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# Celebrating more than 50 years of scientific excellence high temperatures-high pressures thermophysical properties: fundamentals and applications



Co-Editors-in-Chief Iván Egry Jean-François Sacadura

Special Supplemental Issue High Temperature Thermophysical Properties of 22 Pure Metals

> Guest Editor Gernot Pottlacher



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## Editorial

Only a few groups worldwide are engaged in measuring high temperature thermophysical properties of metals; G. Pottlacher's group at the University of Graz is one of them. His group has studied high temperature properties of metals for about 30 years, and its results are summarised in this compilation. The method applied throughout is fast pulse heating, also known as the exploding wire technique. In addition to delivering data in the solid phase, this method provides also access to the liquid phase, thanks to fast data acquisition. It is possible to measure thermal expansion, enthalpy, heat capacity and electrical resistivity of the solid and liquid metal as a function of temperature until the molten wire collapses. This technique is suitable for metals with high melting points and, consequently, the metals investigated are mainly transition, noble and rare-earth metals.

The compilation contains a short introduction, explaining how the data were obtained, and one section for each metal considered. Each section starts with a basic survey, including the metal's history, its common uses, its relevance in daily life, safety and health aspects. The second part is devoted to the measured data. These are presented in graphical form with indicative error bars. In addition, recommended values are provided as polynomial fits. From the data, additional thermophysical properties like thermal conductivity and thermal diffusivity can be derived. It is the strength of this collection that it contains only data measured by the author's group, thus allowing cross-comparisons between the elements without having to worry about potential systematic differences. A comprehensive bibliography, quoting the original publications from which the data were extracted, is also given.

This compilation was first published as a book by Edition Keiper (Austria) in 2010, but can still be regarded as up-to-date. The editors and publishers of *High-Temperatures – High Pressures* are proud to present this work now as a supplement to the journal. They grant open access to this invaluable source of thermophysical property data, making it accessible to a wide readership.

Iván Egry

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Special Supplemental Issue of High Temperatures-High Pressures

# High Temperature Thermophysical Properties of 22 Pure Metals

GUEST EDITOR Gernot Pottlacher

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## 1 Preface

Basic research is always closely connected with experiments. Of course this applies particularly to experimental physics. In this context data collection can be seen as the final output of measurements. But basic research is also done in theoretical and computational physics. Today simulations can already be called 'measurements'. In this context data collection serves as input parameter. Generally, results in the form of data collection are the link between all different fields of science.

In the field of high temperature thermophysics only a few experimental methods deliver data from more than 1000 degrees above the melting point. As in fast pulse-heating, the high temperature region is the focus of interest we consider that the results are worth being published as a compilation. The large temperature range makes this compilation the hottest collection in the world.

Under the supervision of Prof. Pottlacher, the workgroup of subsecond thermophysics at the TU Graz has been working on investigations of metals for more than 20 years. The key features of the measurements have not changed during this time. Hence, the results are obtained under quite homogeneous conditions, which is a valuable point concerning comparison and argumentation. We tried to keep this uniformity in the presentation of the data by selecting only standard quantities to be displayed: volume expansion, specific enthalpy, and electrical resistivity as a function of temperature. Additional information and properties can be found in the original publications which are thoroughly cited.

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#### References

## 2 Introduction

#### 2.1 Fast pulse-heating

Investigations were performed on wire-shaped specimens. The heating was achieved by discharging a capacitor bank  $(500 \,\mu\text{F})$  over the sample. With charging voltages up to  $10 \,\text{kV}$ , the resulting high heating rate  $(10^8 \,\text{K/s})$  led to a rapid increase of the temperature (ohmic heating) of the sample. Heating continued until the end of the liquid phase where, at the transition to the gas phase, the so-called wire explosion took place. The short experimental duration prevented mechanical (and gravitational) disturbances and chemical reactions. Contact-free temperature measurement was performed by means of pyrometry. The ambient atmosphere was usually nitrogen [1].

Some details about data acquisition: The samples were purchased in the highest purity available at the time<sup>1</sup>. Results were average values of several independent measurements. These mean values were fitted either with polynomials of the lowest order possible or according to the theoretical background (e. g. a linear behaviour is expected in the liquid phase).

Temperature was measured contactless with pyrometers operating at 650 nm, 1570 nm or 900 nm. The stated temperatures are 'true temperature' (not radiance temperature). Via ratios of the measured radiance intensity at melting,  $J(T_m)$ , and the measured radiance intensity at temperature T, J(T), one obtains the unknown temperature T using the melting temperature of the investigated material as calibration point:

$$T = \frac{c_2}{\lambda \cdot \ln\left(1 + \frac{J(T_m) \cdot \epsilon(\lambda, T)}{J(T) \cdot \epsilon(\lambda, T_m)} \cdot \left[\exp\left(\frac{c_2}{\lambda \cdot T_m}\right) - 1\right]\right)}$$
(1)

Herin  $c_2$  is the second radiation constant ( $c_2=1.4388 \text{ mK}$ ),  $\lambda$  is the wavelength,  $\epsilon(\lambda, T)$  is the emissivity of the liquid sample, and  $\epsilon(\lambda, T_m)$  is the emissivity at the melting temperature. When applicable we included our measurements on emissivity at 684.5 nm in the calculation of temperature. It is recommended to refer to the respective cited original publications about the details of temperature measurement. To learn more about the influence of emissivity see [3]. The uncertainty bars belong to single data points on the fits and were not converted into an uncertainty of polynomial-parameters. Therefore they are just displayed graphically.

