ZIRCONIUM AND ZIRCONIUM COMPOUNDS

1. Introduction

Zirconium [7440-67-7] is classified in subgroup IVB of the periodic table with its sister metallic elements titanium and hafnium. Zirconium forms a very stable oxide. The principal valence state of zirconium is +4, its only stable valence in aqueous solutions. The naturally occurring isotopes are given in Table 1. Zirconium compounds commonly exhibit coordinations of 6, 7, and 8. The aqueous chemistry of zirconium is characterized by the high degree of hydrolysis, the formation of polymeric species, and the multitude of complex ions that can be formed.

Zirconium occurs naturally as a silicate in zircon [1490-68-2], the oxide baddeleyite [12036-23-6], and in other oxide compounds. Zircon is an almost ubiquitous mineral, occurring in granular limestone, gneiss, syenite, granite, sandstone, and many other minerals, albeit in small proportion, so that zircon is widely distributed in the earth's crust. The average concentration of zirconium in the earth's crust is estimated at 220 ppm, about the same abundance as barium (250 ppm) and chromium (200 ppm) (2).

Zircon has been known as a gem mineral since biblical times and was known as jargon in Sri Lanka (Ceylon) and as hyacinth in France. The name zircon possibly comes from the Arabic *zargon* for the gold or dark amber color of the more common gemstone. Zircons may be colorless, amber, red, reddish

Table 1. **Naturally Occurring Zirconium Isotopes**

Isotope	CAS Registry Number	Occurrence, %[a]	Thermal neutron capture cross section, 10^{-28} m^2[b]
^{90}Zr	[13982-15-5]	51.45	0.03
^{91}Zr	[14331-93-2]	11.32	1.14
^{92}Zr	[14392-15-5]	17.19	0.21
^{94}Zr	[14119-12-1]	17.28	0.055
^{96}Zr	[15691-06-2]	2.76	0.020

[a] Ref. 1.
[b] To convert m^2 to barns, multiply by 10^{28}.

brown, blue, green, or black. In 1789, Klaproth announced that in analyzing jargon from Sri Lanka he had found 68% of an unknown earth which he called zirkonerde (3). In 1797, Vauqelin studied this new earth, to which the name zirconia was given, and published the preparation and properties of some of its compounds (4). In 1824, Berzelius prepared the first crude zirconium metal, a black powder, by heating potassium and potassium hexafluorozirconate [16923-95-8] in a closed pot (5). In 1914, the first relatively pure zirconium was prepared by the reduction of zirconium tetrachloride [10026-11-6] with sodium in a bomb.

High purity zirconium was first produced by van Arkel and de Boer in 1925. They vaporized zirconium tetraiodide [13986-26-0] into a bulb containing a hot tungsten filament which caused the tetraiodide to dissociate, depositing zirconium on the filament.

Approximately 95% of the consumption of zirconium is as zircon, zirconium oxide, or other zirconium chemicals. The remainder is consumed as zirconium metal and zirconium-containing metals.

2. Occurrence and Mining

Zirconium is found in at least 37 different mineral forms (6) but the predominant commercial source is the mineral zircon, zirconium orthosilicate. Other current mineral sources are baddeleyite and eudialyte [12173-26-1].

Zircon occurs worldwide as an accessory mineral in igneous, metamorphic, and sedimentary rocks. Weathering has resulted in segregation and concentration of the heavy mineral sands in layers or lenses of placer deposits in river beds and ocean beaches. Zircon is the primary source of all hafnium. All commercial sources of zircon are derived from the mining of these ancient, unconsolidated beach deposits, the largest of which are in Kerala State in India, Sri Lanka, the east and west Coasts of Australia, on the Trail Ridge in Florida, and at Richards Bay in the Republic of South Africa. These heavy mineral sands are processed for the recovery of the titanium-bearing minerals ilmenite, rutile, and leucoxene, the zircon is obtained as a co-product. The output of zircon depends largely then on the market for these titanium minerals used in producing titanium oxide white pigment and titanium metal.

The deposits, usually ca 4% heavy minerals, are mined with front-end loaders or sand dredges. Typically, the overburden is bulldozed away, the excavation is flooded, and the raw sand is handled by a floating sand dredge capable of dredging to a depth of 18 m. The material is broken up by a cutter head to the bottom of the deposit and the sand slurry is pumped to a wet-mill concentrator mounted on a floating barge behind the dredge. Initial wet concentration using screens, Reichert cones, spirals, and cyclones removes the coarse sand, slimes, and light-density sands to produce a 40 wt% heavy-mineral concentrate. The tailings are returned to the back end of the excavation and used for rehabilitation of worked-out areas. The concentrate is dried and iron oxide and other surface coatings are removed; various combinations of gravity separation, magnetic separation (qv), and electrostatic separation yield individual concentrates of rutile, ilmenite, leucoxene, zircon, monazite, and xenotime. Other heavy minerals such as staurolite, tourmaline, sillimanite, corundum, and magnetite may be recovered as local situations warrant. Typical analyses of zircon sand samples are given in Table 2.

Baddeleyite, a naturally occurring zirconium oxide, has been found in the Poco de Caldas region of the states of Sao Paulo and Minas Geraes in Brazil, Kovdor in Russia, and the northeastern Transvaal of the Republic of South Africa. Brazilian baddeleyite occurs frequently with zircon, and ore shipments are reported to contain 65–85% zirconium oxide, 12–18% silica, and 0.5% uranium oxide. Very little of this ore is exported now because all radioactive minerals are under close control of the Brazilian government. Russia was the sole producer of baddeleyite in 2005 (7).

The Phalaborwa complex in the northeastern Transvaal is a complex volcanic orebody. Different sections are mined to recover magnetite, apatite, a copper concentrate, vermiculite, and baddeleyite, listed in order of annual quantities mined. The baddeleyite is contained in the foskorite ore zone at a zirconium oxide concentration of 0.2%, and at a lesser concentration in the carbonatite orebody. Although baddeleyite is recovered from the process tailings to meet market demand, the maximum output could be limited by the requirements for the magnetite and apatite. The baddeleyite concentrate contains ca 96% zirconium oxide

Table 2. **Typical Analysis of Zircon Sands, %**

Assay	Sri Lanka	India	Nigeria	Republic of South Africa	United States, Florida	Australia	
						East	West
constituents							
$(Zr + Hf)O_2$	64.9	64.4	58.2	65.0	65.3	65.7	64.6
Fe_2O_3	0.16	0.23	0.90	0.18	0.07	0.06	0.28
Al_2O_3	0.20	0.60	0.65	0.15	0.17	0.14	0.25
TiO_2	0.71	0.16	0.05	0.08	0.10	0.17	0.32
P_2O_5	0.18	0.13	0.39	0.13	0.05	0.07	0.08
U_3O_8	0.03	0.04	0.11	0.03	0.03	0.03	0.03
Nb_2O_5	<0.01	<0.01	2.0	<0.01	<0.01	<0.01	<0.01
Hf/Hf + Zr	2.2	2.3	6.8	2.3	2.2	2.2	2.2
size, μm (mesh)							
>149 (+100)	0.1	41.8	97.2	5.6	0.4	83.8	20.2
<74–149 (−100–200)	40.7	48.6	2.7	92.7	91.7	14.2	77.9
<74 (−200)	59.2	9.6	0.1	1.7	7.9	2.0	1.9

with a hafnium content of 2% Hf/Zr + Hf. A comminuted, chemically beneficiated concentrate containing ca 99% zirconium oxide is produced also.

Eudialyte, $(Na,Ca)_6ZrOH(Si_3O_9)_2$, from a large deposit near Narssaq in southwest Greenland, is the source of pure zirconium oxide. The hafnium ratio in the ore is 2.2% Hf/Zr + Hf.

Two zirconium-containing minerals were discovered in North America, namely, welognite [55659-01-3], $(Sr_{2.8}Ca_{0.2})ZrNa_2(CO_3)_6 \cdot 3\,H_2O$, and gittinsite [75331-27-0], $CaZrSi_2O_7$ (8,9). Unlike zircon, the zirconium content of these minerals and eudialyte can be dissolved by strong acid.

3. Physical Properties

Zirconium is a hard, shiny, ductile metal, similar to stainless steel in appearance. It can be hot-worked to form slabs, rods, and rounds from arc-melted ingot. Further cold-working of zirconium with intermediate annealings produces sheet, foil, bar wire, and tubing. Physical properties are given in Table 3.

4. Chemical Properties

Zirconium forms anhydrous compounds in which its valence may be 1, 2, 3, or 4, but the chemistry of zirconium is characterized by the difficulty of reduction to oxidation states less than four. In aqueous systems, zirconium is always quadrivalent. It has high coordination numbers, and exhibits hydrolysis which is slow to come to equilibrium, and as a consequence zirconium compounds in aqueous systems are polymerized.

Zirconium is a highly active metal which, like aluminum, seems quite passive because of its stable, cohesive, protective oxide film which is always present in air or water. Massive zirconium does not burn in air, but oxidizes rapidly above 600°C in air. Clean zirconium plate ignites spontaneously in oxygen of ca 2 MPa (300 psi); the autoignition pressure drops as the metal thickness decreases. Zirconium powder ignites quite easily. Powder ($<44\,\mu m$ or -325 mesh) prepared in an inert atmosphere by the hydride–dehydride process ignites spontaneously upon contact with air unless its surface has been conditioned, ie, preoxidized by slow addition of air to the inert atmosphere. Heated zirconium is readily oxidized by carbon dioxide, sulfur dioxide, or water vapor.

Zirconium reacts more slowly with nitrogen than with oxygen. Heating in nitrogen for 3 min gives a 0.3 μm layer of zirconium nitride [25658-42-8] at 700°C or a 1.2-μm layer at 900°C. The nitriding rate is enhanced by the presence of oxygen in the nitrogen or on the metal surface. Clean zirconium in ultrapure nitrogen reacts more slowly. Although the nitride reaction occurs at 900°C or higher, diffusion of nitrogen into zirconium is slow, and temperatures of 1300°C are needed to fully nitride the metal.

Heated zirconium is readily chlorinated by ammonium chloride, molten stannous chloride, zinc chloride, and chlorinated hydrocarbons and the common chlorinating agents. It is slowly attacked by molten magnesium chloride in the absence of free magnesium, which is always present in the Kroll process.

Table 3. **Physical Properties of Zirconium**

Property	Value	Refs.
atomic weight	91.22	
density at 298.15 K, g/cm^3	6.5107	3,5
crystal structure		
αZr		10
close-packed hexagonal space group	P6_3/mmc	11
a, nm	0.3231	
c, nm	0.5146	
c/a	1.5927	
βZr		11
body-centered cubic space group	Im3m	10
α-β transition temperature, K	1136 ± 5	12
melting temperature, K	2125 ± 10	13
boiling temperature, K	4577 ± 100	13
vapor pressure, $T < 2125$ K, $\log_{10}P_{kPa}$[a]		14
βZr	$8.956 \pm 0.080 \cdot (30810 \pm 240) T^{-1}$	
liquid Zr	$8.547 \pm 0.080 \cdot (29940 \pm 240) T^{-1}$	
heat of transition, kJ/mol[b]	3.89 ± 0.08	13
heat of melting, kJ/mol[b]	18.8 ± 2.1	14
heat of boiling, kJ/mol[b]	573.2 ± 4.6	15
heat of sublimation at 298 K, kJ/mol[b]	600.8	15
heat capacity, $T = 298 - 1136$, J/(mol·K)[b]		12
αZr	$22.857 \pm 8.970 \times 10^{-3}\, T - 0.69 \times 10^5\, T^{-2}$	
βZr	$21.493 \pm 6.586 \times 10^{-3}\, T + 36.718 \times 10^5\, T^{-2}$	
entropy at 298.15 K, J/(mol·K)[b]	38.99 ± 0.46	12
thermal expansion		16
single crystal		
perpendicular to c-axis, $L_{TC} = L_{0^\circ C}$	$1 + 5.145 \times 10^{-6}\, T$	
parallel to c-axis, $L_{TC} = L_{0^\circ C}$	$1 + 9.213 \times 10^{-6}\, T - 6.385 \times 10^{-9}\, T^2 + 18.491 \times 10^{-12}\, T^3 - 9.856 \times 10^{-15}\, T^4$	
volumetric, $V_{TC} = V_{0^\circ C}$	$1 + 19.756 \times 10^{-6}\, T - 7.023 \times 10^{-9}\, T^2 + 19.146 \times 10^{-12}\, T^3 - 9.980 \times 10^{-15}\, T^4$	
polycrystalline		
linear, for random orientation, $L_{TC} = L_{0^\circ C}$	$1 + 6.499 \times 10^{-6}\, T - 2.096 \times 10^{-9}\, T^2 + 6.108 \times 10^{-12}\, T^3 - 3.259 \times 10^{-15}\, T^4$	
thermal conductivity, W/(m·K)		17[c]
0–10 K	$1.08189 \times 10^{-1}\, T + 1.65524 \times 10^{-3}\, T^2 - 2.63239 \times 10^{-4}\, T^3$	
10–25 K	$9.48650 \times 10^{-1} + 3.44316 \times 10^{-1}\, T - 1.79663 \times 10^{-2}\, T^2 + 2.82821 \times 10^{-4}\, T^3$	
25–80 K	$1.80754 - 5.50950 \times 10^{-2}\, T - 7.61839 \times 10^{-4}\, T^2 - 3.72006 \times 10^{-6}\, T^3$	
80–500 K	$5.18009 \times 10^{-1} - 2.36738 \times 10^{-3}\, T + 6.28905 \times 10^{-6}\, T^2 - 5.58159 \times 10^{-9}\, T^3$	
500–1900 K	$2.44486 \times 10^{-1} - 2.3982 \times 10^{-4}\, T + 2.27218 \times 10^{-7}\, T^2 - 6.24923 \times 10^{-11}\, T^3$	
electrical resistivity, Zr, at 5°C, Ω·cm	$43.740.08 \times 10^{-6}$	18
temperature coefficient, 0–200°C, per °C	42.5×10^{-4}	19
elastic moduli, Zr, GPa[d]		20,21

Table 3. (*Continued*)

Property	Value	Refs.
single-crystal adiabatic, 19.7°C, 6.505 g/cm^3		
C_{11}	143.5 ± 0.2	
C_{12}	72.5 ± 0.2	
C_{13}	65.4 ± 0.2	
C_{33}	164.9 ± 0.2	
C_{44}	32.07 ± 0.03	
polycrystalline adiabatic[e]		20
Young's modulus, GPa[e]	97.1	
shear modulus, GPa[e]	36.5	
bulk modulus, GPa[e]	954	
Poisson's ratio	0.33	22
Brinell hardness number, HB[f]	90–130	

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

[c] Tabulated selected experimental values were regressed to give the equation quoted. Estimated values tabulated were not used in the regression. All equations represent tabulated, nonestimated values within ±2% or better.

