powder. Tungsten trioxide is reduced to the metal by carbon above 1050°C and by hydrogen as low as 650°C. At lower temperatures, intermediate oxides are formed. Tungsten trioxide is insoluble in water and in acid solutions except hydrofluoric) but forms a tungstate with strong alkali.

$$2\ NaOH + WO_3 \longrightarrow Na_2WO_4 + H_2O$$

When heated in a hydrogen chloride atmosphere, WO_3 is completely volatilized at $\sim 500°C$, forming the oxydichloride, WO_2Cl_2.

Tungsten dioxide is a brown powder formed by the reduction of WO_3 with hydrogen at 575–600°C. Generally, this oxide is obtained as an intermediate in the hydrogen reduction of the trioxide to the metal. On reduction, first a blue oxide, then a brown oxide (WO_2), is formed. The composition of the blue oxide was in doubt for a long time. However, it has since been resolved that $W_{20}O_{58}$ and $W_{18}O_{49}$ are formed as intermediates. They may also be prepared by the reaction of tungsten with WO_3.

The oxide W_3O is regarded as both an oxide and a metal phase. It is gray and has a density of 14.4 g/cm^3, It is prepared by the electrolysis of fused mixtures of WO_3 and alkali-metal phosphates. At $\sim 700°C$, it decomposes into W and WO_2; β tungsten is W_3O.

3.6. Tungsten Bronzes

Tungsten bronzes (30, 31) constitute a series of well-defined nonstoichiometric compounds of the general formula $M_{1-x}WO_3$, where x is a variable between 0 and 1 and M is some other metal. Generally M is an alkali metal, although many other metals can be substituted.

The systems most extensively investigated are the sodium tungsten bronzes. These compounds are intensely colored, ranging from golden yellow to bluish black, depending on the value of x, and, in crystalline form, exhibit a metallic sheen. They have a positive temperature coefficient of resistance for $Na{:}WO_3$ ratios $> >0.3$, and a negative temperature coefficient of resistance at lower ratios. Sodium tungsten bronzes are inert to chemical attack by most acids, but may be dissolved by basic reagents. Sodium tungsten bronzes serve as promoters for the catalytic oxidation of carbon monoxide and reformer gas in fuel cells (32) (see Batteries, secondary). In general, these bronzes form cubic or tetragonal crystals, the lattice constants increasing with sodium concentration. They are prepared by electrolytic reduction, vapor-phase deposition, fusion, or

Table 2. Properties of Normal Tungstates

Compound	CAS Registry no.	Properties	Specific gravity
$BaWO_4$	[7787-42-0]	Colorless, tetragonal, $a = 0.564$ nm, $c = 1.270$ nm	5.04
$CdWO_4$	[7790-85-4]	Yellow, rhombic	
$CaWO_4$	[7790-75-2]	White, tetragonal, $a = 0.524$ nm, $c = 1.138$ nm, $n_D^{20}1.9263$	6.06
$Ce_2(WO_4)_3$	[52345-28-5]	Yellow, monoclinic, $a = 1.151$ nm, $b = 1.172$ nm, $c = 0.782$ nm, $\beta = 109°48'$, mp 1089°C	6.77
$PbWO_4$	[7759-01-5]	Colorless, monoclinic, mp 1123°C	8.46
Ag_2WO_4	[13465-93-5]	Pale yellow	
Na_2WO_4	[13472-45-2]	White, rhombic, mp 698°C	4.179
$Na_2WO_4{\cdot}2H_2O$	[10213-10-2]	White, rhombic, loses $2H_2O$ at 100°C	3.245
$SrWO_4$	[13451-05-3]	White, tetragonal, $a = 0.540$ nm, $c = 1.190$ nm	6.187

solid-state reaction (33, 34). The latter method is the most versatile, in which the reagents are finely ground and heated at 500–850°C in vacuum for prolonged periods of time.