#### 2.2 Use of this compilation

The pulse-heating results were combined with the Bachelor thesis of Gerald Reif (introduction, history, common uses, relevance in life)[4]. This is in conformity with the academic requirement to start any investigation with a basic survey (Part A:) before passing over to special knowledge. On the one hand, the style of this basic survey was adapted to the easy-going

<sup>&</sup>lt;sup>1</sup>About the influence of supplier and purity see [2].

approaches which are commonly considered nowadays. Hence, we did not exclude internet references like Wikipedia. No responsibility is taken for the accuracy of this information.

On the other hand, our pulse-heating results are pure measurement results performed at our laboratory (Part B:).

Volume expansion as a function of temperature can be converted into density as a function of temperature by dividing density at 20°C by volume expansion.

Specific enthalpy is calculated via equation 2, given in kJ/kg.

$$H(t) - H(293) = \frac{1}{m} \cdot \int I(t) \cdot U(t) \cdot dt$$
(2)

Herein m represents the mass of the sample obtained from geometry and density at room temperature. I is the current. U is the voltage drop.

Enthalpy can be expressed in kJ/mol by multiplying kJ/kg with atomic weight. The enthalpy increase at the melting transition (heat of fusion) was calculated from the polynomials for solid and liquid phase at the melting point  $T_m$ . Specific heat capacity  $c_P$  is the first derivative of the enthalpy polynomials with respect to temperature.

Electrical resistivity was calculated by multiplying resistivity at initial geometry  $\rho_{IG}$  (see equation 3) with volume expansion.

$$\rho_{IG}(T) = \frac{U(T) \cdot \pi \cdot r^2}{I(T) \cdot l} \tag{3}$$

Herein r is the radius of the sample at room temperature, l is the length of the sample.

The resistivity increase at the melting transition was calculated from the polynomials for solid and liquid phase at  $T_{\rm m}$ . Thermal conductivity  $\lambda$ can be calculated from resistivity  $\rho$  using the Wiedemann-Franz law:

$$\lambda = \frac{\mathbf{L} \cdot T}{\rho} \tag{4}$$

with  $L = 2.45 \times 10^{-8} V^2 / K^2$  [5].

Thermal diffusivity a can be calculated by:

$$a = \frac{\lambda}{c_{\rm P} \cdot {\rm d}(T)} = \frac{{\rm L} \cdot T}{c_{\rm P} \cdot \rho_{\rm IG} \cdot d_0} \tag{5}$$

with  $d_0 =$ density at room temperature.

#### 2.3 Abbreviations

at.wt.: atomic weight

- $c_P$ : specific heat capacity at constant pressure
- $C_P$ : molar specific heat capacity at constant pressure
- *H*: specific enthalpy
- $H_{\rm s}$ : enthalpy at  $T_m$  solid phase
- $H_1$ : enthalpy at  $T_m$  liquid phase
- $\Delta H$ : heat of fusion (increase of enthalpy at solid-liquid phase transition)
- $\rho$ : electrical resistivity
- $\rho_{\text{IG}}$ : electrical resistivity with initial geometry
- $\rho_{\rm s}$ : resistivity at  $T_m$  solid phase
- $\rho_{l}$ : resistivity at  $T_{m}$  liquid phase
- $\Delta \rho$ : increase of resistivity at solid-liquid phase transition
- T: temperature in Kelvin
- $T_m$ : melting temperature
- u: unit 1, 'dimensionless' quantity
- $V/V_0$ : volume expansion
- rec.: recommended

#### 2.4 Cited authors at the TU Graz

Michael Beutl Christian Brunner Claus Cagran Ralph Gallob Thomas Hüpf Helmut Jäger Erhard Kaschnitz Wolfgang Neff Theo Neger Gerald Nussbaumer Christian Otter Gernot Pottlacher Gerald Reif Achim Seifter Boris Wilthan Laurentius Windholz

# 3 Elements

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## A: Basic survey

#### The Element

Symbol:	Co
Atomic number:	27
Group:	Transition metal
Atomic weight: [6]	58.933195(5) u
Ground state electron configuration:	$[Ar]3d^74s^2$
Crystal structure at $25^{\circ}$ C: [7]	hcp with $a = 2.5071$ Å
	and $c = 4.0695 \text{ Å}$
Allotropy: [8]	$\alpha$ -Co: hcp; $\beta$ -Co: fcc
	Transition $\alpha \rightarrow \beta$ at 417°C
<b>Density at</b> $20^{\circ}$ C: [6]	$8.9 \text{ g} \cdot \text{cm}^{-3}$
Melting point: [6]	1768 K
Boiling point: [6]	3200 K
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.421 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$24.81 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Curie temperature:	$1115^{\circ}\mathrm{C}$
Isotope range: [9]	50-72 (stable: 59)

#### Introduction

Cobalt (Co) is a bluish steel-gray metal that can be polished to a bright shine. It is brittle and only malleable when alloyed with other metals. It is magnetic, and when alloyed with aluminum and nickel ('alnico' metal) it acts as a super-magnet with many uses in industry. Chemically and physically, cobalt acts much like its two neighbours in the 4th period on the periodic table, iron (Fe) and nickel (Ni). Particularly, iron, cobalt, and nickel are unique in that they possess natural magnetic properties. [10]

#### History

Since ancient times in Egypt and the Middle East, people have known of a mineral that could be used to make a highly prized deep blue glass, but were unaware that this material contained the element cobalt. Alchemists in the 16th century identified a mineral they named 'zaffer' which was used to produce blue pigments and blue glass. They believed, mistakenly, that it contained the element bismuth. Furthermore, German miners and the early smelters of this period also wrongly believed that cobalt ores were really copper ores. They attributed their difficulties with the extraction of copper from this particular ore to mountain gnomes (*Kobolde*, meaning 'goblins' in German). They believed these gnomes had bewitched the ore to prevent them from procuring copper.