[d] To convert GPa to psi, multiply by 145,000.

[e] Calculated from single-crystal adiabatic moduli by the Voight method.

[f] At good Kroll-process purity, lower for iodide zirconium.

Zirconium is readily attacked by acidic solutions containing fluorides. As little as 3 ppm flouride ion in 50% boiling sulfuric acid corrodes zirconium at 1.25 mm/yr. Solutions of ammonium hydrogen fluoride or potassium hydrogen fluoride have been used for pickling and electropolishing zirconium. Commercial pickling is conducted with nitric–hydrofluoric acid mixtures (see METAL SURFACE TREATMENTS).

4.1. Corrosion Resistance. Zirconium is resistant to corrosion by water and steam, mineral acids, strong alkalies, organic acids, salt solutions, and molten salts (28) (see also CORROSION AND CORROSION CONTROL). This property is attributed to the presence of a dense adherent oxide film which forms at ambient temperatures. Any break in the film reforms instantly and spontaneously in most environments.

Zirconium is completely resistant to sulfuric acid up to boiling temperatures, at concentrations up to 70 wt%, except that the heat-affected zones at welds have lower resistance in >55 wt% concentration acid (Fig. 1). Fluoride ions must be excluded from the sulfuric acid. Cupric, ferric, or nitrate ions significantly increase the corrosion rate of zirconium in 65–75 wt% sulfuric acid.

Zirconium resists attack by nitric acid at concentrations up to 70 wt% and up to 250°C. Above concentrations of 70 wt%, zirconium is susceptible to stress-corrosion cracking in welds and points of high sustained tensile stress (29). Otherwise, zirconium is resistant to nitric acid concentrations of 70–98 wt% up to the boiling point.

Zirconium is not attacked by caustics up to boiling temperatures. It is resistant to molten sodium hydroxide to 1000°C, but is less resistant to potassium hydroxide.

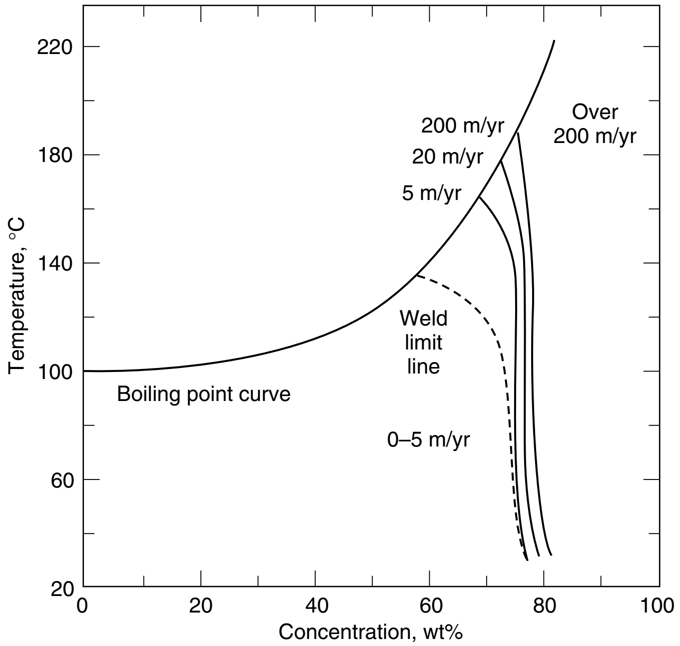


Fig. 1. Corrosion of zirconium in sulfuric acid.

Zirconium is totally resistant to corrosion by organic acids. It has been used in urea-production plants for more than two decades.

Zirconium is totally resistant to attack of hydrochloric acid in all concentrations to temperatures well above boiling (Fig. 2). Aeration has no effect, but oxidizing agents such as cupric or ferric ions may cause pitting. Zirconium also has excellent corrosion resistance to hydrobromic and hydriodic acid.

5. Processing

5.1. Decomposition of Zircon. Zircon is a highly refractory mineral as shown by its geological stability; the ore is cracked only with strong reagents and high temperature.

Electric Furnace. Zircon and coke have reacted in an electric arc furnace to produce a crude zirconium carbide nitride [12713-24-5] (ca 6 wt% C, 2 wt% N, 1 wt% O):

$$\mathrm{ZrSiO_4 + 3\,C \xrightarrow{air} Zr(C,\,N,\,O) + SiO\uparrow\ + 3\,CO\uparrow}$$

With a deficiency of carbon, the silica is not reduced to carbide but converted into silicon monoxide which is vaporized at the reaction temperature, estimated to be 2500°C. In actual operation, the above proportions are optimal. The additional carbon is derived from the graphite electrodes. If more coke is added, more silicon is retained as the carbide in the fused ingot. When feed of the batch charge is completed, the fused ingot is separated from the unreacted charge

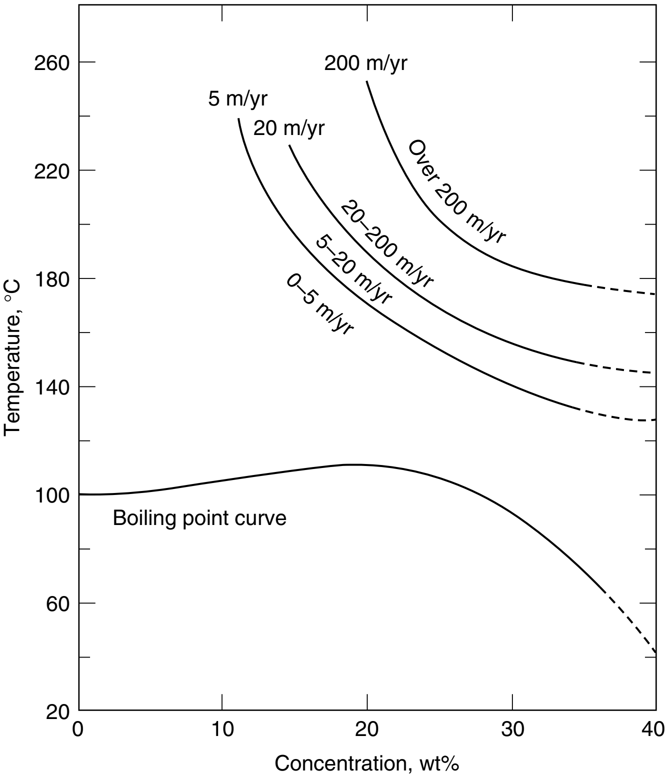


Fig. 2. Corrosion of zirconium in hydrochloric acid.

which had insulated the ingot from the furnace shell, and the hot ingot is allowed to oxidize to crude zirconia. Alternatively, the entire charge is cooled and separated and the ingot is broken into lumps which are subsequently chlorinated.

Mixed zircon, coke, iron oxide, and lime reduced together produce zirconium ferrosilicon [71503-20-3], 15 wt% Zr, which is an alloy agent. Fused zirconia [1314-23-4] has been made from zircon but baddeleyite is now the preferred feed for the production of fused zirconia and fused alumina–zirconia by electric-arc-furnace processing.

Caustic Fusion. Fusion of finely ground zircon with caustic soda at 600°C or with soda ash produces a frit containing sodium silicate, sodium zirconate [12201-48-8], and some sodium silicozirconate (25,26). Water removes most of the sodium and silica, leaving a hydrous zirconium oxide which is soluble in most mineral acids. If the fusion is conducted with less alkali, the resulting frit is essentially Na_2ZrSiO_5 [12027-83-7] which can be ground and treated with a strong mineral acid to solubilize and extract the zirconium. These two methods are most commonly used to produce aqueous zirconium solutions, hydrated zirconium compounds, and zirconium oxide.

Similarly, fusion of milled zircon with dolomite or lime forms $CaSiO_3$ and $MgZrO_3$ [12032-31-4], $CaZrO_3$ [12013-47-7], and $CaO{\cdot}Ca_2SiO_4$ or $CaSiO_3$ and ZrO_2, and is used to prepare zirconium oxide, usually as calcia-stabilized cubic zirconia because of the calcia left in solid solution in the zirconia (27–29).

Fluorosilicate Fusion. The fusion reaction of milled zircon with potassium hydrogen fluoride was used to prepare potassium hexafluorozirconate [16923-95-8] for studies leading to the first separation of hafnium and zirconium (30). Similar reactions using potassium hexafluorosilicate have been used (31,32) commercially in the United States and the former USSR:

$$K_2SiF_6 + ZrSiO_4 \longrightarrow K_2ZrF_6 + 2\,SiO_2$$

The use of potassium hexafluorosilicate is preferred over sodium hexafluorosilicate because of the lower tendency of the potassium compound to dissociate the lose silicon tetrafluoride by sublimation. The addition of potassium carbonate or chloride to the fusion mix further reduces this tendency and promotes completion of the reaction. The reaction is conducted in a rotary furnace operating at 700°C. The product is crushed prior to leaching with acidified hot water. The hot slurry is filtered to remove the silica, and potassium hexafluorozirconate crystallizes as the solution cools.

Chlorination. Historically, the production of zirconium tetrachloride from zircon sand involved first a reduction to carbide nitride (see above) followed by the very exothermic reaction of the crushed carbide nitride with chlorine gas in a water-cooled vertical shaft furnace:

$$Zr(C, N, O) + 2\,Cl_2 \xrightarrow{700-1200^\circ C} ZrCl_4 + (CO + N_2)\uparrow$$

In the current practice, milled zircon and coke are chlorinated in fluidized beds using chlorine as the fluidizing medium:

$$ZrSiO_4 + 4\,C + 4\,Cl_2 \xrightarrow{1100^\circ C} ZrCl_4 + SiCl_4 + 4\,CO$$

Additional energy to sustain the endothermic reaction is provided chemically by the addition of silicon carbide grain or electrically by use of electrothermal fluidized beds (33,34), induction heating, or resistance heating. Chlorine efficiencies are typically 98% or better.

The product gases are first cooled below 200°C to selectively condense so-called zirconium tetrachloride snow in a large space condenser. The silicon tetrachloride subsequently is condensed in a quench condenser wherein the warm gases are countercurrently scrubbed with liquid silicon tetrachloride at −20°C. The silicon tetrachloride is purified by stripping and distillation.

Thermal Dissociation. The thermal dissociation of zircon into zirconia and cristobalite or liquid silica above 1650°C has been studied as a means of producing zirconia, but the process was hampered by the partial recombination of the two phases during cooling. Passing particulate zircon through the intense heat of a plasma and immediately thereafter quenching the molten droplet results in the formation of dissociated zircon particles of generally spheroidal configuration (35). The spheroids consist of a fused, amorphous silica mass in which radiating crystallites of monoclinic zirconia are dispersed.

This dissociated zircon is amenable to hot aqueous caustic leaching to remove the silica in the form of soluble sodium silicate. The remaining skeletal structure of zirconia is readily washed to remove residual caustic. Purity of this zirconia is directly related to the purity of the starting zircon since only silica, phosphate, and trace alkalies and alkaline earth are removed during the leach. This zirconia, and the untreated dissociated zircon, are both proposed for use in ceramic color glazes (36) (see COLORANTS FOR CERAMICS).

5.2. Separation of Hafnium.

Zirconium and hafnium always occur together in natural minerals and therefore all zirconium compounds contain hafnium, usually about 2 wt% Hf/Hf + Zr. However, the only applications that require hafnium-free material are zirconium components of water-cooled nuclear reactors.

Zirconium and hafnium have very similar chemical properties, exhibit the same valences, and have similar ionic radii, ie, 0.074 mm for Zr^{4+}, 0.075 mm for Hf^{4+} (see HAFNIUM AND HAFNIUM COMPOUNDS). Because of these similarities, their separation was difficult (37–40). Today, the separation of zirconium and hafnium by multistage counter-current liquid–liquid extraction is routine (41) (see EXTRACTION, LIQUID–LIQUID).

In the initial thiocyanate-complex liquid–liquid extraction process (42,43), the thiocyanate complexes of hafnium and zirconium were extracted with ether from a dilute sulfuric acid solution of zirconium and hafnium to obtain hafnium. This process was modified in 1949–1950 by an Oak Ridge team and is still used in the United States. A solution of thiocyanic acid in methyl isobutyl ketone (MIBK) is used to extract hafnium preferentially from a concentrated zirconium–hafnium oxide chloride solution which also contains thiocyanic acid. The separated metals are recovered by precipitation as basic zirconium sulfate and hydrous hafnium oxide, respectively, and calcined to the oxide (44,45).