3.7. Tungsten Blue

The mild reduction, for example, by Sn(II), of acidified solutions of tungstates, tungsten trioxide, or tungstic acid in solutions gives intense blue products, which are referred to by the general term *tungsten blues*. Thus they resemble molybdenum blues in many respects. Tungsten trioxide acquires a bluish tint merely on exposure to underwater ultraviolet radiation. If hydrogen is produced in a tungstate solution by means of zinc and hydrochloric acid, blue precipitates form that are stable in air. These are believed to be hydrogen analogues of the tungsten bronzes. These blue hydrogen tungsten bronzes, $H_{1-x}WO_3$, are prepared by the wet reduction of tungstic acid and are structurally related to the alkali tungsten bronzes (35–37). Tungsten blues have a strong tendency to form colloids.

3.8. Tungstic Acid and Tungstates

Tungstic acid, H_2WO_4 or $WO_3{\cdot}H_2O$, is an amorphous yellow powder that is practically insoluble in water or acid solution, but dissolves readily in a strongly alkaline medium. It may be precipitated from hot tungstate solutions with strong acids. However, if the tungstate solution is acidified in the cold, a white voluminous precipitate of hydrated tungstic acid forms, which has the formula $WO_3{\cdot}xH_2O$, where x is ~ 2. It is converted to the yellow form by boiling in an acid medium. Both the yellow and white forms tend to become colloidal on washing. Tungstic acid forms a series of stable salts of the types $M(I)_2WO_4$, $M(II)WO_4$, and $M(III)_2(WO_4)_3$, of which some also exist in the hydrated form. Except for tungstates of the alkali metals and magnesium, these salts are generally sparingly soluble in water. They are decomposed by hot mineral acids (except phosphoric) to tungstic acid. The insoluble tungstates are prepared by adding a sodium tungstate solution to a solution of the appropriate salt. Some properties of these tungstates are given in Table 2.

Ammonium tungstate [11140-77-5], $(NH_4)_2WO_4$), cannot be obtained from an aqueous solution since it decomposes when such a solution is concentrated. It is prepared by the addition of hydrated tungstic acid to liquid ammonia.

Anhydrous sodium tungstate, Na_2WO_4, is prepared by fusing tungsten trioxide in the proper proportion with sodium hydroxide or sodium carbonate:

$$WO_3 + 2NaOH \longrightarrow Na_2WO_4 + H_2O$$

Table 3. Polytungstates in Order of Increasing Ratio of $H_3O^+ : WO_4^{2-}$

$H_3O^+:WO_{2-4}^-$	Polytungstate	CAS Registry no.	Common name
0.333	$W_{12}O_{20\text{—}46}$		Para-Z
0.667	W_3O_{4--11}	[39898-14-1]	Tritungstate
	$H_4W_3O_{4\text{—}13}$		
1.167	$H_{10}W_{12}O_{10--46}$	[12401-49-9]	Para-B
	HW_6O_{5--21}	[11080-77-6]	Para-A
1.33	$W_{12}O_{8--40}$		
1.50	$H_4W_3O_{4\text{—}13}$	[12207-61-3]	Meta
	$H_4W_3O_{4\text{—}13}$	[12273-48-2]	Pseudometa
2.0	$WO_3{\cdot}H_2O(H_2WO_4)$	[7783-03-1]	Tungstic acid

$$WO_3 + Na_2CO_3 \longrightarrow Na_2WO_4 + CO_2$$

On crystallization from aqueous solution, the dihydrate is generally obtained.

The tungstates are of particular interest in electronic and optical applications. They are also used for ceramics, catalysts, pigments, and corrosion; as fire inhibitors; and in other applications.

3.9. Polytungstates

An important and characteristic feature of the tungstate ion is its ability to form condensed complex ions of isopolytungstates in acid solution (38). As the acidity increases, the molecular weight of the isopolyanions increases until tungstic acid precipitates. Extensive investigations on these systems have been hampered by lack of well-defined solid derivatives.