Georg Brandt (1694-1768) of Sweden in 1739 investigated a bluish mineral he wanted to winnow from the element bismuth, being mined in the same regions where cobalt minerals were found. Cobalt was the first metal to be discovered which was not yet known to ancient alchemists. Brandt is credited with the discovery of the element cobalt, albeit it was a known mineral for many centuries. He isolated the new element, and its name, originating from *Kobold* goblins, has been used ever since. [10] Brandt, Georg (1694-1768)

## Common Uses

About 65% of the total consumption of cobalt accounts for alloys and powder metallurgical (P/M) products:

- High-temperature alloys (650 to 1150°C), such as *Haynes*<sup>®</sup> 188 (39Co-22Ni-22Cr-14W-3Fe-1.25Mn-0.35Si-0.1C-0.03La) and the alloy *MAR M509* (Co -22.5Cr -10Ni -7W -3.5Ta -1.5Fe -1Mo -0.6C 0.4Si -0.1Mn), are well established in the gas turbine industry, the latter is also applied in combustor cans and afterburner liners in high-performance aircraft gas turbines. [11] [12]
- Wear-resistant alloys: The very hard and customized alloy *Stellite®* 100 (Co-34Cr-19W-2C) was designed for metal-cutting purposes, but also applied in tool bits and milling cutter blades. *Stellite®* 12 (Co-29Cr-8.3W-3Ni-3Fe-2Si-1.8C-1Mo-1Mn) is used for hardfacing applications such as facing the cutting edges of knives utilized in the carpet, plastics and paper industries. [11]
- **Permanent magnets**: Nickel-iron-aluminum-cobalt (*Alnico*, 20-25% Co) alloys are very brittle but possesses a high coercive force. Whereas iron-cobalt alloys (30-50% Co) are **soft magnetic**, in which cobalt increases the Curie temperature and the saturation magnetization of iron [13] [14].
- In tool steels, i.e. P/M high-speed tool steels, cobalt increases the solidus temperature and enhances hot hardness and temper resistance. Alloys like *CPM Rex 76* (Fe 1.5C 3.75Cr 10W 5.25Mo 3.1V 9Co 0.06S) and *HAP 70* (Fe 2C 4Cr 12W 10Mo 4.5V 12Co) are two examples, offering exceptional hot hardness and wear resistance. Cobalt thereby increases the solubility of carbon in austenite ( $\gamma$ -Fe). [15]
- Cemented carbides, in which cobalt is a binding metal. Applied as 97WC-3Co, 90WC-10Co or 71WC-12.5TiC-12TaC-4.5Co, they find application in mining, oil and gas drilling as well as in metal cutting and machining. [12]

Other important end products include:

- The dental alloy *Vitallium*<sup>TM</sup>(64% Co, 30% Cr and 5% Mo) is used for cast denture base and bridgework because of its light weight and resistance to corrosion. Its high temperature resistance also makes it a suitable material for components of turbochargers. [9]
- The addition of cobalt oxide to a glass melt and to enamel yields a blue pigmentation. Glass with 0.5% Co is very suitable for welders' goggles; and the same glass but with a few milligramms of Co per kilogramme is used for camera lenses. [9]
- Black cobalt oxide Co<sub>3</sub>O<sub>4</sub> is used as a coating on high-temperature solar collectors for this specific purpose, it is even superior to black chromium coatings. [9]
- Moisture Detectors: Cobalt chloride mixed with silica gel displays the characteristic blue color of anhydrous chloride CoCl<sub>2</sub>. When this gel absorbes moisture, pink (almost invisible) cobalt chloride hexahydrate CoCl<sub>2</sub>·6H<sub>2</sub>O is formed. [9]
- Co-60 is used as an agent against cancer in radiotherapy ('cobalt therapy'). [9]
- The element cobalt is inclined to form complexes and to draw different ligands to these complexes. This makes the metal suitable as a catalyst. Cobalt can change between the oxidation states +2 and +3. The element is an efficient catalyst for oxidation reactions. The element is in fact an additive to virtually all catalysts for oxidation reactions in organic chemistry. [16]
- Usage in salt licks in the form of cobalt-sulfates in agriculture, as well as other compounds are used in agricultural industries. [16]

## Relevance in Life

Occupational cobalt poisoning is basically caused by the inhalation of dust. Long-term exposure to cobalt powder may produce allergic sensibilization and chronic bronchitis. Metallic cobalt and its oxide as well as its sulfide have not been classified as carcinogenic even though some experiments with animals indicate that.

Cobalt is an essential element for life on earth, and important for humans and animals. It is present mainly in the form of vitamin  $B_{12}$ . Careful application in the form of the chloride, sulfate, acetate, or nitrate has been found effective in correcting a certain mineral deficiency disease in animals. [9] [17]

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 1: Volume expansion results of cobalt, polynomials taken from [2]. Density at  $20 \,^{\circ}\text{C}$ : 8900 kg·m<sup>-3</sup> [18].

	$T_m = 1768 \mathrm{K} [19]$	
solid	$V/V_0(T) = 0.967 + 4.835 \times 10^{-5} \cdot T$	
	$+4.105 \times 10^{-9} \cdot T^2$	$1450{\rm K} < T < 1768{\rm K}$
liquid	$V/V_0(T) = 0.918 + 9.269 \times 10^{-5} \cdot T$	$1768{\rm K} < T < 2200{\rm K}$



Figure 1: Volume expansion of cobalt.

## Enthalpy

Table 2:	Specific enthalpy	results of coba	$\operatorname{lt}, H \operatorname{in} \mathrm{kJ} \cdot \mathrm{kj}$	$g^{-1}$ , polynomials to	$\operatorname{aken}$
from $[2]$					

	$T_m = 1768 \mathrm{K}  [19],  at.wt. = 58.933  [18]$	
solid	$H(T) = -337.1 + 0.714 \cdot T$	$1450{ m K} < T < 1768{ m K}$
	$c_p = 714 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 42.078  \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
liquid	$H(T) = -212.5 + 0.793 \cdot T$	$1768{ m K} < T < 2200{ m K}$
	$c_p = 793  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 46.734  \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 924.6, H_{\rm l} = 1189.3$	
	$\Delta H = 264.7$	



Figure 2: Specific enthalpy of cobalt as a function of temperature.