In the tributyl phosphate extraction process developed at the Ames Laboratory, Iowa State University (46–48), a solution of tributyl phosphate (TBP) in heptane is used to extract zirconium preferentially from an acid solution (mixed hydrochloric–nitric or nitric acid) of zirconium and hafnium (45). Most other impurity elements remain with the hafnium in the aqueous acid layer. Zirconium recovered from the organic phase can be precipitated by neutralization without need for further purification.

High molecular weight primary, secondary, and tertiary amines can be employed as extractants for zirconium and hafnium in hydrochloric acid (49–51). With similar aqueous-phase conditions, the selectivity is in the order tertiary > secondary > primary amines. The addition of small amounts of nitric acid increases the separation of zirconium and hafnium but decreases the zirconium yield. Good extraction of zirconium and hafnium from ca 1 *M* sulfuric acid has been effected with tertiary amines (52–54), with separation factors of 10 or more. A system of this type, using trioctylamine in kerosene as the organic solvent, has been used in Japan in the production of zirconium (55).

Zirconium and hafnium are separated by fractional distillation of the anhydrous tetrachlorides in a continuous molten solvent salt $KCl-AlCl_3$ system at atmospheric pressure (56,57). Zirconium and hafnium tetrachlorides are soluble in $KCl-AlCl_3$ without compound formation and are produced simultaneously.

Pure zirconium tetrachloride is obtained by the fractional distillation of the anhydrous tetrachlorides in a high pressure system (58). Commercial operation of the fractional distillation process in a batch mode was proposed by Ishizuka Research Institute (59). The mixed tetrachlorides are heated above 437°C, the triple point of zirconium tetrachloride. All of the hafnium tetrachloride and some of the zirconium tetrachloride are distilled, leaving pure zirconium tetrachloride. The innovative aspect of this operation is the use of a double-shell reactor. The autogenous pressure of 3–4.5 MPa (30–45 atm) inside the heated reactor is balanced by the nitrogen pressure contained in the cold outer reactor (60). However, previous evaluation in the former USSR of the binary distillation process (61) has cast doubt on the feasibility of also producing zirconium-free hafnium tetrachloride by this method because of the limited range of operating temperature imposed by the small difference in temperature between the triple point, 433°C, and critical temperature, 453°C, a hafnium tetrachloride.

5.3. Reduction. Brezelius attempted the first reduction of zirconium in 1824 by the reaction of sodium with potassium fluorozirconate. However, the first pure ductile metal was made in 1925 by the iodide thermal-dissociation method. The successful commercial production of pure ductile zirconium via the magnesium reduction of zirconium tetrachloride vapor in an inert gas atmosphere was the result of the intense research efforts of Kroll and co-workers at the U.S. Bureau of Mines in 1945–1950 (62–67).

Obtaining pure ductile zirconium by reduction of the oxide is particularly difficult because of the tendency of hot zirconium to dissolve considerable amounts of oxygen, making the metal brittle at room temperature. Therefore, it is common practice to reduce oxygen-free zirconium tetrachloride.

Kroll Process. Hafnium-free zirconium dioxide is mixed with pulverized coke and fed into an induction-heated chlorinator where the mixture is fluidized by chlorine gas; reaction at 900°C gives zirconium tetrachloride and carbon dioxide. The product gas passes through a nickel-lined condenser where zirconium tetrachloride powder is formed by cooling below 200°C. It is purified by subliming and recondensing in a nitrogen–hydrogen atmosphere to reduce the aluminum and phosphorus contents. The tetrachloride powder is charged into the upper chamber of a vertical cylindrical steel retort which contains cast ingots of magnesium in a stainless-steel liner within the lower chamber. The retort is sealed and evacuated and backfilled with argon several times at 200°C. Heat applied to the lower retort chamber melts the magnesium which in turn reduces the zirconium tetrachloride vapors as they sublime out of the upper chamber. The retort is cooled and unloaded. The stainless-steel liner is peeled from the reduction mass and the bulk of the magnesium chloride salt is physically separated from the Zr–Mg regulus. Several reduction reguli are stacked and loaded into a furnace for removal of residual magnesium chloride. The distillation is conducted in a vacuum <1.3 Pa (<10 μm Hg). As the temperature is gradually increased to 980°C, the magnesium chloride melts and drains and the magnesium metal is distilled and condensed on the cold lower retort wall, leaving porous zirconium sponge. After cooling and conditioning, the sponge is removed from the retort and broken into chunks using a hydraulic chisel. The chunks are graded, crushed to ca 1 cm dia, and sampled before blending and melting.

Other Reductions. Ductile, pure zirconium has been made by a two-stage sodium reduction of zirconium tetrachloride (68) in which the tetrachloride and sodium are continuously fed into a stirred reactor to form zirconium dichloride

[13762-26-0]; heating with additional sodium yields zirconium metal. Leaching with water removes the sodium chloride from the zirconium. Bomb reduction of pure zirconium tetrafluoride with calcium also produces pure metal (69).

Finely divided zirconium powder is made by bomb reduction of zirconium oxide with magnesium or calcium. The powder is separated by leaching with cold hydrochloric acid. Because of its large surface area, it is extremely pyrophoric and hazardous to produce. Zirconium powder made by this technique is used in ordnance fuses and incendiaries, but it contains considerable oxygen and therefore cannot be converted into ductile mill products.

Electrolysis. Electrowinning of zirconium has long been considered as an alternative to the Kroll process, and at one time zirconium was produced electrolytically in a prototype production cell (70). Electrolysis of an all-chloride molten-salt system is inefficient because of the stability of lower chlorides in these melts. The presence of fluoride salts in the melt increases the stability of Zr^{4+} in solution, decreasing the concentration of lower valence zirconium ions, and results in much higher current efficiencies. The chloride–electrolyte systems and electrolysis approaches are reviewed in References 71 and 72. The recovery of zirconium metal by electrolysis of aqueous solutions in not thermodynamically feasible, although efforts in this direction persist.

Refining. Zirconium sponge produced by the Kroll process has adequate purity and ductility for most uses. For applications requiring extremely soft metal and for research studies on the properties of the pure metal, it can be further purified by the van Arkel-de Boer (iodide-bar) process using a selective vapor transport (73–76). Zirconium sponge is loaded into a cylindrical Inconel vessel. The vessel lid contains insulated electrical lines from which a zirconium wire filament in a hairpin shape is suspended. Iodine is added to the evacuated vessel which then is heated to 250°C in a molten-salt bath. Volatile zirconium tetraiodide forms and diffuses to the central zirconium filament which is resistance-heated to 1200–1500°C. The tetraiodide thermally dissociates at the hot filament, depositing zirconium and releasing iodine to react again with the sponge feed. The deposition rate is controlled by the feed-bed temperature, filament temperature, iodine concentration, filament-to-bed distance, and the presence of other gases. Ordinarily, bars of 40 mm dia are grown from 3-mm filament wire. Under conditions optimized for zirconium transfer, the impurity metals and metallic oxides, carbides, and nitrides transfer poorly so that the zirconium filament is much softer and purer than the starting sponge.

Electron-beam melting of zirconium has been used to remove the more volatile impurities such as iron, but the relatively high volatility of zirconium precludes effective purification. Electrorefining is fused-salt baths (77,78) and purification by d-c electrotransport (79) have been demonstrated but are not in commercial use.

6. Economic Aspects

Global production of zircon increased to 870,000 tons, slightly more than that of 2004, while demand increased 3% compared with that of 2004. Demand for zircon continued to surpass the available supply in 2005 (see Table 4). The shortage was

Table 4. **World Zirconium Mine Production, Reserves, and Reserve Base**[a]

Country	Mine production, 10^3 t, 2004	Mine production, 10^3 t, 2005	Reserves, × 10^6 t, ZrO_2	Reserve base, × 10^6 t, ZrO_2
United States	W[b]	W[b]	3.4	5.7
Australia	441	450	9.1	30
Brazil	26	35	2.2	4.6
China	17	15	0.5	3.7
India	20	20	3.4	3.8
South Africa	300	305	14	14
Ukraine	35	35	4.0	6.0
Other countries	10	10	0.9	4.1
World total (rounded)	*850*	*870*	*38*	*72*

[a] From Ref. 7.

[b] W = withheld, proprietary data.

caused by increased demand, the closure of several zircon-producing mines, and record-high levels in 2005 in response to the worldwide supply shortfall. In 2005, U.S. imports of zirconium ores and concentrates decreased about 15%, while exports increased 24% (see Table 5). Imports declined as a result of continued high output from recent expansions in Georgia and Virginia and lower domestic demand. A number of new projects to expand the availability of zircon are underway in Australia, Canada, Kenya, Madagascar, Malawi, and Mozambique. Production from a number of these projects was expected to begin in 2006. The availability of hafnium, produced as a byproduct during zirconium metal processing, continued to exceed demand.

7. Specifications and Standards

The U.S. specifications for zirconium are listed in Table 6. For nuclear power use, each reactor vendor issues particular, detailed specifications which usually include the pertinent ASTM nuclear specifications.

The four ASTM-specified grades of commercial zirconium and zirconium alloys are given in Table 7. The unalloyed Zr 702, the most commonly used commercial grade, has the best overall chemical corrosion resistance but it is the lowest in strength; Zr 705 has similar corrosion resistance in most environments but its strength is almost double that of Zr 702. It has better formability in applications requiring bending through a sharp radius. Both Zr 702 and 705 are approved for use in the construction of pressure vessels according to the American Society of Mechanical Engineers Boiler and Pressure Vessel Code, Section VIII.

The chemical corrosion resistance of Zr 704 is slightly less than that of Zr 702 in some environments but Zr 704 is superior in high temperature, high pressure water, and steam. A softer version of Zr 705 is Zr 706, developed specifically for severe forming applications such as panel-type heat exchangers.

Table 5. **United States: Salient Statistics**[a,b]

Statistics	2001	2002	2003	2004	2005
production, zircon (ZrO_2 content)	W	W	W	W	W
imports:					
zirconium, ores and concentrates (ZrO_2 content)	39,400	22,900	24,300	22,900	19,400
zirconium, unwrought, powder, and waste and scrap	145	82	75	89	266
zirconium, wrought	571	474	468	708	643
zirconium oxide (ZrO_2 content)[c]	2,950	2,900	2,350	3,960	3,190
exports:					
zirconium ores and concentrates (ZrO_2 content)	43,500	30,600	45,900	44,700	55,600
zirconium, unwrought, powder, and waste and scrap	186	208	204	233	310
zirconium, wrought	1,190	1,430	1,490	1,470	1,660
zirconium oxide (ZrO_2 content)[c]	2,400	1,950	1,520	1,600	2,340
consumption, zirconium ores and concentrates, apparent (ZrO_2 content)	W	W	W	W	W
prices:					
zircon, dollars per metric ton (gross weight):					
domestic	340	350	360	557	662
imported, f.o.b.[d]	356	397	396	477	673
zirconium, unwrought, dollars per kilogram[e]	31	39	44	31	22
net import reliance as a percentage of apparent consumption:					
zirconium	E	E	E	E	E

[a] From Ref. 7, Data for 2005 are estimated.

[b] W = withheld, proprietary data; E = net exporter.

[c] Includes germanium and zirconium oxides.

[d] U.S. Census Bureau data.

[e] Unit value based on U.S. imports.

Table 6. **U.S. Specifications for Zirconium**

	ASTM				
Form	Nuclear	Commercial	ASME	DOE	AWS[a]
sponge	B 349	B 494			
ingot	B 350	B 495		M 10-1T	
bars, rod, and wire	B 351	B 550	SB550	M 7-9T	
flat rolled products	B 352	B 551	SB551	M 5-6T	
tubing	B 353	B 523	SB523	M 3-8T	
forging and extrusions		B 493	SB493	M 2-9T	
bare welding rods			SFA5.24	M 1-16T	A5.24
descaling and cleaning		B 614			
welding fittings		B 653			
seamless and welded pipe		B 658	SB658		
aqueous corrosion testing	G 2	G 2			

[a] American Welding Society.

Table 7. **ASTM Grades and Commercial Designations of Commercial Zirconium and Alloys**

Nominal composition, wt%	R 60702, Zr 702	R 60704, Zr 704	R 60705, Zr 705	R 60706, Zr 706
Zr + Hf, min	99.2	97.5	95.2	95.5
Fe + Cr	<0.2	0.3	<0.2	<0.2
Sn		1.5		
Nb			2.5	2.5
Hf	2.0	2.0	2.0	2.0

There are no industry-wide specifications for zirconium metal castings, or for zirconium chemicals.

For nuclear applications, hafnium-free zirconium is used, mostly as Zircaloy 2 and Zircaloy 4, in alloys developed in the U.S. Naval Nuclear Propulsion Program. The nickel-free Zircaloy 4 absorbs less of the hydrogen generated by steam corrosion, and is used increasingly. Zr-2.5Nb was adapted by Atomic Energy of Canada, Ltd., for use in Candu reactor pressure tubes (see NUCLEAR REACTORS). Excel is a newer, stronger, creep-resistant alloy developed in Canada as a pressure-tube material. Ozhennite 0.5 is another zirconium alloy from the former USSR for nuclear applications. A UK zirconium alloy, A.T.R., is used in carbon dioxide−cooled reactors. The alloying compositions are given in Table 8.

8. Analytical Methods

Zirconium is often determined gravimetrically. The most common procedure utilizes mandelic acid (81) which is fairly specific for zirconium plus hafnium. Other precipitants, including nine inorganic and 42 organic reagents, are listed in Reference 82. Volumetric procedures for zirconium, which also include hafnium as zirconium, are limited to either EDTA titrations (83) or indirect procedures (84). X-ray fluorescence spectroscopy gives quantitative results for zirconium, without including hafnium, for concentrations from 0.1 to 50% (85). Atomic absorption determines zirconium in aluminum in the presence of hafnium at concentrations of 0.1−3% (86).