The chemistry of tungsten in solution has recently been studied by chromatography and spectroscopy (39, 40). Much of the reported work concerns the existence of tungstate species in acid solutions with particular reference to the molar ratio of soluble tungstate species.

If polytungstates are considered as formed by the addition of acid to $WO_4{}^{2-}$, then a series of isopolytungstates appears, in which the degree of aggregation in solution increases with decreasing pH. The relationships of the species, in order of increasing $H_3O^+:WO_4{}^{2-}$ ratio, are shown in Table 3.

Metatungstates of the alkali, alkaline-earth, rare-earth, and transition metals have been reported. However, conventional synthesis rarely gives high yields of the pure compounds. The rare-earth tungstates, for example $La_2(H_2W_{12}O_{40}){\cdot}xH_2O$, may be prepared by the action of lanthanide carbonates on metatungstic acid, $H_6(H_2W_{12}O_{40})$ [12299-86-4]. Other salts are prepared by the action of carbonates or sulfates of the corresponding metal on metatungstic acid or metatungstates. Generally, these compounds are heat-sensitive and should be recovered by freeze drying. Alkali metal and ammonium metatungstates, $M_6(H_2(W_{12}O_{40}){\cdot}xH_2O$, may be prepared by the digestion of hydrated tungsten trioxide with the corresponding base (42–47). These salts are generally known for their high solubility in water; the most important is ammonium metatungstate [12028-48-7], $(NH_4)_6(H_2W_{12}O_{40})$.

The paratungstates are generally crystallized from slightly basic solutions. By far the most important salt is ammonium paratungstate [1311-93-9], $(NH_4)_{10}W_{12}O_{40}{\cdot}5H_2O$, which is usually known as the “heavy form” of commercial ammonium paratungstate. It is usually formed by crystallization from a boiling solution. However, if crystallization is allowed to take place slowly at room temperature, an undecahydrate, $(NH_4)_{10}W_{12}O_{40}{\cdot}11H_2O$ [12383-34-5], is formed. This hydrate is known as the “light” form of ammonium paratungstate. Both forms are insoluble in water and decompose in acid or alkali. They are reduced to the metal by heating in a

Table 4. Principal Species of Heteropolytungstates

Ratio of heteroatoms to W atoms	Principal central atoms, X	Typical formulas	Structure by X ray
1:12	P^{5+}, As^{5+}, Si^{4+}, Ge^{4+}, Ti^{4+}, Co^{3+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Ga^{3+}, Te^{4+}, B^{3+}	$[X^{n+}(W_{12}O_{40})]^{(8-n)}$	Known
1:10	Si^{4+}, Pt^{4+}	$[X^{n+}(W_{10}O_x)]^{(2x-60-n)}$	Unknown
1:9	Be^{2+}	$[X^{2+}(W_9O_{31})]^{6-}$	Unknown
1:6	Series A: Te^{6+}, I^{7+}	$[X^{n+}(W_6O_{24})]^{(12-n)}$	Isomorphous with 6-molybdates
	Series B: Ni^{2+}, Ga^{3+}	$[X^{n+}(W_6O_{24}H_6)]^{(6-n)}$	Known
2:18	P^{5+}, As^{5+}	$[X_2^{n+}(W_{18}O_{62})]^{(12-n)}$	Known
2:17	P^{5+}, As^{5+}	$[X_2^{n+}(W_{17}O_x)]^{(2x-102-2n)}$	Unknown
$1m{:}6m^a$	As^{3+}, P^{3+}	$[X^{n+}(W_6O_x)]_m^{m(2x-36-n)}$	Unknown

[a] m = unknown·

hydrogen atmosphere. Ammonium paratungstate is widely used as a catalyst. Peroxytungstic acid [41486-83-3], $H_2WO_2(O_2)_2$. Peroxytungstates are known but tend to be unstable; the instability increases with increasing ratio of oxygen to tungsten (48).