## Resistivity

 [-].		
	$T_m = 1768 \mathrm{K}  [19]$	
solid	$\rho_{\rm IG}(T) = 0.484 + 2.703 \times 10^{-4} \cdot T$	$1450{\rm K} < T < 1768{\rm K}$
	$\rho(T) = 0.420 + 3.420 \times 10^{-4} \cdot T$	
liquid	$\rho_{\rm IG}(T) = 0.961 + 6.593 \times 10^{-5} \cdot T$	$1768{\rm K} < T < 2200{\rm K}$
	$\rho(T) = 0.858 + 1.738 \times 10^{-4} \cdot T$	
	$\rho_{\rm IG,s} = 0.962,  \rho_{\rm IG,l} = 1.078$	
	$\Delta \rho_{\rm IG,s-l} = 0.116$	
	$ \rho_{\rm s} = 1.025,  \rho_{\rm l} = 1.166 $	
	$\Delta \rho_{ m s-l} = 0.141$	

Table 3: Electrical resistivity results of cobalt,  $\rho$  in  $\mu\Omega$ ·m, polynomials taken from [2].



Figure 3: Electrical resistivity of cobalt as a function of temperature. Dashed line: values including volume expansion.

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## A: Basic survey

#### The Element

Symbol:	Cu
Atomic number:	29
Group:	Transition metal
Atomic weight: [6]	63.546(3) u
Ground state electron configuration:	$[Ar]3d^{10}4s^{1}$
Crystal structure at $25^{\circ}$ C: [7]	fcc with $a = 3.6149$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$8.96 \mathrm{g\cdot cm^{-3}}$
Melting point: [6]	$1084.62^{\circ}C$
Boiling point: [6]	$2562^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.385 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$24.440 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	57-79 (stable: $63, 65$ )

#### Introduction

Copper (Cu) is an easy to find and versatile metal of unmistakable reddishto-brown color. It is malleable, ductile, and easily formed to a variety of shapes, from ingots over wire to powder, as coins, sheets, or rods, to mention a few. It is resistant to weak acids, but will dissolve in strong or hot acids. To atmospheric corrosion copper resists better than iron does. When exposed to moist air or sea water, it forms a bluish-green film ('patina') over its surface. This coating of copper carbonate and copper sulfate provides a protective layer for the underlying metal. One of copper's most useful characteristics is that it is an excellent conductor of electricity and heat. [10]

## History

The name and symbol for copper come from the Latin *cuprum* (former *cyprium*), referring to the island of Cyprus, where copper was found in the ancient world. This island was sacred to Aphrodite (Roman: Venus), Greek goddess of love, sex, and beauty. At that time copper was used to manufacture mirrors, so the metal was associated with the goddess in mythology and alchemy, marked by the  $\mathfrak{P}$  symbol. [20]

Since prehistoric times native copper has been used as adornment, e.g copper pendants found in the Middle East dating back to 9000 BCE. As the extraction of the copper ore was simple and the further precipitation was relatively easy, it was one of the reasons that copper became one of the earliest metals known to have been mined and refined. Later on, humans learned to smelt copper from high-grade ores, as well as to harden pure copper by mixing it with other substances for use in weapons and tools.

By mixing it with arsenic and later with tin ores, they gained an alloy that was more suitable for tools, namely bronze (about 3000 BCE, Middle East). In about 500 BCE, copper was mixed with 5 wt% to 45 wt% zinc (Zn), so a new alloy - known as brass - was invented.

Nowadays, copper alloys such as copper-aluminum and copper-nickel are utilized. [10] [21]

#### Common Uses

The properties of copper make it the third most used industrial metal after iron and aluminum in terms of quantity. Its formability makes copper a suitable metal for the production of a wide range of components (e.g. foils and wires of 0.02 mm thickness), but on the other hand, its softness limits its suitability for certain applications. In alloys like bronze and brass, solidity is increased significantly.

- Copper Metal: The main usage of copper is for electrical and electronic products ( $\approx 75\%$ ). There is a wide spectrum of applications, from roofing to decorative elements in architecture to tubes and pipes for air conditioning and refrigeration, fire sprinklers and solar energy systems. [22]
- Copper is second only to silver as an excellent conductor of electricity and heat (electrical resistivity at 293 K: Ag:  $\rho = 1.587 \cdot 10^{-8} \Omega m$ , Cu:  $\rho = 1.678 \cdot 10^{-8} \Omega m$  [6], thermal conductivity at 300 K: Ag:  $k = 4.28 \text{ W cm}^{-1} \text{ K}^{-1}$ , Cu:  $k = 3.98 \text{ W cm}^{-1} \text{ K}^{-1}$ [6]).
- Copper-nickel-alloys are widely used for marine appliances due to their excellent resistance to seawater corrosion and high inherent resistance to biofouling. Further usages include coinage alloy and cladding material (CuNi25), thermocouples and heating elements (CuNi44) or electrical resistors and heating wires or cables (CuNi23Mn). In the automotive industry, hydraulic brake tubes made of copper-nickel-alloys were found to be superior to commonly used low-carbon steel. [22].
- Brass (copper-zinc-alloy) is the most used copper alloy. There are two forms of this alloy,  $\alpha$  and  $\alpha/\beta$ -brass.  $\alpha$ -brass consists of up to 38 wt% of zinc ( $\alpha$ -phase), whereas the most common brass has a zinc concentration of 37 wt%.