Emission spectroscopy is used for lower concentrations and trace levels. Methods, as outlined in ASTM procedures (87), include zirconium in aluminum and aluminum alloys, ceramics, sand, magnesium alloys, and titanium.

Table 8. **Hafnium-Free Zirconium Alloys for Nuclear Service**

Element	Zircaloy 2	Zircaloy 4	Zr-2.5 Nb	Excel	A.T.R.	Ozhennite 0.5
Sn	1.5	1.5	<0.02	3.5	<0.01	0.02
Fe	0.14	0.22	<0.08	<0.08	<0.05	0.1
Cr	0.1	0.1	<0.02	<0.02	<0.01	<0.02
Ni	0.05	<0.004	<0.007	<0.007	<0.004	0.1
Nb			2.5	0.8		0.1
Cu					0.55	
Mo				0.8	0.55	

Colorimetric methods always include hafnium. Most methods employ a separation step such as solvent extraction. The three reagents used successfully are 8-hydroxyquinoline (88), alizarin red S (89), and catechol violet (90).

Impurities in zirconium and zirconium alloys and compounds are often determined by emission spectroscopy. Both carrier distillation techniques and point-to-plane methods are available (91,92). Several metallic impurities can be determined instantaneously by this method. Atomic absorption analysis has been used for iron, chromium, tin, copper, nickel, and magnesium (93). The interstitial gases, hydrogen, nitrogen, and oxygen are most often determined by chromatography (81). Procedures for carbon, chloride, fluoride, phosphorus, silicon, sulfur, titanium, and uranium in zirconium are given in the literature (81,94–96).

9. Health and Safety Factors

Zirconium is generally nontoxic as an element or in compounds (97,98). At pH normally associated with biological activity, zirconium chiefly exists as the dioxide which is insoluble in water and in this form zirconium is physiologically inert.

Chelated complexes such as sodium zirconium lactate [15529-67-6] or ammonium zirconium carbonate [22829-17-0], and acidic forms such as zirconium hydroxy oxide chloride [18428-88-1] have been used in preparations in deodorants or for treatment for poison oak and poison ivy dermatitis. In such occasions, when the skin had been cut or abraded, a few users developed granulomas which have been identified as a delayed hypersensitivity to zirconium (99). These may take several weeks to develop, and commonly persist for 6 months to over a year.

The oral toxicity is low; OSHA standards for pulmonary exposure specify a TLV of 5 mg (Zr)/m^3. STEL is 10 mg (Zr)/m^3 (100).

In massive form, zirconium is commonly brought to red heat before forging, swaging, or other hot working with only slight surface oxidation of the ingot or slab. Conversely, zirconium metal with a high surface area such as sponge, foil, fine powder, fine machining chips, and grinding dust is extremely flammable and often pyrophoric, especially when slightly damp. Many unexpected ignitions have occurred caused by improper handling of finely divided forms of zirconium metal, resulting in more than one incident of fatal flash burns to metal workers. Very fine dusts of zirconium ignite when dispersed in air. Fires can be extinguished with a blanket of argon or a layer of dry salt or sand. Water is hazardous unless the zirconium can be quenched below its ignition temperature. A settled 25-kg mass of 20-μm particles ignited in the bottom of a water-filled 55-gal (208-L) drum burns for hours. A stream of water results in the generation of hydrogen and steam which disperse the burning fragments and spread the fire (101). Safe handling of zirconium has been discussed in several publications (101–103).

Zirconium powder reacts exothermically with many other elements, including hydrogen, boron, carbon, nitrogen, and the halogens, although the ignition temperature is usually above 200°C. The reaction between zirconium powder and platinum is especially violent.

Finely divided zirconium is classified as a flammable solid and shipping regulations are prescribed accordingly (104). Metal powder finer than 74 μm (270 mesh) is limited to 2.26 kg per individual container.

10. Uses

Zircon ceramics, opacifiers, refractories, and foundry applications are the leading end uses for zirconium. Other end uses of zirconium include abrasives, chemicals, metal alloys, welding rod coatings, and sandblasting. The leading market for hafnium metal is as an addition in superalloys (7).

Zircon, used for facings on foundry molds, increases resistance to metal penetration and gives a uniform finish to castings. Milled or ground zircon is used in refractory paints for coating the surfaces of molds. Zircon, in the form of refractory bricks and blocks, is used in furnaces and hearths for containing molten metals. Glass tank furnaces use fused-cast and bonded alumina-zirconia-silica-base refractories. Baddeleyite is used principally in the manufacture of alumina-zirconia abrasive and in ceramic colors and refractories (80).

Stabilized zirconium oxide exhibits high-light reflectivity and good thermal stability and is primarily used as an opacifier and pigment in glazes and colors for pottery and other ceramic products (105–107). Yttria-stabilized zirconia (YSZ) is used in the manufacture of oxygen sensors that control combustion in furnaces and automobile engines. YSZ is also used in the manufacture of a diverse array of products, including high-temperature, high-strength structural ceramics, heat- and break-resistant shirt buttons, golf shoe spikes, golf putters, fiber optic connector components, coatings for the hot sections of jet engines, and cubic zirconia, a gemstone simulant for diamonds and colored gemstones (108). YSZ is increasingly used in dental applications as inlays, crowns, and bridges as it has two to three times the fracture resistance and 1.4 times the strength of similar alumina products (109,110).

Ammonium- and potassium-zirconium carbonate are used as paper and board coatings or insolubilizers for high-quality print performance. Zirconium chemicals are also used in inks to promote adhesion to metals and plastics and as crosslinkers in polymers and printing inks.

Because of its low thermal neutron absorption cross section, hafnium-free zirconium metal is used as cladding for nuclear fuel rods. A zirconium alloy used in aggressive coolant stage in fuel cladding (111) has been reported. Commercial-grade zirconium, unlike nuclear grade, contains hafnium and is used in the chemical process industries because of its excellent corrosion resistance.

Hafnium is used in nuclear control rods because of its high-thermal neutron absorption cross section. However, the leading end use for hafnium metal is as an alloy addition in superalloys.

Zirconate compounds exhibit several interesting properties. Lead zirconate–titanate [12626-81-2] compositions display piezoelectric properties which are utilized in the production of FM-coupled mode filters, resonators in microprocessor clocks, photoflash actuators, phonograph cartridges, gas ignitors, audio tweeters and beepers, and ultrasonic transducers. Lanthanum-modified lead zirconate–titanate ceramics have been studied for photoferroelectric image storage (112) (see FERROELECTRICS). Alkaline-earth zirconate dielectrics are used in ceramic capacitors.

The uses of other zirconium compounds result primarily from the ability of zirconium to complex with carboxyl groups and to form an insoluble organic compound. Ammonium zirconium carbonate enhances the fungicidal action of copper salts on cotton cloth (113) and zirconium acetate has been used as an algicide. Both ammonium zirconium carbonate and zirconium acetate [14311-93-4] have been used in the waterproofing of fabrics (114). Freshly prepared zirconium sulfate solutions are preferred over chromium solutions in the tanning of leather to prepare white leathers, although other mixed sulfate solutions containing zirconium, chromium, and aluminum have been proposed. In the retanning of chrome-treated leather (qv), an intermediate treatment with ammonium zirconium carbonate improves the results obtained during the second chrome tanning (115). Zirconium carbonate produces durable acrylic-emulsion floor polishes which are easily stripped by treatment with household ammonia (see POLISHES). Polyurethane cured with zirconium carbonate for improved floor finishes has been reported (116). Both zirconium sulfate [14644-61-2] and potassium hexafluorozirconate have been used for flame-resistant treatment of wool fabric. Very dilute fluoride solutions containing zirconium and gluconic acids are used for the preparation of clean aluminum surfaces to be subsequently painted or overcoated (117). Similarly, an aqueous solution of zirconium nitrate [13746-89-9] and poly(vinyl alcohol) is applied as a precoating on glass surfaces before the application of phosphor photobinder in the production of cathode-ray tubes.

Zirconium tetrafluoride [7783-64-4] is used in some fluoride-based glasses. These glasses are the first chemically and mechanically stable bulk glasses to have continuous high transparency from the near uv to the mid-ir (0.3–6 μm) (118). Zirconium oxide and tetrachloride have use as catalysts (119), and zirconium sulfate is used in preparing a nickel catalyst for the hydrogenation of vegetable oil. Zirconium 2-ethylhexanoate [22464-99-9] is used with cobalt driers to replace lead compounds as driers in oil-based and alkyd paints (see DRIERS AND METALLIC SOAPS).

Sodium hydrogen zirconium phosphate [34370-53-1] is an ion-exchange material used in portable kidney dialysis systems which regenerate and recirculate the dialysate solution. The solution picks up urea during the dialysis. The urea reacts with urease to form ammonia, which is absorbed by the sodium hydrogen zirconium phosphate.

Zirconium phosphate [13772-29-7] also absorbs cesium and other radioactive-decay daughter products, and has been proposed as part of permanent disposal systems for nuclear fuel waste processing.

Zirconium metal is marketed in three forms: zirconium-containing silicon–manganese, iron, ferrosilicon, or magnesium master alloys; commercially pure zirconium metal; and hafnium-free pure zirconium metal. The use of zircon for the production of zirconium metal of all three types is ca 5–8% of the total U.S. zircon consumption.

Silicon–manganese–zirconium, ferrozirconium, and ferrosilicon–zirconium (and some pure zirconium) are used in the steel industry for deoxidizing. Magnesium–zirconium is added to magnesium and aluminum alloys for grain refining and strengthening. Most magnesium alloys used at elevated temperatures contain zirconium.

Because of its flammability, zirconium is used in military ordnance including percussion-primer compositions, delay fuses, tracers, and pyrophoric shrapnel, in getters for vacuum tubes, inert-gas glove boxes, and sodium-filled hollow-shaft exhaust valves, and as shredded foil in flashbulbs for photography and excitation of lasers. Alloying applications of pure zirconium include zirconium–niobium superconductors, titanium aircraft alloys, and strengthening of copper alloys. Pure zirconium is being increasingly used as a corrosion-resistant metal in fabricating columns, pumps, pipe, valves, heat exchangers, and tanks for severe chemical environments, particularly sulfuric and hydrochloric acids, except those containing fluorides. In this capacity, it is also used in facilities producing urea, hydrogen peroxide, methyl methacrylate, or acetic acid.

11. Compounds

The numerous intermetallic compounds of zirconium, from $ZrAl_3$ to $ZrZn_6$, are reviewed in References 120–123.

11.1. Hydrides. Zirconium hydride [7704-99-6] in powder form was produced by the reduction of zirconium oxide with calcium hydride in a bomb reactor. However, the workup was hazardous and many fires and explosions occurred when the calcium oxide was dissolved with hydrochloric acid to recover the hydride powder. With the ready availability of zirconium metal via the Kroll process, zirconium hydride can be obtained by exothermic absorption of hydrogen by pure zirconium, usually highly porous sponge. The heat of formation is 167.4 J/mol (40 kcal/mol) hydrogen absorbed.

Zirconium absorbs or desorbs hydrogen reversibly. Provided the metal surface is clean, equilibrium is attained quickly above 400°C, and very slowly below 250°C. The hydrogen solubility limit in alpha zirconium has been expressed (124) as solubility, ppm $= 1.61 \times 10^5 \exp(-8959/RT)$. The addition of hydrogen lowers the $\alpha \rightarrow \beta$ transition from 876 to 550°C at 6 at.% hydrogen. Further hydrogen addition causes the formation of hydride phases, culminating in the body-centered tetragonal epsilon phase as the hydrogen content approaches the limiting concentration of ZrH_2 (125,126). Hydrogen is removed by heating and evacuating. To reduce the hydrogen content to 10 ppm, the specimen must be heated to 900°C at 1 Pa (ca 10^{-2} mm Hg) (see HYDRIDES).

Zirconium hydride is not a true compound of fixed stoichiometry but rather a series of crystalline phases through which zirconium metal transforms with changing hydrogen concentration and temperature. The γ-phase hydride exists below 250°C in the narrow composition range $ZrH_{0.9}$ to $ZrH_{1.1}$, the δ-phase has a compositional range $ZrH_{1.5}$ to $ZrH_{1.7}$, and the ϵ-phase has a compositional range $ZrH_{1.8}$–ZrH_2. Most commercial hydride powder contains δ- and ϵ-phase.

Above 40 wt% hydrogen content at room temperature, zirconium hydride is brittle, ie, has no tensile ductility, and it becomes more friable with increasing hydrogen content. This behavior and the reversibility of the hydride reaction are utilized in preparing zirconium alloy powders for powder metallurgy purposes by the hydride–dehydride process. The mechanical and physical properties of zirconium hydride, and their variation with hydrogen content of the hydride, are reviewed in Reference 127.

Intermetallic compounds of zirconium with iron, cobalt, and manganese absorb and desorb considerable amounts of hydrogen, up to $ZrMn_{2.4}H_3$ [68417-38-9] (128) and $ZrV_2H_{5.3}$ [63440-37-9] (129). These and other zirconium intermetallic compounds are being extensively studied for possible hydrogen storage applications (130).

The metallic monohalides zirconium chloride [14989-34-5], ZrCl, and zirconium bromide [31483-18-8], ZrBr, reversibly absorb hydrogen up to a limiting composition of ZrXH (131). These hydrides are less stable than the binary hydride ZrH_2, and begin to disproportionate above 400°C to ZrH_2 and ZrX_4 in a hydrogen atmosphere (see also HYDRIDES).