Heteropolyanions are closely related to the isopolyanions, and over 30 elements are known to function as the heteroatom with many stoichiometric ratios between the heteroatom and the anion. Both the acids and the salts are known and are usually hydrated when crystallized from aqueous solutions. As a class, heteropoly compounds are characterized by a number of properties independent of the heteroatom and the metallic component. Typically, heteropoly tungsten compounds show the following characteristics: high molecular weight, usually >3000; a high degree of hydration; unusually high solubility in water and some organic solvents; strong oxidizing action in aqueous solution; strong acidity in free acid form; decomposition in strongly basic aqueous solutions to give normal tungstate solutions; and highly colored anions or colored reaction products.

Heteropoly anions may be classified according to the ratio of the number of central atoms to tungsten, as shown in Table 4.

Structures of heteropolytungstate and isopolytungstate compounds have been determined by X-ray diffraction. The anion structures are represented by polyhedra that share corners and edges with one another. Each W is at the center of an octahedron, and an O atom is located in each vertex of the octahedron. The central atom is similarly located at the center of an XO_4 tetrahedron or XO_6 octahedron. Each such polyhedron containing the central atom is generally surrounded by WO_6 octahedra that share corners edges (or both) with it and with one another; thus, the correct total number of oxygen atoms is utilized. Each WO_6 octahedron is directly attached to a central atom through a shared oxygen atom. In the actual structures, the octahedra are frequently distorted. The oxygens are relatively large spheres, and practically all space within the anion structure is taken up by the bulky oxygens, which are close-packed or nearly so. When the large heteropolytungstate anions are packed together as units in a crystal, the interstices between the anions are very large compared to water molecules or most simple cations. In most compounds, there is apparently no direct linkage between the individual heteropoly anions, such as in the structures of $K_6CoW_{12}O_{40}{\cdot}20H_2O$ [37346-54-6] and $K_6P_2W_{18}O_{62}$ [60748-58-5]. Instead, the complexes are joined by hydrogen bonding through some molecules of water of hydration. These principles are illustrated in the crystal structure of $H_3PW_{12}O_{40}{\cdot}xH_2O$ [12501-23-4], as determined by X-ray diffraction (49, 50).

Heteropoly salts of large cations, such as cesium, frequently crystallize as acid salts regardless of the ratio of cations to anions in the mother liquor. Furthermore, salts of these cations are frequently less highly hydrated than salts of smaller cations. Apparently, the larger cations take up so much of the space between the heteropoly anions that there is less room for water. There is often not enough room for the large cations required to form a normal salt. Instead, solvated hydrogen ions fill in to balance the negative charge of the anions, and a crystalline acid salt results.

Commercially, heteropolytungstates, particularly the heteropolytungstates, are produced in large quantities as precipitants for basic dyes, with which they form colored lakes or toners (see also Dyes and dye intermediates). They are also used in catalysis, passivation of steel and other procedures.

4. Sulfides

Tungsten disulfide [12138-09-9], WS_2, although found in nature, is usually prepared by heating tungsten powder with sulfur at 900°C. It is a soft, grayish-black powder, relatively inert and unreactive, with sp gr 7.5. It is insoluble in water, hydrochloric acid, alkali, and organic solvents or oils, and decomposes in hot, strong oxidizing agents, such as aqua regia, concentrated sulfuric acid, and nitric acid. Heating in air or in the presence of oxygen yields WO_3. However, its thermal stability in air is $\sim 90°C$ higher than that of MoS_2. Tungsten disulfide forms adherent, soft, continuous films on a variety of surfaces and exhibits good lubricating properties similar to molybdenum disulfide and graphite (51) (see also Lubrication and lubricants). It is also reported to be a semiconductor (qv).