By increasing the zinc content above 38 wt%, a new structural component called  $\beta$ -phase is formed. Between 38 wt% and 45 wt% of zinc content, the structure consists of a mixture of *alpha*- and  $\beta$ -phases, and therefore is called  $\alpha/\beta$ -brass. Its advantage is enhanced strength, but corrosion resistance is reduced in it.

- Nickel-Brass (copper-zinc-nickel-alloy) is a composite of 64 wt% Cu, 24 wt% Zn and 12 wt% Ni. Its features are high strength and good corrosion resistance and can be used as a material for mechanical springs, e.g. contact springs. It looks like silver and therefore is often used as an alternative for silver. By applying a final silver plating on the formed component, it is known as argentan, electroplated nickel silver (EPNS) or German silver.
- Bronze (copper-tin-alloy), its prototype is tin bronze, an alloy with 90 wt% Cu and 10 wt% Sn. By blending it with aluminum, beryllium, nickel or iron, special bronzes for a diversified range of applications are obtained. It is used for durable tools because it does not generate sparks when struck against a hard surface.[9][22]
  - Tin bronze is used for pump housings, impellers, slide bearings, springs, blades, turbines, hammers and many more, customized by adding different quantities of lead and zinc.
  - Aluminum bronze possesses high strength similar to steel and has good wear resistance
  - Nickel-aluminum bronze has very good corrosion resistance, especially in marine environments
  - Phosphor bronze is used for guitar and piano strings and especially for precision-grade bearings and springs.

## Relevance in Life

Copper as dust or powder, as well as some of its compounds, is flammable or even explosive when ignited. Many of copper's compounds are extremely toxic, poisoning occurs through skin contact or when inhaled or ingested. On the other hand, plants as well as animals and humans require traces of copper in order to properly metabolize their food.

Copper is a component in many metalloenzymes and other proteins, therefore as a trace element, it is essential for life. Several copper-containing enzymes catalyze redox reactions.

Copper deficiency is not unusual in grazing animals, especially sheep, and is treated by dietary supplements. In pigs, copper has been observed to have a strong growth-promoting effect.

Toxication occurs at high concentrations of copper. The higher evolved an organism, the bigger is its uptake regulation ability. A special protein called 'metallothionein' is synthesized in the liver, protecting the organism against harm from intake of sulfide-forming metals (e.g. cadmium, copper, lead and mercury).[9]

Copper compounds (e.g. copper sulphate) have a wide spectrum of applications, like protection against fabric decay, as preventative of algae development in potable water reservoirs or as molluscicide for the control of slugs and snails. [22]

# B: Thermophysical properties obtained by Pulse - heating

#### Volume expansion

Table 4: Volume expansion results of copper, polynomials taken from [23], [24], [25]. Density at 20 °C: 8960 kg·m<sup>-3</sup> [18].

	$T_m = 1356 \mathrm{K} [23]$	
	rec. $T_m = 1357.77 \mathrm{K} [26]$	
solid	$V/V_0(T) = 0.9907 + 3.2232 \times 10^{-5} \cdot T$	
	$-4.5658 \times 10^{-9} \cdot T^2 + 5.2713 \times 10^{-12} \cdot T^3$	$300{\rm K} < T < 1356{\rm K}$
liquid	$V/V_0(T) = 1.0085 + 6.3923 \times 10^{-5} \cdot T$	$1356{\rm K} < T < 1900{\rm K}$



Figure 4: Volume expansion of copper.

## Enthalpy

taken nom [20].					
	$T_m = 1356 \mathrm{K} [23],  at.wt. = 63.546 [18]$				
	rec. $T_m = 1357.77 \mathrm{K} [26]$				
solid	$H(T) = -207.894 + 0.4809 \cdot T$	$1100{\rm K} < T < 1356{\rm K}$			
	$c_p = 480.9 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$				
	$C_p = 30.559  \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$				
liquid	$H(T) = -45.463 + 0.53145 \cdot T$	$1356{\rm K} < T < 2200{\rm K}$			
	$c_p = 531.5 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$				
	$C_p = 33.775 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$				
	$H_{\rm s} = 444,  H_{\rm l} = 675,  \Delta H = 231$				

Table 5: Specific enthalpy results of copper, H in kJ·kg<sup>-1</sup>, polynomials taken from [23].



Figure 5: Specific enthalpy of copper as a function of temperature.

## Resistivity

Table 6:	Electrical	resistivity	results	of	copper,	ρ	in	$\mu \Omega \cdot m$ ,	polynor	$\mathbf{nials}$
taken from	m [23].									

	$T_m = 1356 \mathrm{K} [23]$	
	rec. $T_m = 1357.77 \mathrm{K}  [26]$	
solid	$\rho_{\rm IG}(T) = -0.0214 + 9.1542 \times 10^{-5} \cdot T$	$1100{\rm K} < T < 1356{\rm K}$
	$\rho(T) = -0.02861 + 9.98873 \times 10^{-5} \cdot T$	
liquid	$\rho_{\rm IG}(T) = 0.1092 + 6.5009 \times 10^{-5} \cdot T$	$1356{\rm K} < T < 1900{\rm K}$
	$\rho(T) = 0.11031 + 7.83066 \times 10^{-5} \cdot T$	
	$\rho_{\rm IG,s} = 0.103, \ \rho_{\rm IG,l} = 0.197$	
	$\Delta \rho_{\rm IG,s-l} = 0.095$	
	$\rho_{\rm s} = 0.107, \ \rho_{\rm l} = 0.216, \ \Delta \rho_{\rm s-l} = 0.109$	



Figure 6: Electrical resistivity of copper as a function of temperature. Dashed line: values including volume expansion.