11.2. Carbide. Zirconium carbide [12020-14-3], nominally ZrC, is a dark gray brittle solid. It is made typically by a carbothermic reduction of zirconium oxide in a induction-heated vacuum furnace. Alternative production methods, especially for deposition on a substrate, consist of vapor-phase reaction of a volatile zirconium halide, usually $ZrCl_4$, with a hydrocarbon in a hydrogen atmosphere at 900–1400°C.

Once initiated, zirconium and carbon powders react exothermically in a vacuum or inert atmosphere to form zirconium carbide. With the greater availability of relatively pure metal powders, this technique is coming into common use for the production of several refractory carbides. Zirconium carbide is not a fixed stoichiometric compound, but a defect compound with a single-phase composition ranging from $ZrC_{0.6}$ to $ZrC_{0.98}$ at 2400°C.

Zirconium carbide is inert to most reagents but is dissolved by hydrofluoric acid solutions which also contain nitrate or peroxide ions, and by hot concentrated sulfuric acid. Zirconium carbide reacts exothermically with halogens above 250°C to form zirconium tetrahalides, and with oxidizers to zirconium dioxide in air above 700°C. Zirconium carbide forms solid solutions with other transition-metal carbides and most of the transition-metal nitrides without the formation of compounds. When heated in a vacuum, zirconium carbide, $ZrC_{0.6-0.98}$, moves to the congruent composition $ZrC_{ca\ 0.85}$, with a melting point of 3420°C.

As a hard, high melting carbide and possible constituent of UC-fueled reactors, zirconium carbide has been studied extensively. The preparation, behavior, and properties of zirconium and other carbides are reviewed in Reference 132, temperature-correlated engineering property data in Reference 133 (see also CARBIDES, CEMENTED).

11.3. Nitride. Cubic zirconium nitride, ZrN, a brittle, yellow solid, is prepared by heating zirconium turnings or loose sponge to 1100–1500°C in a nitrogen or ammonia atmosphere. The reaction is slow because of the slow diffusion of nitrogen through the protective nitride layer, and nitrogen contents approaching stoichiometric require time or higher temperatures such as those of a plasma torch. Zirconium tetrachloride and nitrogen is a hydrogen atmosphere above 1000°C yield zirconium nitride films or powders; impurity effects cause the growth of nitride whiskers (134). Ammonia and zirconium tetrachloride forms adducts which on heating to 750°C give $ZrN_{1.3}$ [25658-42-8], which in turn yields ZrN at 1200°C (135). Unlike its analogues, TiN and HfN, which are being used as wear-resistant surface layers on cemented-carbide tool bits, no significant commercial applications for ZrN have been developed (see also NITRIDES).

Zirconium nitride is dissolved by concentrated hydrofluoric acid, dissolved slowly by hot concentrated sulfuric acid, and oxidizes to zirconium oxide above 700°C in air.

11.4. Borides. Zirconium forms two borides: zirconium diboride [12045-64-6], ZrB_2, and zirconium dodecaboride [12046-91-2], ZrB_{12}. The diboride is synthesized from the elements, by vapor-phase coreduction of zirconium and boron halides, or by the carbothermic reduction of zirconium oxide and boron carbide; boric oxide is avoided because of its relatively high vapor pressure at the reaction temperature.

$$2\,ZrO_2 + B_4C + 3\,C \xrightarrow{1400^\circ C} 2\,ZrB_2 + 4\,CO$$

The diboride has a hexagonal structure and melts at 3245°C (136); it is considered to have the best oxidation resistance of all the refractory hard metals. The dodecaboride has a cubic structure.

11.5. Phosphides. Zirconium forms several phosphides: ZrP_3 [39318-19-9], ZrP_2 [12037-80-8], and $ZrP_{0.6}$ [12066-61-4]; they are part of the Zr–P phase diagram (137). The solubility of phosphorus in zirconium metal is low, ca 50 ppm, and at higher concentrations it collects as separate globules at the metal grain boundaries. Analysis indicates that this material is Zr_3P.

11.6. Chalcogenides. The reactions of pure zirconium turnings with threefold quantities of elemental sulfur, selenium, or tellurium give ZrS_3 [12166-31-3], $ZrSe_3$ [12166-53-9], and $ZrTe_3$ [39294-10-5] (138). Zirconium disulfide [12039-15-5] is made from the elemental powders and by the action of carbon disulfide on zirconium oxide above 1200°C (139); some ZrOS [12164-95-3] is usually also obtained. The higher sulfides disproportionate at ca 700°C; synthesis reactions at 900–1000°C with S:Zr ratios between 0.2 and 2.3 produced crystals that were identified as Zr_9S_2 [12595-12-9], $Zr_{21}S_8$ [12595-19-6], Zr_2S [12334-07-5], ZrS_{1-x}, ZrS [12067-18-4], and $ZrS_{1.3}$ [37244-09-0] (140). Zirconium disulfide is a semiconductor with a cadmium–iodide-type layered structure consisting of stacked sandwiches each containing single sheets or metal cations between two sheets of anions.

Several compounds such as $BaZrS_3$ [12026-44-7], $SrZrS_3$ [12143-75-8], and $CaZrS_3$ [59087-48-8], have been made by reacting carbon disulfide with the corresponding zirconate at high temperature (141), whereas $PbZrS_3$ [12510-11-1] was produced from the elements zirconium and sulfur plus lead sulfide sealed in a platinum capsule which was then pressurized and heated (142). Lithium zirconium disulfide [55964-34-6], $LiZrS_2$, was also synthesized. Zirconium disulfide forms organometallic intercalations with a series of low ionization (<6.2 eV)-sandwich compounds with parallel rings (143).

The dichalcogenides are hexagonal, the diamagnetic trichalcogenides are monoclinic. The compound sulfides $BaZrS_3$ [12026-44-7], $SrZrS_3$ [12143-75-8], and $CaZrS_3$ [59087-48-8] have an orthorhombic distorted perovskite structure, although $BaZrS_3$ prepared at 1000°C displayed a tetragonal perovskite structure which was attributed to a sulfur deficiency (141).

11.7. Oxides. Zirconium dioxide [1314-23-4], ZrO_2, is the most important oxide of zirconium. It melts at $2710 \pm 35^\circ C$, and in the pure state exists in four solid phases: monoclinic, tetragonal, orthorhombic, and a cubic fluorite structure. The monoclinic phase is stable up to ca 1100°C, and transforms to tetragonal as the temperature increases to 1200°C. The proportion of tetragonal during the transformation is temperature dependent and not time-related (144). The transformation temperature exhibits a large hysteresis, and the tetragonal-to-monoclinic transition occurs between 1000 and 850°C; it is a martensitic transformation. The volume expansion resulting from the tetragonal-to-monoclinic transition can be restrained by high external pressure, increasing the stability of the tetragonal phase at lower temperatures (145). At higher pressures, an orthorhombic (cotunnite-type) structure has been identified (146) and it has been suggested that at 1000°C the zirconium oxide pressure-transformations are

$$\text{monoclinic} \xleftarrow{\text{GPa (ca } 10^4 \text{ atm)}} \text{tetragonal} \xleftarrow{10\,\text{GPa (ca } 10^5 \text{ atm)}} \text{orthorhombic}$$

The tetragonal-to-cubic reversible transformation occurs at 2370°C. The existence of cubic zirconia was proven by high temperature x-ray diffraction studies but little is known about the transformation. The cubic structure can be stabilized at lower temperatures by the introduction of vacancies in the anion lattice. The existence of cubic zirconia down to 1525°C has been shown in substoichiometric ZrO_{2-x} (147–149) and zirconium nitride-stabilized cubic zirconia (150). Vacancies are also generated by adding alkaline-earth oxides or rare-earth oxides to form stable solid solution cubic zirconia. Although these materials were initially considered stable at room temperature, more recent studies indicate that the kinetics of change are slow and that the lower temperature stability ranges from 280 to 1400°C, depending on the stabilizing oxide (151). Fully stabilized cubic magnesia–zirconia ceramics do not withstand thermal cycling, whereas CaO- and Y_2O_3-stabilized oxides exhibit higher thermal stability.

Partially stabilized zirconias are formed by adding insufficient yttria, calcia, or magnesia to completely stabilize the zirconia, firing the mix, and then slowly cooling the sintered material in order to precipitate tetragonal zirconia within the grains of stabilized zirconia. The improved toughness of partially stabilized zirconias is the result of stress-induced martensitic transformation of the tetragonal particles to the monoclinic form in the stress field of a propagating crack. Their commercial application is based on their high strength and thermal shock resistance.

Zirconia prepared by the thermal decomposition of zirconium salts is often metastable tetragonal, or metastable cubic, and reverts to the stable monoclinic form upon heating to 800°C. These metastable forms apparently occur because of the presence of other ions during the hydrolysis of the zirconium; their stability has been ascribed both to crystallite size and surface energy (152,153) as well as strain energy and the formation of domains (154).

Zirconium oxide is stable to most reagents but dissolves slowly in hot concentrated sulfuric acid and in concentrated hydrofluoric acid. Carbon tetrachloride or phosgene above 300°C, or chlorine and carbon above 600°C give $ZrCl_4$. Above 1400°C, zirconium oxide is reduced by carbon to zirconium carbide. At high temperatures, zirconium oxide reacts with many metal oxides, including BaO, CaO, MgO, SrO, Y_2O_3, Re_2O_3, and PbO, to form solid solution oxides and, with the exception of magnesium, zirconate compounds. Molten-salt synthesis procedures give uniform, stoichiometric, finely divided alkaline-earth zirconate powders for use as a dielectric (155).

Although lower oxides do not occur terrestrially, they can be produced at high temperature. Zirconium monoxide [12036-01-0], ZrO, has been observed in the sun's spectra, and in the spectra of zirconium oxide being evaporated from the surface of a tungsten filament (156). As oxygen is added to alpha zirconium, additional diffraction lines appear at Zr_3O [12059-93-7] and higher oxygen contents (157,158); Zr_3O occurs as an ordered super lattice in zirconium, representing the limit of oxygen solubility in zirconium. Other lower oxide compounds that are considered stable are Zr_8O [53801-45-9] and Zr_2O [12412-49-6] (159).

11.8. Silicates. Zirconium silicate, $ZrSiO_4$, occurs naturally as zircon. Zircon is tetragonal, with the zirconium and silicon linked through oxygen atoms to form edge-sharing alternating SiO_4 tetrahedra and ZrO_8 triangular dodecahedra (160). Zircon is isomorphous with xenotime which occurs in solid solution in zircon crystals (161).

Upon heating to 900°C, zircon is transformed to a scheelite-type structure at 12 GPa (ca 120,000 atm), and a further transformation to the $KAlF_4$ structure at 17 GPa (ca 170,000 atm) has been predicted (162).

Zircon is synthesized by heating a mixture of zirconium oxide and silicon oxide to 1500°C for several hours (163). The corresponding hafnium silicate, hafnon, has been synthesized also. Zircon can be dissociated into the respective oxides by heating above 1540°C and rapidly quenching to prevent recombination. Commercially, this is done by passing closely sized zircon through a streaming arc plasma (38).

Zircon silicate is highly stable. Decomposition of zircon is accomplished only by very aggressive chemical attack, usually at high temperature.

Many other silicate minerals contain zirconium as a constituent (164,165). These minerals may be altered or metamict zircons such as cyrtolite or malacon.

11.9. Halides. *Quadrivalent.* Zirconium tetrafluoride is prepared by fluorination of zirconium metal, but this is hampered by the low volatility of the tetrafluoride which coats the surface of the metal. An effective method is the halogen exchange between flowing hydrogen fluoride gas and zirconium tetrachloride at 300°C. Large volumes are produced by the addition of concentrated hydrofluoric acid to a concentrated nitric acid solution of zirconium; zirconium tetrafluoride monohydrate [14956-11-3] precipitates (69). The recovered crystals are dried and treated with hydrogen fluoride gas at 450°C in a fluid-bed reactor. The thermal dissociation of fluorozirconates also yields zirconium tetrafluoride.

The physical properties of zirconium tetrafluoride are listed in Table 9.

Zirconium tetrafluoride dissolves in dilute acid without hydrolysis, and can be recovered as the monohydrate [14956-11-3] by crystallization from nitric acid solutions. If the solution is acidified with hydrofluoric acid, $ZrF_4 \cdot 3\,H_2O$ [14517-16-9] crystallizes at 10–30 wt% HF; $HZrF_5 \cdot 4\,H_2O$ [18129-16-9] crystallizes at 30–35 wt% HF, and at higher HF concentrations $H_2ZrF_6 \cdot 2\,H_2O$ [12021-95-3] can be recovered.

Potassium hexafluorozirconate, K_2ZrF_6, can be crystallized from a zirconium oxide chloride [7699-43-6] solution by addition of excess hydrofluoric acid and a stoichiometric amount of potassium fluoride. Industrially, it is produced by the fusion of zircon flour with potassium fluorosilicate as described above (31). Sodium fluorozirconates can be produced by equivalent processes, or by adding sodium fluoride to a warm acidified solution of potassium fluorozirconate to precipitate

Table 9. **Physical Properties of Zirconium Tetrahalides**

Property	ZrF_4	$ZrCl_4$	$ZrBr_4$	ZrI_4
color	white	white	white	orange-yellow
melting point, °C	932	437	450	499
sublimation temperature at 101.3 kPa (= 1 atm), °C	903	331	357	431
density, g/cm^3	4.43	2.80		4.85
critical temperature, °C		503.5	532	686
critical pressure, MPa[a]		5.7	4.3	4.1
critical density, g/cm^3		0.76	0.97	1.13
vapor pressure				
$\log P_{\mathrm{kPa}} = A - B/T$[b]				
A	12.682	10.891	11.393	8.695
B	12430	5400	5945	6700
range t, °C	408–640	207–416	216–332	137–307
crystal structure	monoclinic (B)	monoclinic	cubic	cubic
space group, nm	I 2/a	P 2/c	P a3	P a3
a	0.957	0.6361	1.095	1.179[c]
b	0.993	0.7407		
c	0.773	0.6256		
β[c]	99.47	109.30		
Zr–X bond distance, nm	0.210 avg	2.307[d] 2.498[e] 2.665[e]		

[a] To convert MPa to atm, divide by 0.101.