Tungsten trisulfide [12125-09-8], WS_3, is a chocolate-brown powder, slightly soluble in cold water, but readily forming a colloidal solution in hot water. It is prepared by treating an alkali-metal thiotungstate with HCl (52). Tungsten trisulfide is soluble in alkali carbonates and hydroxides.

Tungsten forms thiotungstates corresponding to the tungstates, but one, two, three, or all of the oxygen atoms are replaced by sulfur. These compounds form with solutions of the alkali or alkaline-earth tungstates saturated with hydrogen sulfide. They vary in color from pale yellow to yellowish-brown and, in general, crystallize well. Acidifying a solution of these salts precipitates tungsten trisulfide.

Potassium tetrathiotungstate [14293-75-5], K_2WS_4, forms yellow rhombic crystals that are soluble in water. Ammonium tetrathiotungstate [13862-78-7], $(NH_4)_2WS_4$, forms bright orange crystals that exhibit a metallic iridescence. These crystals are stable in dry air and soluble in water. Ammonium tetrathiotungstate is generally prepared by treating a solution of tungstic acid with excess ammonia and saturating with hydrogen sulfide. It is readily decomposed in a nonoxidizing atmosphere to WS_2, for which it is a convenient source.

5. Interstitial Compounds

Tungsten forms hard, refractory, and chemically stable interstitial compounds with nonmetals, particularly C, N, B, and Si. These compounds are used in cutting tools, structural elements of kilns, gas turbines, jet engines, sandblast nozzles, protective coatings, and other components (see also Refractories; Refractory coatings).

5.1. Carbides

Tungsten and carbon form two binary compounds, tungsten carbide [12070-12-1], WC, sp gr 15.63, and ditungsten carbide [12070-13-2], W_2C, sp gr 17.15; both are prepared by heating tungsten and carbon at high temperatures. The presence of hydrogen or a hydrocarbon gas promotes the reaction. The relative quantities of the reactants and the temperature determine the phase formed. Tungsten carbide may also be prepared from oxygen-containing compounds of tungsten, but because of the tendency to form oxycarbides, a final heating in vacuum above 1500°C is necessary. Both carbides melt at $\sim 2800°C$ and have a hardness approaching that of diamond. Tungsten carbides are insoluble in water, but are readily attacked by HNO_3–HF. The most important commercial application is in hard metals. Tungsten carbides are brittle, but combination with, for example, cobalt decreases the brittleness. Approximately 65% of tungsten production is for the manufacture of WC (see Carbides).

5.2. Nitrides

The nitrides of tungsten are quite similar to the carbides. Although nitrogen does not react directly with tungsten, the nitrides can be prepared by heating tungsten in ammonia. The two phases, ditungsten nitride [12033-72-6], W_2N, and tungsten nitride [12058-38-7], WN, have been studied extensively (53, 54) (see Nitrides).

5.3. Borides

Ditungsten boride [12007-09-9], W_2B, and tungsten boride, WB, are prepared by hot-pressing tungsten and boron. Ditungsten pentaboride [12007-98-6], W_2B_5, is prepared by heating tungsten trioxide, graphite, and boron carbide *in uacuo*. Tungsten borides are extremely hard and exhibit almost metallic electrical conductivity. Recently, the formation of tungsten boride phases in the manufacture of boron filaments for structural composites for space vehicles and aircraft has been reported (55) (see Boron compounds, refractory boron compounds).

5.4. Silicides

Tungsten silicides form a protective oxide layer over tungsten to prevent destructive oxidation at elevated temperatures. The layer fails to protect at lower temperatures, a behavior referred to as *disilicide pest*. This failure can be explained by the silicon being initially oxidized to SiO_2 at the surface and depleting the surface of Si, forming pentatungsten trisilicide [12039-95-i], W_5Si_3. At high temperatures, a uniform layer of W_5Si_3 is formed, but at lower (pest) temperatures, the attack is not uniform and seems to follow grain boundaries or subgrain boundaries in the disilicide. The next stage is the rapid growth and penetration of the complex oxide into the disilicide layer. This process ultimately consumes the disilicide, causing oxidation of the tungsten substrate. The existence of tritungsten disilicide [12509-47-6], W_3Si_2, and ditungsten silicide [56730-24-6], W_2Si, has been reported (56).