3.3 Gold

## A: Basic survey

#### The Element

Symbol:	Au
Atomic number:	79
Group:	Transition metal
Atomic weight: [6]	196.966569(4) u
Ground state electron configuration:	$[Xe]4f^{14}5d^{10}6s^{1}$
Crystal structure at $25^{\circ}$ C: [7]	Cubic fcc with $a = 4.0782$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$19.30 \mathrm{g\cdot cm^{-3}}$
Melting point: [6]	$1064.18^{\circ}\mathrm{C}$
Boiling point: [6]	$2856^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.129 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.418 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	172-205 (stable: 197)

#### Introduction

Gold is a soft and shiny metal with a yellow color. It is dense, malleable and ductile. The name is derived from the Anglo-Saxon word *geolo* meaning 'yellow', the symbol is from the Latin word *aurum*, which means 'shining dawn'. Correspondingly, also based on its shine and value, it was construed as the element referring to the sun  $\mathbf{O}$  by alchemists and in mythology - *Aurora*, the Roman goddess of the light of dawn.

Gold is chemically inert, but will react with chlorine and cyanide solutions and can be dissolved in aqua regia. Apart from its outward appearance, gold is a good electrical conductor as well as a formidable heat reflector for infrared radiation, and used as reflection coating on glass in construction. The purity of gold is measured in *carats* (one carat is equal to one part in twenty-four). [9] [10]

#### History

Gold is considered to be one of the first metals used by humans, found as pebble-like nuggets of metal, which they admired for its color. Egyptian hieroglyphs from around 2600 BCE mention gold, the Sumerian civilization forged it into ornaments and it appears several times in the Old Testament of the Christian Bible.

Since about 2700 BCE, formed gold rings, squares, later coins have been circulating for payment purposes. From Macedonia, amply supplied with gold in its area, Philip II, and later on his son Alexander the Great, the

coin gold stater became universal currency. Later, the expanding Roman Empire spread the usage of gold as money - along with silver and copper. Subsequently new sources of gold were found - gold remained the object for money, decoration and jewelry up to the present time, where banknotes, paper money and other means of payment are still guaranteed by their equivalent in gold. [9] [10]

#### Common Uses

In almost all applications gold is used alloyed with other components, being harder and providing better abrasion resistance.

• In jewelry, gold is commonly alloyed with other metals in order to increase strength and a variety of pigments. An alloy of gold, silver, and copper is called *green gold* when the amounts of silver predominates and *red gold* in case of a copper dominance. The alloy of gold and nickel is called *white gold*.

Gold-palladium alloys offer very good formability and are preferred by jewelers, as well as by persons suffering from allergies. [11]

- Gold alloys are used for unique braze and solder applications, e.g.  $BM~2050^{\textcircled{C}}$  (Au50Pd25Ni25) for stainless and superalloys,  $BM~1860^{\textcircled{C}}$  (Au37.5Cu62.5) for copper, nickel, Kovar, and Mo-Mn metallized ceramics [27]
- In photography, gold is used to shift the color of silver bromide black and white prints towards brown or blue tones, as well as to increase their stability.
- Gold's ability to reflect electromagnetic radiation, such as infrared and visible light as well as radio waves, is used for protective coatings, e.g. on artificial satellites.
- In dentistry, gold alloys (e.g. Apollo 4CF<sup>©</sup>, Au 68 Ag 21.4 Pd 6 Pt 1 Zn 3.4) are used in tooth restorations, such as crowns and permanent bridges. Furthermore, porcelain is veneered with gold alloys (e.g. Cera F<sup>©</sup>, Au 58 Ag 27.3 Pd 7 Pt 3 Zn 2.3 In 0.2) [28]
- Gold is edible in small quantities, and can therefore be used to decorate food (E 175)
- In aerospace applications, thin gold films (as coating) are used as lubrication in high-temperature, high vacuum and radiation environments, because gold is chemically inert, has a considerably high melting point offering long-term stability without evaporation. In electronics, thin layers of gold (0.05 to 0.25  $\mu$ m) as top layers are used in spring socket contacts. [29]

- In alkaline electrolytes, gold is an effective oxygen reduction catalyst and is also capable of catalysing the direct oxidation of sodium borohydride with high utilisation in proton-exchange membrane (PEM) fuel cells - carbon supported Pd80Au20 alloys are used. [30]
- On some high-end compact discs gold is used as the reflective layer.
- Gold chloride and gold oxide are used to make high-valued cranberry or red pigment (ruby glass). [31]

#### Relevance in Life

Gold is the most frequent sensitizer in the common population (15%), significantly more frequent in patients with gold in dental restorations. Inflammatory arthritides can be treated with Au salts, especially sodium aurothiomalate. Other salts have been used for therapeutic purposes against tuberculosis and rheumatoid arthritis when applied in correct concentrations (greater quantities are toxic). [17] [9]

# B: Thermophysical properties obtained by Pulse - heating

#### Volume expansion

Table 7: Volume expansion results of gold, polynomials taken from [32]. Density at 20 °C: 19300 kg·m<sup>-3</sup> [18].

	$T_m = 1337 \mathrm{K} [26]$	
liquid	$V/V_0(T) = 1.0265 + 6.1608 \times 10^{-5} \cdot T$	
	$+1.1306 \times 10^{-8} \cdot T^2$	$1337{\rm K} < T < 4300{\rm K}$



Figure 7: Volume expansion of gold.

## Enthalpy

om [32].	r,	0 /1 /
	$T_m = 1337 \mathrm{K} [26]$	
	at.wt. = 196.9665 [18]	
liquid	$H(T) = 0.157 \cdot T$	$1337{\rm K} < T < 4300{\rm K}$
	$c_p = 157 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 30.924 \mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$	
	$H_{\rm s} = 148, H_{\rm l} = 210, \Delta H = 62$	

Table 8: Specific enthalpy results of gold, H in kJ·kg<sup>-1</sup>, polynomials taken from [32].