[b] To convert kPa to mm Hg, multiply by 7.5. T = K.

[c] Ref. 167.

[d] Between terminal chlorine atoms.

[e] Between bridging chlorine atoms.

the less soluble sodium salt. Several different sodium salts can be precipitated, depending on the sodium fluoride concentration: $NaZrF_5 \cdot H_2O$ [20982-58-5] is recovered from sodium fluoride concentration less than 0.21%, Na_2ZrF_6 [16925-26-1] is recovered from concentrations between 0.21 and 0.4%, and $Na_5Zr_2F_{13}$ [12022-20-7] from concentrations between 0.47 and 1.18%. At higher sodium fluoride concentrations, Na_3ZrF_7 [17442-98-7] precipitates. All of these solutions must remain acidic to prevent the formation of oxide fluorides. The solubilities and equilibrium phases for $ZrF–Na(K,Rb,Cs)F–H_2O$ systems are given in Reference 168. For comparison with the aqueous system, the molten $NaF \cdot ZrF_4$ salt system had the following stable phases: $Na_3Zr_4F_{19}$ [12140-35-1], $Na_7Zr_6F_{31}$ [12140-37-3], $Na_3Zr_2F_{11}$ [12140-29-3], Na_2ZrF_6, $Na_5Zr_2F_{13}$, and Na_3ZrF_7 (169). (In addition, Na_4HfF_8 has been found in the hafnium system.)

Zirconium tetrachloride, $ZrCl_4$, is prepared by a variety of anhydrous chlorination procedures. The reaction of chlorine or hydrogen chloride with zirconium metal above 300°C, or phosgene or carbon tetrachloride on zirconium oxide above 450°C, or chlorine on an intimate mixture of zirconium oxide and carbon above 700°C are commonly used.

Zirconium tetrachloride is a tetrahedral monomer in the gas phase, but the solid is a polymer of $ZrCl_4$ octahedra arranged in zigzag chains in such a way that each zirconium has two pairs of bridging chlorine anions and two terminal or t-chlorine anions. The octahedra are distorted with unequal Zr–Cl bridge bonds of 0.2498 and 0.2655 nm. The physical properties of zirconium tetrachloride are given in Table 9.

Zirconium tetrachloride is instantly hydrolyzed in water to zirconium oxide dichloride octahydrate [13520-92-8]. Zirconium tetrachloride exchanges chlorine for oxo bonds in the reaction with hydroxylic ligands, forming alkoxides from alcohols (see ALKOXIDES, METAL). Zirconium tetrachloride combines with many Lewis bases such as dimethyl sulfoxide, phosphorus oxychloride and amines including ammonia, ethers, and ketones. The zirconium organometallic compounds are all derived from zirconium tetrachloride.

Zirconium tetrachloride forms additional compounds with phosphorus pentachloride: $ZrCl_4 \cdot PCl_5$ and $ZrCl_4 \cdot 2\,PCl_5$. However, the alleged $2\,ZrCl_4 \cdot PCl_5$ has been found to be a low boiling azeotrope of $ZrCl_4$ and $ZrCl_4 \cdot PCl_5$ (170).

Zirconium tetrachloride forms hexachlorozirconates with alkali-metal chlorides, eg, Li_2ZrCl_6 [18346-96-8], Na_2ZrCl_6 [18346-98-0], K_2ZrCl_6 [18346-99-1], Rb_2ZrCl_6 [19381-65-8], and Cs_2ZrCl_6, and with alkaline-earth metal chlorides: $SrZrCl_6$ [21210-13-9] and $BaZrCl_6$ [21210-12-8]. The vapor pressure of $ZrCl_4$ over these melts as a function of the respective alkali chlorides and of $ZrCl_4$ concentration were studied as potential electrolytes for the electrowinning of zirconium (72). The zirconium tetrachloride vapor pressure increased in the following sequence: $Cs < Rb < K < Na < Li$. The stability of a hexachlorohafnate is greater than that of a comparable hexachlorozirconate (171), and this has been proposed as a separation method (172).

Zirconium tetrabromide [13777-25-8], $ZrBr_4$, is prepared directly from the elements or by the reaction of bromine on a mixture of zirconium oxide and carbon. It may also be made by halogen exchange between the tetrachloride and aluminum bromide. The physical properties are given in Table 9. The chemical behavior is similar to that of the tetrachloride.

Zirconium tetraiodide [13986-26-0], ZrI_4, is prepared directly from the elements, by the reaction of iodine on zirconium carbide, or by halogen exchange with aluminum triiodide. The reaction of iodine with zirconium oxide and carbon does not proceed. The physical properties are given in Table 9.

Zirconium tetraiodide is the least thermally stable zirconium tetrahalide. At 1400°C, it disproportionates to Zr metal and iodine vapor. This behavior is utilized in the van Arkel-de Boer process to refine zirconium. As with the tetrachloride and tetrabromide, the tetraiodide forms additional adducts with gaseous ammonia which, upon heating, decompose through several steps ending with zirconium nitride.

Lower Valent Halides. Zirconium trichloride [10241-03-9], $ZrCl_3$, tribromide [24621-18-9], $ZrBr_3$, and triiodide [13779-87-8], ZrI_3, are produced from zirconium metal and tetrahalide in sealed tantalum tubes at 500–700°C. The hafnium trihalides are made in the same manner. These reactions are slow, and may not reach equilibrium for days. Zirconium monohalides as the reductant increase the reaction rates. Another procedure uses quartz tubes with double bulbs; the halide is kept at the sublimation temperatures and the metal at 700°C. In a procedure employing comparatively low temperatures, the tetrahalides are dissolved in the corresponding liquid aluminum halide at the eutectic and reduced by metallic zirconium or aluminum between 220 and 300°C. The zirconium trihalides and $ZrI_{3.40}$ [29950-62-7] were prepared in this manner (173). Zirconium trichloride, tribromide, and triiodide have been made from their respective tetrahalides by atomic hydrogen reduction (174).

The trichloride and tribromide disproportionate above 200°C at or below 101.3 kPa (1 atm) (175):

$$12\,ZrCl_3 \xrightarrow{200^\circ C} 10\,ZrCl_{2.8} + 2\,ZrCl_4$$
$$10\,ZrCl_{2.8} \xrightarrow{300^\circ C} 5\,ZrCl_{1.6} + 5\,ZrCl_4$$
$$5\,ZrCl_{1.6} \longrightarrow 4\,ZrCl + ZrCl_4$$
$$4\,ZrCl \xrightarrow[\text{vac}]{600^\circ C} 3\,Zr + ZrCl_4$$

Other researchers have reported the trihalides to be nonstoichiometric with composition ranges of $ZrCl_{2.94}$–$ZrCl_{3.03}$, $ZrBr_{2.87}$–$ZrBr_{3.23}$, and $ZrI_{2.83}$–$ZrI_{3.43}$ (176). The composition ranges of the lower iodides were reported to be $ZrI_{1.9}$–$ZrI_{2.1}$, and $ZrI_{1.1}$–$ZrI_{1.3}$ (177).

Zirconium dichloride, $ZrCl_2$, has been made by a month-long reaction of ZrCl and $ZrCl_3$ at 650–750°C. The product has a three-layer sheet structure of close-packed Cl–Zr–Cl (178).

The first known cluster ion for group IVB elements is $ZrCl_{2.5}$, produced similarly to $ZrCl_2$: $(Zr_6Cl_{12})^{3+}$ $(Cl^-)_3$, with nine delocalized bonding electrons in the metal cage (178). ZrI_2 also contains the 12-electron cage Zr_6I_{12}, as does the isostructural Zr_6Cl_{12}.

Attempts to prepare zirconium trifluoride, ZrF_3, by the zirconium reduction of zirconium tetrafluoride were unsuccessful, but it has been made by heating zirconium hydride to 750°C in a stream of hydrogen and hydrogen fluoride (179).

Monovalent Halides. Zirconium monochloride [14989-34-5], ZrCl, was discovered during electrorefining studies of zirconium in a $SrCl_2$–NaCl–$ZrCl_4$ melt intended to produce pure ductile hafnium-depleted zirconium from crude zirconium anodes (180,181). The monochloride is also called Zirklor. It is obtained as black flakes with a graphite slip-plane behavior and was proposed as a lubricant (182,183).

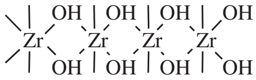
Zirconium monochloride and zirconium monobromide [31483-18-8] are prepared in better purity by equilibration of mixed lower halides with zirconium foil at 625°C (184,185) or by slowly heating zirconium tetrahalide with zirconium turnings at 400–800°C over a period of two weeks and holding at 800–850°C for a few additional days (186). Similar attempts to produce zirconium monoiodide [14728-76-8] were unsuccessful; it was, however, obtained from the reaction of hydrogen iodide with metallic zirconium above 2000 K (187).

Zirconium chloride and bromide have closely related but dissimilar structures. Both contain two metal layers enclosed between two nonmetal layers which both have hexagonal structure. In ZrCl, the four-layer sandwich repeats in layers stacked up according to /abca/bcab/cabc/, whereas the ZrBr stacking order is /abca/cabc/bcab/ (188). Both are metallic conductors, but the difference in packing results in different mechanical properties; the bromide is much more brittle.

Zirconium monochloride is reported to disproportionate at 610°C in a high vacuum (184) and to exert a $ZrCl_4$ pressure of 101.3 kPa (1 atm) at 900°C and 293.7 kPa (2.9 atm) at 975°C, and to melt at 1100°C in an autogenous $ZrCl_4$ pressure of 1.5–2 MPa (15–20 atm) (185). The disproportionation proceeds at a lower temperature in the presence of copper or silver (182).

Zirconium monochloride reacts with sodium ethoxide to form additional adducts which hydrolyze in water. The monochloride does not react with benzene in a Friedel-Crafts reaction, and does not enter into intercalation reactions similar to those of zirconium disulfide. Both monohalides add hydrogen reversibly up to a limiting composition of ZrXH (131).

11.10. Hydroxyl Compounds. The aqueous chemistry of zirconium is complex, and in the past its understanding was complicated by differing interpretations. In a study of zirconium oxide chloride and zirconium oxide bromide, the polymeric cation $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ was identified (189); the earlier postulated moiety $[Zr{=}O]^{2+}$ was discarded. In the tetramer, the zirconium atoms are connected by double hydroxyl bridges (shown without the coordinating water molecules):



The tetramer exists in two-molal zirconium chloride and nitrate solutions, but it polymerizes into cross-linked chains on hydrolysis (190,191); in strong acid solutions, the hydroxyl bridges can be replaced by other anions to form trimers (192) and monomers (192,193).

11.11. Hydrous Oxides and Hydroxides. Hydroxide addition to aqueous zirconium solutions precipitates a white gel formerly called a hydroxide, but now commonly considered hydrous zirconium oxide hydrate [12164-98-6], $ZrO_2{\cdot}nH_2O$. However, the behavior of this material changes with time and temperature.

The freshly precipitated material with four hydroxyl groups titratable with potassium fluoride for each zirconium atom can be considered a true hydroxide (194,195). When the freshly precipitated hydroxide was kept in water for two to three days before titration, two hydroxyl groups were titrated quickly, and two slowly on mixing for 30 h. These were called α- and γ-hydroxides. An intermediate β-hydroxide with three hydroxyl groups per zirconium could be produced only by precipitation from solutions of zirconium oxide chloride or nitrate in methanol, with extremely high zirconium concentrations. Drying these hydroxides in air gave a powder, which no longer contained any titratable hydroxyl groups; the material was very sparingly soluble in acid.

The hydroxides as precipitated are amorphous, but if they are refluxed in a neutral or slightly acidic solution they convert to a mixture of cubic and monoclinic hydrous zirconia crystallites; on continued refluxing, only the monoclinic form persists (196). If the refluxing is conducted in an alkaline solution, metastable cubic zirconia is formed (197).

11.12. Oxide Chlorides. Zirconium oxide dichloride, $ZrOCl_2 \cdot 8\,H_2O$ [13520-92-8], commonly called zirconium oxychloride, is really a hydroxyl chloride, $[Zr_4(OH)_8{\cdot}16H_2O]Cl_8{\cdot}12H_2O$ (189). Zirconium oxychloride is produced commercially by caustic fusion of zircon, followed by water washing to remove sodium silicate and to hydrolyze the sodium zirconate; the wet filter pulp is dissolved in hot hydrochloric acid, and $ZrOCl_2{\cdot}8H_2O$ is recovered from the solution by crystallization. An aqueous solution is also produced by the dissolution and hydrolysis of zirconium tetrachloride in water, or by the addition of hydrochloric acid to zirconium carbonate.

Tetragonal prisms of $ZrOCl_2{\cdot}8H_2O$ crystallize from hot hydrochloric acid solutions by cooling or by increasing the acidity; in >32% hydrochloric acid transparent hexagonal plates are formed probably as $ZrOCl_2 \cdot 2\,HCl \cdot 10\,H_2O$ (198).

