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Analytical Chemistry of Zirconium and Hafnium

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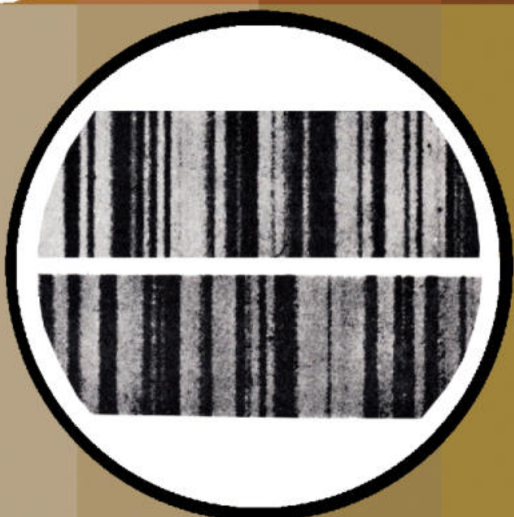

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BY

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TO JETU

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PREFACE

ZIRCONIUM and hafnium have many interesting physical and mechanical properties such as corrosion resistance and mechanical strength of metals and alloys at both low and elevated temperatures. The transparency of zirconium to thermal neutrons has found its greatest use as a construction material in nuclear reactors. Hafnium is always associated with zirconium and their separation from each other remained a challenge to analytical chemists for several years. Hafnium has been used as control rods in nuclear reactors because of its large neutron cross-section. Less interest has been shown in the chemical and physical properties of hafnium through the years. This may, however, change as its applications widen. Hafnium can absorb and give up heat more than twice as fast as zirconium or titanium and seems very promising as a construction material for jet engines and space technology.

The monograph presents a collection and comparison of available literature on the characterization and analysis of zirconium and hafnium. The aqueous chemistry of zirconium and hafnium has been discussed to draw attention to the complications of hydrolysis and polymerization and their effect on analytical procedures. Classical methods such as gravimetric, titrimetric and absorptiometric are presented along with spectrographic, X-ray and neutron activation methods. Techniques for the separation, of zirconium from hafnium have been discussed. The monograph covers important literature up to 1967.

Thanks are due to Professor Henry Freiser for his valuable criticism of the manuscript.

Philadelphia,
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Physical Properties of Zirconium and Hafnium

Property	Zirconium	Hafnium
Atomic number	40	72
Atomic weight	91.22	178.6
Atomic radius	1.452 Å	1.442 Å
Ionic radius (M^{4+})	0.74 Å	0.75 Å
Density	Close-packed hexagonal structure, 6.489 g/cm^3 (low hafnium) to 6.574 g/cm^3 (high hafnium); body-centered cubic high-temperature structure at 979°C, 6.046 g/cm^3	13.09 ± 0.01 g/cm^3 at 20°C
Melting point	1852 ± 2°C	2222°C
Boiling point	3580°C	5400°C
Vapor pressure	1949–2054°K $\log P\ (\text{atm}) = \frac{31{,}066}{T} + 7.3551 - 2.415 \times 10^{-4}\,T$	10^{-10} atm at 1867°C; 10^{-9} atm at 2007°C
Thermal expansion	Alpha, 5.85×10^{-6} per °C for heterogenously oriented polycrystals; body-centered cubic alpha, 9.7×10^{-6} per °C between 870 and 1337°C	Alpha phase, 0.000519 per °C between 20 and 200°C
Thermal expansion perpendicular to C-axis	Alpha, 6.96×10^{-6} per °C	—
Specific heat	At room temperature, 0.067 ± 0.001 cal/g C°; above 862°C, 0.08 cal/g °C	0.0351 cal/g °C between 25° and 100°C
Specific heat vs. temperature	Between 1.8° and 4.2°K, $C_v = 6.92 \times 10^{-4}T + 464.5\ (T/265)$ cal/mole/°C. $Cp = 0.070 + 3.6 \times 10^{-5}T$ cal/g °C	—
Latent heat of fusion	5.5 kcal/mole (estimated)	—
Latent heat of vaporization	142,150 ± 350 cal/mole	—

PHYSICAL PROPERTIES OF ZIRCONIUM AND HAFNIUM—*cont.*

Property	Zirconium	Hafnium
Thermal conductivity	At 24°C—, 0.211 W/cm °C A 100°C—, 0.204 W/cm °C At 300°C—, 0.187 W/cm °C $K = 0.0308\ (\rho\text{-}0.00327)T + 0.0381$, where ρ is the electrical conductivity in reciprocal microohm-cm and T is temperature in °K.	At 50°C, 0.233 W/cm °C
Electrical resistivity at room temperature	40 microohm-cm	35.1 microohm-cm
Temperature coefficient of electrical resistivity	44×10^{-4} per °C	0.0038 per °C
Electrochemical equivalent	Valence 4, 0.2363 mg/coulomb	Valence 4, 0.4626 mg/coulomb
Superconductivity critical temperature	0.546°K in zero magnetic field	—
Paramagnetic susceptibility	At 25°C, 1.3×10^{-6} cgs At 700°C, 1.53×10^{-6} cgs At 862°C, 1.9×10^{-6} cgs	0.42×10^{-6} emu/g at 20°C
Thermal neutron cross-section	0.18 barns	105 barns
Ionization potential	34.33 eV for valence 3	—
Crystal structure	Close-packed hexagonal at 25°C; $a = 3.2312$ Å $c = 5.1477$ Å, $c/a = 1.5931$ Å; body-centered cubic at 862°C; $a = 3.6090$ Å	Close-packed hexagonal, alpha phase, $a = 3.1883$ Å $c = 5.0422$ Å; body-centered cubic, beta phase, $a = 3.50$ Å.
Modulus of elasticity	13.7×10^6 psi	—
Hardness	87–98 B	100 B

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