	700 F	
	600 -	
kg_1	ŀ	
/ kJ	500 -	
lalpy	ł	
Specific Enthalpy / kJ kg <sup>-1</sup>	400 -	
cific	-	
Spe	300 -	
	-	
	200	
		1500         2000         2500         3000         3500         4000         4500
		Temperature / K

Figure 8: Specific enthalpy of gold as a function of temperature.

## Resistivity

Table 9: Electrical resistivity results of gold,  $\rho$  in  $\mu\Omega{\cdot}m,$  polynomials taken from [32].

	$T_m = 1337 \mathrm{K} [26]$	
liquid	$\rho_{\rm IG}(T) = 0.1216 + 1.3044 \times 10^{-4} \cdot T$	$1337{ m K} < T < 4300{ m K}$
	$\rho(T) = 0.1473 + 1.1270 \times 10^{-4} \cdot T$	
	$+2.09539 \times 10^{-8} \cdot T^2$	
	$ ho_{ m IG,l} = 0.30$	
	$ \rho_{\rm l} = 0.33 $	



Figure 9: Electrical resistivity of gold as a function of temperature. Dashed line: values including volume expansion.

## A: Basic survey

#### The Element

Symbol:	Hf
Atomic number:	72
Group:	Transition metal
Atomic weight: [6]	178.49(2) u
Ground state electron configuration:	$[Xe]4f^{14}5d^26s^2$
Crystal structure at $25^{\circ}$ C: [7]	hcp with $a = 3.1964$ Å
	and $c = 5.0511$ Å
Allotropy: [8]	$\alpha$ -Hf: hcp; $\beta$ -Hf: bcc
	Transition $\alpha \rightarrow \beta$ at 1742°C
<b>Density at</b> $20^{\circ}$ C: [6]	$13.31 \text{ g} \cdot \text{cm}^{-3}$
Melting point: [6]	$2233^{\circ}\mathrm{C}$
Boiling point: [6]	$4603^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.144 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.73 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	154-185 (stable: 176-180)

#### Introduction

Hafnium is a ductile metal with the look and feel of stainless steel, but which is significantly heavier. Freshly exposed to air it shines like silver, but reacts immediately by forming a protective oxide coating. The chemical and physical properties are very similar to that of the element zirconium, resulting in the almost impossible task of gaining pure samples of one of these elements - they are always doted by the other in small quantities. [10] In aqueous solutions, hafnium is soluble in HF and concentrated  $H_2SO_4$ , as well as in aqua regia, while resistant to HCl and  $H_2SO_4$  and is unaffected by HNO<sub>3</sub> in all concentrations and by alkalies.[8]

#### History

Henry Moseley's research in 1914 using X-ray spectroscopy confirmed the systematic design of the periodic table, determined the number of lanthanoids and disclosed gaps at atomic number 43, 61, 72, and 75.

Nils Bohr was able to predict the properties of all chemical elements as being similar to zirconium - according to his atomic theory. His prediction disagreed with the pronouncement of experimentalists in England and France that element 72 belonged to the group of rare earths. Finally in 1923, element 72 was discovered by the Dutch spectroscopist Dirk Coster (1889-1950) and the Hungarian physical chemist George Charles von Hevesy (1885-1966) at Niels Bohr's laboratory in Copenhagen in zircon through X-ray spectroscope analysis. They named the element after the town - Copenhagen, *Hafnia* in Latin. [33]

Coster, Dirk (1889-1950) Bohr, Nils (1885-1962) von Hevesy, George Charles (1885-1966) Moseley, Henry (1887-1913)

## Common Uses

The major use of hafnium is as an alloying additive to nickel-based superalloys (1-2 wt%), in thermal barrier and diffusion coatings because hafnium is the only option for geting the required grain boundary refinement ([34]). These alloys and coatings are used in turbine vanes in the combustion zone of jet aircraft engines as well as in industrial gas turbines. Adding hafnium to some alloys increases the allowable operating temperature by 50°C. [13] [35]

Another eminent use of hafnium is in nuclear reactors as a control-rod material. Early reactors were equipped with long crosswise formed control rods made of bare hafnium metal. A high thermal neutron absorption cross section (113 barn [12]) was accompanied by excellent hot water corrosion resistance, grindability and good ductility. Nowadays, stainless steel-clad silver-indium-cadmium and boron carbide, respectively, is replaced by stainless steel clad hafnium. [13]

Other usages for hafnium are: [34]

- Pure Hafnium is used as the active tip for plasma arc cutting tools.
- $\bullet$  Hafnium oxide (HfO<sub>2</sub>), resistant to heat and corrosion, is used as lining for refractory furnaces.
- Hafnium oxide-based compounds are practical high-k dielectrics, resulting in a reduction of the gate leakage current in field effect transistors and accordingly improve their performance.[36]
- It is used in gas-filled and incandescent lamps.
- As an efficient getter material for scavenging oxygen and nitrogen.
- Hafnium dioxide is a high-refractive-index, low light absorption material suited to use as a hard, scratch-free coating for optical devices, such as the metal mirrors used in the near-ultraviolet-to-infrared part of the spectrum. [34]

## Relevance in Life

Hafnium itself is not harmful, however its powder and dust are toxic if inhaled and even explosive in wet conditions. [9]

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 10: Volume expansion results of hafnium, polynomials taken from [1]. Density at  $20 \,^{\circ}$ C: 13310 kg·m<sup>-3</sup> [18].

	$T_m = 2471 \mathrm{K} [37]$	
solid	$V/V_0(T) = 0.996 + 1.288 \times 10^{-5} \cdot T$	
	$+2.766 \times 10^{-9} \cdot T^2$	$1500{\rm K} < T < 2471{\rm K}$
liquid	$V/V_0(T) = 0.972 + 3.623 \times 10^{-5} \cdot T$	$2471{\rm K} < T < 3500{\rm K}$



Figure 10: Volume expansion of hafnium.