Ditungsten trisilicide [12138-30-6], W_2Si_3, gray, sp gr alkaline solutions. It is readily attacked by HNO_3–HF and hydroxides.

Tungsten disilicide [12039-88-2], WSi_2, forms bluish-gray tetragonal crystals ($\alpha 0.3212$ nm, $c = 0.7880$ nm). It is insoluble in water and melts at 2160°C. The compound is attacked by fluorine, chlorine, fused alkalies, and HNO_3–HF. It may be used for high-temperature thermocouples in combination with $MOSi_2$ in an oxidizing atmosphere.

5.5. Anionic Complexes

Compounds of tungsten with acid anions other than halides and oxyhalides are relatively few in number, and are known only in the form of complex salts. A number of salts containing hexavalent tungsten are known. Potassium octafluorotungstate [57300-87-5], K_2WF_8, can be prepared by the action of KI on $W(CO)_6$ in an IF_5 medium. The addition of tungstates to aqueous hydrofluoric acid gives salts that are mostly of the type $M(I)_2(W_2F_4)$. Similarly, double salts of tungsten oxydichloride are known.

Salts containing pentavalent tungsten may be obtained by the reduction of alkali tungstate in concentrated hydrochloric acid. Salts of type $M(I)_2(WOCl_5)$ (green), $M(I)(WOCl_4)$ (brown-yellow), and $M(I)(WOCl_4{\cdot}H_2O)$ (blue) have been isolated. Thiocyanato and bromo salts are also known.

Salts containing tetravalent tungsten have been prepared by various methods. The most important are the octacyanides, $M(I)_4(W(CN)_8)$. They form yellow crystals and are very stable. They are isolated as salts or free acids and can be oxidized by $KMnO_4$ in H_2SO_4 to compounds containing pentavalent tungsten, $M(I)_3(W(CN)_8)$ (yellow).

The only known trivalent tungsten complex is of the type $M(I)_3(W_2Cl_9)$. It is prepared by the reduction of strong hydrochloric acid solutions of K_2WO_4 with tin. If the reduction is not sufficient, a compound containing tetravalent tungsten, $K_2(WCl_5(OH))$ [84238-10-0], is formed (57).

Hazards encountered with tungsten may be caused by substances associated with the production and use of tungsten, including As, Sb, Pb, and other impurities in tungsten ores; Co aerosols and dust in the carbide industry; and thoria used in welding elecrodes. Lanthanum is being promoted as a substitute for thoria in this application.

A considerable difference in the toxicity of soluble and insoluble compounds of tungsten has been reported (58). For soluble sodium tungstate, $Na_2WO_4{\cdot}2H_2O$, injected subcutaneously in adult rats, LD_{50} is 140–160 mg W/kg. Death is due to generalized cellular asphyxiation. Guinea pigs treated orally or intravenously with $Na_2WO_4{\cdot}2H_2O$ suffered anorexia, colic, incoordination of movement, trembling, and dyspnea.

Orally in rats, the toxicity of sodium tungstate was highest, tungsten trioxide was intermediate, and ammonium tungstate [15855-70-6] least (59, 60). In view of the degree of systemic toxicity of soluble compounds of tungsten, a threshold limit of 1 mg of tungsten per cubic meter of air is recommended. A threshold limit of 5 mg of tungsten per cubic meter of air is recommended for insoluble compounds (61).

6. Uses

Tungsten compounds, especially the oxides, sulfides, and heteropoly complexes, form stable catalysts for a variety of commercial chemical processes, such as, petroleum processing (62). The tungsten compounds may function as principal catalysts or as promoters of other catalysts. The blue oxide, $W_{20}O_{58}$, is an important catalyst in industrial chemical synthesis involving hydration, dehydration, hydroxylation, and epoxidation (63). It is expected that the application of tungsten catalysts will increase greatly since many tungsten compounds are commercially available.