Zirconium oxychloride is an important intermediate from which other zirconium chemicals are produced. It readily effloresces, and hydrates with 5–7 H_2O are common. The salt cannot be dried to the anhydrous form, and decomposes to hydrogen chloride and zirconium oxide.

Zirconium hydroxy oxychloride [18428-88-1], nominally ZrO(OH)Cl, is produced by dissolving hydrous zirconia in hydrochloric acid in an equal molar proportion, and is available only in solution. Other oxychlorides with Cl:Zr ratios <2 are discussed in Reference 199.

Anhydrous zirconium oxide chloride, $ZrOCl_2$ [7699-43-6], has been prepared by the reaction of dichlorine oxide with a zirconium tetrachloride suspension in carbon tetrachloride starting at −30°C and slowly rising to room temperature. The white solid is extremely hygroscopic and decomposes to $ZrCl_4$ and ZrO_2 at 250°C (200).

11.13. Nitrates. Anhydrous zirconium tetranitrate [12372-57-5], $Zr(NO_3)_4$, is prepared from zirconium tetrachloride and nitrogen pentoxide (201). The hydrated compounds are obtained from aqueous nitric acid (165); $ZrO(NO_3)_2 \cdot 2\,H_2O$[20213-65-4] is most commonly used; $Zr(NO_3)_4 \cdot 5\,H_2O$ [12372-57-5] can be produced from strong nitric acid.

Aqueous solutions of zirconium oxide dinitrate [13826-66-9] (zirconium oxynitrate) and zirconium oxychloride behave very similarly; these two compounds have been cocrystallized in solid solution (202) where $ZrO(NO_3)_2 \cdot 5\,H_2O$ was the stable hydrate.

11.14. Carbonates. Basic zirconium carbonate [37356-18-6] is produced in a two-step process in which zirconium is precipitated as a basic sulfate from an oxychloride solution. The carbonate is formed by an exchange reaction between a water slurry of basic zirconium sulfate and sodium carbonate or ammonium carbonate at 80°C (203). The particulate product is easily filtered. Freshly precipitated zirconium hydroxide, dispersed in water under carbon dioxide in a pressure vessel at ca 200–300 kPa (2–3 atm), absorbs carbon dioxide to form the basic zirconium carbonate (204). Washed free of other anions, it can be dissolved in organic acids such as lactic, acetic, citric, oxalic, and tartaric to form zirconium oxy salts of these acids.

Basic zirconium carbonate is nominally $2ZrO_2{\cdot}CO_2{\cdot}xH_2O$ but the ZrO_2:CO_2 ratio may range from 4:1 to 1:1 depending on the methods and techniques of preparation.

Basic zirconium carbonate reacts with sodium or ammonium carbonate solutions to give water-soluble double carbonates. The ammonium double carbonate is nominally $NH_4[Zr_2O(OH)_3(CO_3)_3]$. These solutions are stable at room temperature, but upon heating they lose carbon dioxide and hydrous zirconia precipitates.

In a study of zirconium double carbonates (205), a family of carbonates with CO_3:Zr ratios of 1, 1.5, 2, 2.5, 3, 3.5, and 4:1 were identified. None of these compounds combined with ammonia, confirming the absence of HCO_3^-.

11.15. Sulfates. Sulfate ions strongly complex zirconium, removing hydroxyl groups and forming anionic complexes. With increasing acidity, all hydroxyl groups are replaced; zirconium sulfate [7446-31-3], $Zr(SO_4)_2 \cdot 4\,H_2O$, with an orthorhombic structure (206), can be crystallized from a 45% sulfuric acid solution. Zirconium sulfate forms various hydrates, and 13 different crystalline $Zr(SO_4)_2 \cdot nH_2O$ [14644-61-2] systems are described in Reference 207. The tetrahydrate loses three hydration waters above 100°C and becomes anhydrous at 380°C. Many complex sulfates are formed with alkali-metal sulfates.

Basic zirconium sulfates are formed by hydrolysis of zirconium sulfate, which is broken up into fragments that undergo further hydrolysis to yield a series of basic sulfates with the generic formula $Zr_n(OH)_{2n+2}(SO_4)_{n-1}$ (190).

Basic zirconium sulfate is also considered to be strands of $[Zr(OH)_2^b]_n^{2n+}$ joined by bridging sulfates (208). The resulting formula is $Zr(OH)_2^b - (OH)^t(SO_4)_{0.5}^b \cdot nH_2O$, where b are bridging anions and t are terminal anions.

The most common basic sulfate is $5ZrO_2{\cdot}3SO_3{\cdot}nH_2O$ [84583-91-5] which is precipitated in good yield when a zirconium oxychloride solution is heated with the stoichiometric amount in sulfate ion. It is used to prepare high purity oxides and ammonium zirconium carbonate.

The stability of zirconium sulfate solutions to spontaneous precipitation when heated to 70°C for 2 h was studied as a function of SO_3:ZrO_2 ratio and metal concentrations (209). The zirconium solutions were considered unstable at metal concentrations below 0.64 M or at SO_3:ZrO_2 ratios <1.2.

11.16. Phosphates. Phosphate ions precipitate group IVB metals from strongly acid solutions. This ability is used in analytical procedures to separate zirconium from other elements, and to prepare zirconium phosphates. The precipitate is a gelatinous amorphous solid of variable composition. However, when refluxed in strong phosphoric acid, a crystalline, stoichiometrically constant compound forms of composition $Zr(HPO_4)_2{\cdot}H_2O$, known as zirconium bis(monohydrogen phosphate) [13772-31-1] or α zirconium phosphate (210), or αZP. This compound is also obtained by gradual precipitation of the phosphate from a heated zirconium fluoride solution (211). On heating, the αZP undergoes three transformations, losing water and finally converting to cubic zirconium pyrophosphate [33712-62-8], ZrP_2O_7, at 1000°C (212).

The main interest in zirconium phosphates relates to their ion-exchange properties. If amorphous zirconium phosphate is equilibrated with sodium hydroxide to pH 7, one hydrogen is displaced and $ZrNaH(PO_4)_2 \cdot 5\,H_2O$ [13933-56-7] is obtained. The spacing between the zirconium layers is increased from 0.76 to 1.18 nm, which allows this phosphate to exchange larger ions.

The gels precipitated as described above are not useful in ion-exchange systems because their fine size impedes fluid flow and allows particulate entrainment. Controlled larger-sized particles of zirconium phosphate are obtained by first producing the desired particle size zirconium hydrous oxide by sol–gel techniques or by controlled precipitation of zirconium basic sulfate. These active, very slightly soluble compounds are then slurried in phosphoric acid to produce zirconium bis(monohydrogen phosphate) and subsequently sodium zirconium hydrogen phosphate pentahydrate with the desired hydraulic characteristics (213,214).

Although zirconium phosphate is insoluble in acids, it is easily hydrolyzed in excess caustic to give hydrous zirconium oxide. Zirconium phosphate forms soluble complexes with a large excess of zirconium oxide chloride, and therefore separation of phosphorus from zirconium oxide chloride solutions is difficult (215).

The properties and behavior of double phosphates such as $Na_{1+x} - Y_xZr_{2-x}(PO_4)_3$ (216), sodium–zirconium phosphate–silicates (217), and alkali-modified zirconium pyrophosphates (218) have been studied as potential solid electrolytes in high temperature batteries.

11.17. Alkoxides. Zirconium alkoxides are part of a family of alcohol-derived compounds (219). The binary zirconium compounds have the general formula $ZRX_4–n(OR)_n$. They are easily hydrolyzed and must be prepared under anhydrous conditions. They are prepared by the reaction of zirconium tetrahalides and alcohols:

$$ZrCl_4 + 3\,C_2H_5OH \longrightarrow \underset{[87227\text{-}58\text{-}5]}{ZrCl_2(OC_2H_5)_2\cdot C_2H_5OH} + 2\,HCl\uparrow$$

All four chlorines can be substituted if anhydrous ammonia is added to combine with the hydrogen chloride:

$$ZrCl_4 + 4\,CH_3OH + 4\,NH_3 \longrightarrow \underset{[28469\text{-}78\text{-}5]}{Zr(OCH_3)_4} + 4\,NH_4Cl$$

Alkoxides of other alcohols are formed by alcohol exchange. The general stability of the alcohols in exchange is primary > secondary > tertiary, although the reaction can be driven in the opposite direction by removal of the more volatile alcohol:

$$\underset{[18267\text{-}08\text{-}8]}{Zr(OC_2H_5)_4} + 3\,(CH_3)_3COH \longrightarrow \underset{[87227\text{-}52\text{-}9]}{Zr(OC_2H_5)[OC(CH_3)_3]_3} + 3\,C_2H_5OH$$

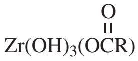
Alkoxides can be formed also by reaction of zirconium dialkylamines with alcohols, and alkoxides can be exchanged also be transesterification reactions.

Double alkoxides of zirconium with alkali metals of the type $MZr_2(OR)_9$ have been obtained by reaction of alkali metal alkoxides with zirconium alkoxides (220). Although these usually are monomeric derivatives, the reaction between zirconium tetra-*t*-butoxide [1071-76-7] and sodium *t*-butoxide was found (221) to form dimeric $[NaZr(OC(CH_3)_3)_5]_2$.

Zirconium alkoxides readily hydrolyze to hydrous zirconia. However, when limited amounts of water are added to zirconium alkoxides, they partially hydrolyze in a variety of reactions depending on the particular alkoxide (222).

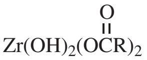
Zirconium tetraisopropoxide [2171-98-4] reacts with fatty acids to form carboxylates (223), and with glycols to form mono- and diglycolates (224).

11.18. Carboxylates. Zirconium hydroxy carboxylates of the generic type



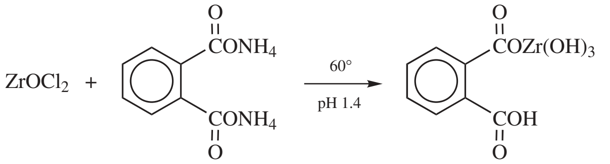
$$\mathrm{Zr(OH)_3(O\overset{O}{\overset{\|}{C}}R)}$$

and



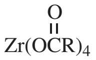
$$\mathrm{Zr(OH)_2(O\overset{O}{\overset{\|}{C}}R)_2}$$

are precipitated by adding carboxylic salts to hydrochloric acid solutions of zirconium. With larger organic ligands, these compounds are water insoluble. They have been used for gravimetric determination, such as trihydroxyzirconium mandelate [87227-59-6] or for industrial purification precipitations, such as hydrogen trihydroxyzirconium phthalate [62313-97-7]:



Zirconium oxalates exist as compounds, double compounds, and mixed oxalato complexes (165,195,225,226). When the carboxylate ligand is a longer alkyl chain, the materials often are called zirconium soaps.

Zirconium tetracarboxylates,



$$\mathrm{Zr(O\overset{O}{\overset{\|}{C}}R)_4}$$

are prepared by reactions of zirconium tetraalkoxides or zirconium tetrachloride with anhydrous carboxylic acids (223).

11.19. Amides, Imides, Alkamides. When zirconium tetrachloride reacts with liquid ammonia, only one chloride is displaced to form a white precipitate, insoluble in liquid ammonia (227):

$$\mathrm{ZrCl_4} + (x + 2)\,\mathrm{NH_3} \longrightarrow \underset{[87319\text{-}91\text{-}3]}{\mathrm{ZrCl_3(NH_2)}\cdot x\mathrm{NH_3}} + \mathrm{NH_4Cl}$$

Upon heating in vacuum to 100°C, this material loses several ammonia moieties to give $\mathrm{ZrCl_3(NH_2)\cdot NH_3}$.

The presence of $\mathrm{NH_4Cl}$ causes the formation of a complex which is soluble in excess liquid ammonia (228):

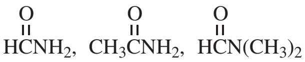
$$\underset{[19381\text{-}66\text{-}9]}{\mathrm{(NH_4)_2ZrCl_6}} + \mathrm{NH_3} \rightarrow \underset{[87247\text{-}93\text{-}2]}{\mathrm{(NH_4)_2[ZrCl_5(NH_2)]}} + \mathrm{NH_4Cl}$$

Additional halides can be removed from the above insoluble ammonolysis product by reaction with potassium imide to form zirconium imide [87227-54-1] $Zr(NH_2)_2$:

$$\begin{aligned} ZrBr_3NH_2 + KNH_2 &\longrightarrow ZrBr_2(NH_2)_2 + KBr \\ ZrBr_2(NH_2) + 2\,KNH_2 &\longrightarrow Zr(NH_2)_4 + 2\,KBr \\ Zr(NH_2)_4 &\longrightarrow Zr(NH_2)_2 + 2\,NH_3 \end{aligned}$$

Zirconium dichlorobis(dimethylamide) [87227-57-4], $ZrCl_2[N(CH_3)_2]_2$ is made directly from methylamine and zirconium tetrachloride but all of the halogens can be substituted by treating zirconium tetrachloride with the appropriate lithium alkylamide (229). Zirconium arylamines are made from zirconium alkoxides which first are converted to aryloxides (230).

The zirconium–nitrogen bond is weaker than the zirconium–oxygen bond even under anhydrous conditions. When zirconium tetrachloride reacts with carbonyl-containing amides such as



$$\mathrm{H\overset{O}{\overset{\|}{C}}NH_2,\ CH_3\overset{O}{\overset{\|}{C}}NH_2,\ H\overset{O}{\overset{\|}{C}}N(CH_3)_2}$$

or

$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}N(CH_3)_2}$$

all the bonding to zirconium is through carbonyl groups (231).