Tungsten hexachloride is used for preparing tungsten metathesis catalysts, which are technically very interesting because they form double and triple bonds with carbon. It is claimed that these catalysts permit the systematic control of a class of compounds used in the production of petroleum, plastics, synthetic fibers, and detergents. The improved control is expected to cut costs by providing more efficient use of raw materials (1). Films of tungsten deposited on various substrates improve the electrical conductivity of transparent tin oxide coatings on aircraft windows and windshields (see Film deposition techniques). Other uses include fire-retardant catalysts and as a fluxing agent in welding.

Tungsten disulfide forms adherent, soft, continuous films on a variety of substrates and exhibits good lubrication under extreme conditions of temperature, load, and vacuum. Applied as a dry powder, suspension, bonded film, or aerosol, it can be an effective lubricant in wire drawing, metal forming, valves, gears, bearings, packing materials, and other applications. Oil-soluble tungsten compounds, such as the ammonium salts of tungstate or tetrathiotungstate, are reported to be effective lubricating-oil additives.

Sodium tungstate is used in the manufacture of *heteropolyacid color lakes*, which are used in printing inks, plants, waxes, glasses, and textiles. It is also used as a fuel-cell electrode material and in cigarette filters. Other uses include the manufacture of tungsten-based catalysts, the fireproofing of textiles, and as an analytical reagent for the determination of uric acid.

Calcium tungstate is fluorescent when exposed to ultraviolet radiation and is therefore widely used in the manufacture of phosphors. It is used in lasers, fluorescent lamps, high-voltage sign tubes, and oscilloscopes for high-speed photographic processes. Small crystals have been used for injection into malignant tumors, thus affording by transillumination a means of X-ray treatment. Other uses include screens for X-ray observations and photographs, luminous paints, and scintillation counters.

Ammonium paratungstate is of commercial significance because it is the precursor of high-purity tungsten oxides, tungsten, and tungsten carbide powders. It is slightly soluble in water but reacts with hydrogen peroxide to produce soluble peroxytungsten compounds.

Ammonium metatungstate is of commercial significance because of its high solubility in water. This property, as well as its acid characteristics, make ammonium metatungstate a very desirable starting material for catalysts and the impregnation of catalyst carriers with alkali-free solutions of tungsten. Other uses include nuclear shielding, corrosion inhibitors, and the preparation of other tungsten chemicals.

Tungsten trioxide is a source material for preparation of tungsten metal and tungsten carbide powders. Because of its bright yellow color, it is used as a pigment in oil and water colors (see Pigments). It is used in a wide variety of catalysts; the most recent application is in the control of air pollution and industrial hygiene.

Tungsten carbides are widely used in the manufacture of hard carbides for high-speed machining tools, wire-drawing dies, wear surfacing, drills and microdrills down to 0.2 mm diameter for circuit-board drilling, and similar applications.

Heteropoly tungstic acids particularly the heteropolys, are useful in analytical chemistry and biochemistry as reagents; in atomic-energy work as precipitants and inorganic ion exchangers; in photographic processes as fixing agents and oxidizing agents; in plating processes as additives; in plastics, adhesives, and cements for imparting water resistance; and in plastics and plastic films as curing or drying agents. An important use for tungstophosphoric acid [12067-99-1] and its sodium salts is the manufacture of organic pigments. These compounds are also used extensively for the surface treatment of furs. In the textile industry, the salts are useful as antistatic agents. The acids are used in diverse applications, such as printing inks, paper coloring, nontoxic paints, and wax pigmentation.

The tungstates and molybdates are good corrosion inhibitors and have been used for some time in antifreeze solutions. In addition, they are used as laser-host materials, phosphors, and for the flameproofing of textiles.

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