11.20. Organometallic Compounds.

Certain zirconium organometallic compounds are highly reactive toward low molecular weight unsaturated molecules. Some of these compounds are useful in various organic syntheses; others function effectively as catalysts for polymerization, hydrogenation, or isomerization.

Some simple zirconium organometallic compounds, such as tetramethylzirconium [6727-89-5], are known. In general, these compounds are very unstable. It appears that zirconium must be π-bonded to at least one moderately large ligand, such as a cyclopentadienyl group, for the compound to be stable. The abbreviation Cp is used here for the cyclopentadienyl group (C_5H_5), and Cp′ for $[C_5(CH_3)_5]$.

The metallocene complexes of M = Ti, Zr, and Hf are most stable when the two Cp groups are not parallel, in contrast to most other transition metal–Cp complexes. The most stable angle for the zirconium metallocenes is ca 40°, which partially accounts for the more interesting chemistry of these compounds compared to other transition metallocenes.

Cyclopentadienyl zirconium compounds are similar in structure and behavior to their titanium analogues. The increasing strength of the M–H and M–C bonds in the series M = Ti, Zr, and Hf makes the zirconium and hafnium compounds slightly more stable and thus somewhat less reactive than their titanium analogues. For example, ferrocenyl lithium reacts with Cp_2MCl_2 to give

$Cp_2M(Fc)_2$. The colors of these compounds, green for Ti and red for Zr and Hf, are the results of electron transitions from a ferrocene orbital to a Cp_2M orbital (232), and is a measure of the relative bond energies. In general, the zirconium compounds are more complex and less reactive than the titanium analogues.

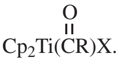
Hydrides. Zirconium hydrides react easily with unsaturated molecules. This process, termed hydrozirconation, replaces the hydrogen with the unsaturated group:

$$\underset{[37342\text{-}97\text{-}5]}{Cp_2ZrHCl} + R \rightarrow Cp_2ZrRCl$$

The oxidative addition reactions of $Cp_2M(CO)_2$ show some interesting differences between the Ti and Zr analogues. For $Cp_2Ti(CO)_2$, both ($R = CH_3$, C_6H_5)

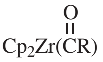
$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl}$$

and $RX(R = CH_3$, C_2H_5, Pr^i, $Bu^s)$ react to give acyls,



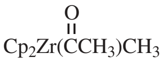
$$\mathrm{Cp_2Ti(}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R)X.}$$

In contrast, $Cp_2Zr(CO)_2$ [59487-85-3] reacts with CH_3I, without CO insertion, to give Cp_2ZrCH_3I [63643-49-2]. Reaction with $P(CH_3)_3$ gives $Cp_2Zr(CO)[P(CH_3)_3]$ [63637-45-6]; diphenylacetylene gives the metallocycle $Cp_2Zr[C_4(C_6H_5)_4]$ [63637-34-3] (243,244).



$$\mathrm{Cp_2Zr(}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R)}$$

R is formed by carbonylation of Cp_2ZrR_2 ($R = CH_3$ [12636-72-5], $CH_2C_6H_5$ [37206-41-0], and C_6H_5 [51177-89-0]) and is reversible for the alkyls, but not for aryls. Equilibrium and thermodynamic data were published for the alkyls. A crystal structure



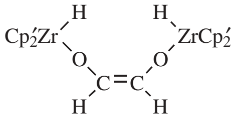
$$\mathrm{Cp_2Zr(}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3)CH_3}$$

for

$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}$$

[60970-97-0] is used as support for interpreting the failure to eliminate the ketone as occurs in the Ti analogue, in terms of stabilization resulting from the side-bonded acyl group (245).

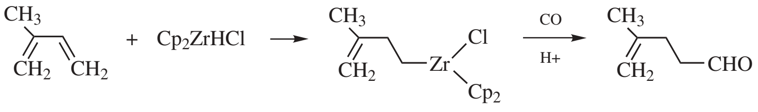
A Zr(IV) carbonyl, $Cp_2ZrH_2(CO)$ [61396-35-8], was formed by exposing a solution of Cp_2ZrH_2 [61396-34-7] to CO at −80°C. The structure was inferred by observation of ^{13}C–H coupling when ^{13}CO was used. No ir spectra could be obtained. Warming $Cp_2ZrH_2(CO)$ gives the dimer [61396-37-0] (246):



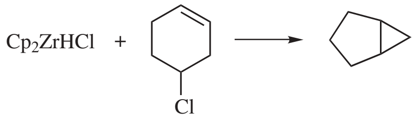
The CO stretching frequency of $Cp'_2ZrH_2(CO)$ was observed by other workers at 2044 cm^{-1} (the Hf analogue was observed at 2036 cm^{-1}) (247). RCO_2H, $R_2C{=}O$, and $RC{\equiv}N$ react to give Cp_2ZrXCl complexes where X = RCO_2-, R_2CHO-, and $RCH{=}N-$, respectively. Esters RCO_2R' give a mixture of $Cp_2ZrCl(OCH_2R)$ and $Cp_2ZrCl(OR')$; CO_2 is reduced to formaldehyde, with formation of $(Cp_2ZrCl)_2O$ [12097-04-0]; cyclopentadiene produces Cp_3ZrCl [69005-93-2]; and ethylene gives $Cp_2ZrCl(CH_2CH_3)$ [12109-84-1] (233).

The hydrides can also be used to form primary alcohols from either terminal or internal olefins. The olefin and hydride form an alkenyl zirconium, Cp_2ZrRCl, which is oxidized to the alcohol. Protonic oxidizing agents such as peroxides and peracids form the alcohol directly, but dry oxygen may also be used to form the alkoxide which can be hydrolyzed (234).

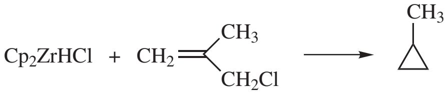
Zirconium hydrides undergo 1,2-addition with 1,3-dienes to give γ,δ-unsaturated complexes in 80–90% yield. Treatment of these complexes with CO at 20°C and 345 kPa (50 psi) followed by hydrolysis gives γ,δ-unsaturated aldehydes (235).



Cyclopropanes can be generated in high yield by treatment of halogen-containing alkenes with Cp_2ZrHCl; eg,



(41%)



(31%)

Alkenes and alkanes are also produced (236). The procedures for the synthesis of Cp_2ZrH_2 [37342-98-6] and Cp_2ZrHCl have been published in detail (237).

Carbonyl Complexes. $Cp_2M(CO)_2$ complexes (M = Ti, Zr [59487-85-3], and Hf) have been prepared by three different methods with varying yields: reduction of Cp_2MCl_2 (when M = Zr [1291-32-3]) with Na(Hg) under CO at 101.3 kPa (1 atm) gives 80% with Ti, 9% with Zr, and 30% with Hf (238); reduction of Cp_2MCl_2 with Li under CO at 20 MPa (200 atm) gives 80% with Zr and 2% with Hf (239); and treatment of Cp_2MBH_4 with $(C_2H_5)_3N$ under CO at 101.3 kPa (1 atm) gives 80% with Ti and 15% with Zr (240). The nmr and ir spectra are similar for all three analogues, with the CO stretching frequencies decreasing in the order Ti > Zr > Hf (238).

An x-ray study of the structure of $Cp_2Hf(CO)_2$ revealed the expected tetrahedral disposition of ligands with OC–Hf–CO and (centroid Cp)–Hf–(centroid Cp) angles of 89.3° and 141°, respectively, and mean bond lengths for both bond types of 0.216 nm (241). The Zr analogue is isomorphous with bond lengths of 0.2187 nm and a OC–Zr–CO bond angle of 89.2° (242).

$Cp_2Zr(CO)_2$ in hot toluene reacts with CO to give a cyclic trimer $(Cp_3ZrO)_3$. The Zr_3O_3 ring in this unusual compound is nearly planar, with Zr–O–Zr and O–Zr–O bond angles of 142.5° and 97.5°, respectively. The mean Zr–O bond length (0.196 nm) seems to indicate a large degree of Zr–O double bonding (243).

Dinitrogen Complexes. The relative inertness of molecular nitrogen is well known, however, some Cp′–Zr compounds coordinate dinitrogen and substantially increase its reactivity. The nitrogen molecule can be coordinated either in a terminal position or as a bridge in dimeric structures.

Bridging and terminal nitrogens have been compared in $[Cp_2Zr(N_2)]_2N_2$. The bridging N_2 has a longer N–N distance (0.118 vs 0.1115 nm) and shorter Zr–N distances. In addition, the bridging N_2 stretching frequency is very low, 1578 cm^{-1} (248).

The increase in reactivity of coordinated N_2 has been assumed to be associated with increased bond length and decreased stretching frequency. A labeling study has shown that this is an oversimplification. In the protonolysis of $[Cp'_2Zr(N_2)]_2N_2$, the hydrazine produced comes equally from terminal and bridging N_2. An intermediate, such as $Cp'_2Zr(N_2H)_2$ [86165-22-2], was proposed where the bridging and terminal N_2 have become equivalent. Furthermore, careful carbonylation of the dimer produces $[Cp'_2Zr(CO)]_2N$ which on protonolysis gives no reduced form of N_2, indicating that both bridging and terminal N_2 are required for reduction (249).

A similar process has been patented covering Cp'_2ZrR [86165-24-4], $Cp'_2ZrR(N_2)$ [86165-25-5], and $(Cp'_2ZrR)_2N_2$ [86165-23-3], where $R = CH[Si(CH_3)_3]_2$. Protonolysis of the dinitrogen complexes gives hydrazine and ammonia (250).

Alkyl and Aryl Complexes. Cp_2MR_2 and Cp_2MRCl, $[R = CH(C_6H_5)_2$, $CH(Si(CH_3)_3)_2]$ have been prepared and studied by nmr, and crystal structures for $R = CHC_6H_5$ have been reported. For Zr, the metal–carbon distance (0.2388 nm) is substantially longer than for $R = CH_3$, whereas no increase is observed with Hf (251).

The thermal decomposition of several Cp_2ZrR_2 compounds has been studied; RH is formed and the hydrogen derives from either a Cp or another R group and not from a solvent molecule (252).

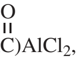
Mixed-Metal Systems. Mixed-metal systems, where a zirconium alkyl is formed and the alkyl group transferred to another metal, are a new application of the hydrozirconation reaction. These systems offer the advantages of the easy formation of the Zr–alkyl as well as the versatility of alkyl–metal reagents. For example, Cp_2ZrRCl (R = alkyl or alkenyl) reacts with $AlCl_3$ to give an Al–alkyl species which may then be acylated with

$$R'\overset{O}{\overset{\|}{C}}Cl$$

to give ketones,

$$\mathrm{R'}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}$$

in up to 98% yield. In contrast, direct acylation of the Zr compounds is difficult (R = alkyl) or impossible (R = alkenyl). The carbon configuration is retained during the transmetallation step which is faster for alkenyls, suggesting a bridged Zr–R–Al intermediate (253). Acyl–aluminum compounds,



$$(\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})\mathrm{AlCl_2},$$

which have potential use in organic synthesis as acyl anion equivalents, can be prepared by a similar reaction (254).

Alkenyl groups have also been transferred to Cu or Pd, leading to alkenyl dimers RCH=CH–CH=CHR in high yield (255). Alkenyls undergo conjugate addition to enones in the presence of catalytic amounts of nickel acetylacetonate in high yield and selectivity (256). Nickel tetralithium catalyzes the reaction of Zr–alkenyls with aryl halides to give the cross-coupling products RCH=CHAr (257). The reaction proceeds much more efficiently if the Ni catalyst is first reduced with diisobutyl aluminum hydride (258).

Alkenyl zirconium complexes derived from alkynes form C–C bonds when added to allylic palladium complexes. The stereochemistry differs from that found in reactions of corresponding carbanions with allyl–Pd in a way that suggests the Cp_2ZrRCl alkylates first at Pd, rather than by direct attack on the allyl group (259).

Catalysts. Several types of zirconium organometallic compounds are useful catalysts. In addition to the catalytic properties of the molecules, the fact that they can be bound to a relatively inert substrate increases their utility. A polymer-bound Cp-complex can be obtained through Cp–ring exchange. Treatment of Cp_2MCl_2 (M = Ti, Zr, Hf) with two equivalents of NaC_5D_5, followed by HCl, gives a mixture of $(C_5H_5)_2$–, $(C_5H_5)(C_5D_5)$–, and $(C_5D_5)_2$–MCl_2 (260). Although this indicates that ring exchanges in Cp_4M is fast, other studies have shown that the ratio of exchange products depends upon whether H- or D-substituted Cp_2MCl_2 is used as a reactant (261). Though Cp-ring exchange is not simply a matter of a Cp_4M intermediate, the products may nonetheless be used to bind Cp–Zr complexes to various substrates.

Polymer–Cp–MCl_3 complexes have been formed with the Cp-group covalently bound to a polystyrene bead. The metal complex is uniformly distributed throughout the bead, as shown by electron microprobe x-ray fluorescence. Olefin hydrogenation catalysts were then prepared by reduction with butyl lithium (262).

Ziegler polymerization catalysts may be prepared from Cp–Zr complexes and trialkylaluminum. The molecular weight of the polymers can be controlled over a wide range by varying the temperature. The activity of these catalysts is considerably increased by the addition of small amounts of water (263,264) (see OLEFIN POLYMERS, INTRODUCTION).

Zirconium–allyl complexes also have catalytic properties. Tetraallylzirconium [12090-34-5] on a silica substrate catalyzes ethylene polymerization

(265). Supported on silica, ZrR_4 (R = allyl or neopentyl) catalyzes olefin isomerization (266).

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