## Enthalpy

oun	ch non	· [±]•	
		$T_m = 2471 \mathrm{K} [37]$	
		at.wt. = 178.49 [18]	
	solid	$H(T) = -142.0 + 0.234 \cdot T$	$2150{\rm K} < T < 2471{\rm K}$
		$c_p = 234 \mathrm{J\cdot kg^{-1}\cdot K^{-1}}$	
		$C_p = 41.766 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	liquid	$H(T) = -121.5 + 0.259 \cdot T$	$2471 < T < 3500  {\rm K}$
		$c_p = 259 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
		$C_p = 46.229  \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
		$H_{\rm s} = 436.2, \ H_{\rm l} = 518.5, \ \Delta H = 82.3$	

Table 11: Specific enthalpy results of hafnium, H in kJ·kg<sup>-1</sup>, polynomials taken from [1].



Figure 11: Specific enthalpy of hafnium as a function of temperature.

#### Resistivity

Table 12: Electrical resistivity results of hafnium,  $\rho$  in  $\mu\Omega{\cdot}m,$  polynomials taken from [1].

	$T_m = 2471 \mathrm{K} [37]$	
solid	$\rho_{\rm IG}(T) = 1.389 + 7.753 \times 10^{-5} \cdot T$	$2200{\rm K} < T < 2471{\rm K}$
	$\rho(T) = 1.352 + 1.212 \times 10^{-4} \cdot T$	
liquid	$\rho_{\rm IG}(T) = 1.642 - 3.142 \times 10^{-5} \cdot T$	$2471{\rm K} < T < 3500{\rm K}$
	$\rho(T) = 1.606 + 2.219 \times 10^{-5} \cdot T$	
	$\rho_{\rm IG,s} = 1.581,  \rho_{\rm IG,l} = 1.564$	
	$\Delta \rho_{\mathrm{IG,s-l}} = 0.017$	
	$\rho_{\rm s} = 1.651,  \rho_{\rm l} = 1.661,  \Delta \rho_{\rm s-l} = 0.01$	



Figure 12: Electrical resistivity of hafnium as a function of temperature. Dashed line: values including volume expansion.

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## A: Basic survey

#### The Element

Symbol:	In
Atomic number:	49
Group:	Metal
Atomic weight: [6]	114.818(3) u
Ground state electron configuration:	$[Kr]4d^{10}5s^{1}5p^{1}$
Crystal structure at $25^{\circ}$ C: [7]	tetragonal with $a = 3.2523$ Å
	and $c = 4.9461$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$7.31 \mathrm{g} \cdot \mathrm{cm}^{-3}$
Melting point: [6]	$156.60^{\circ}\mathrm{C}$
Boiling point: [6]	$2072^{\circ}C$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.233 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$26.74 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	100-134 (stable: 113, $115^2$ )

#### Introduction

Indium resembles aluminum and tin in appearance, being silvery-white with a brilliant luster. The metal is soft, even softer than lead, noncorrosive and does not oxidize at room temperature but at higher temperatures. Furthermore it is soluble in acids, but not in alkalis or hot water. It is available in ultrapure form and when bent, the pure metal makes a high-pitched noise. Like gallium, it wets glass. [9] [6] [10]

#### History

At Bergakademie Freiberg (Saxony, oldest Technical University in the world), in 1863, Ferdinand Reich (1799-1882) researched elements contained in some zinc ore, mined in the area, for comparison with other zinc ores. At that time spectroscopes were being used to identify elements by their unique color spectrum, but being color blind, his assistant Hieronymous Theodor Richter (1824-1898) did the experiment. They anticipated observing the green line of thallium, as found by Sir William Crookes in London two years earlier. But the radiation they observed showed as a blue line, an indigo blue more precisely, which did not coincide with some of cesium's blue lines at all. A new element was discovered, and named after its color, as the Latin word for indigo is *indicum.* [9] [10]

 $<sup>^2\</sup>mathrm{In}\xspace$  115 represents 95.71% of natural indium. This isotope is slightly radioactive with a very long half-life.
Reich, Ferdinand (1799-1882) Richter, Hieronymous Theodor (1824-1898) Crookes, William (1832-1919)

### Common Uses

A major use of indium is in low-melting alloys, followed by alloys for bearings, in electronics (dry batteries, semiconductors, LCDs) and in dental alloys. An overview of specific applications is given below: [13] [9]

- Indium is added to solder alloys (tin and lead as main component) to increase thermal fatigue resistance as well as to improve malleability at low temperature and corrosion resistance. In electronics, indium solders are mainly used in the form of a paste. Applications are: sealing glass to metal in vacuum tubes, fixing semiconductor chips to a base, assembly of semiconductor devices and hybrid integrated circuits.
- Fusible indium alloys are based on bismuth alloyed with lead, cadmium, tin, and indium. They are used to bend thinwalled tubes without wrinkling the wall or changing the original cross section. Because of their low melting point, they are also used in fire-control systems as restraining links that hold alarm, water valve, and door operating mechanisms in place.

Another usage is the fabrication of disposable patterns and dies for the founding of ferrous and non-ferrous metals.

- As temperature measuring utility when other methods are impracticable, small alloy-rods with melting point exactly known are inserted into the equipment (aircraft header tanks, test bearings, or experimental rigs) to indicate if a certain temperature had been reached in certain parts of the equipment.
- Adding indium to lead-tin bearings provides particularly high resistance to fatigue and seizure for heavy-duty and high-speed applications like pistontype aircraft engines, high-performance automobile engines (e.g. formula 1) and in turbo-diesel truck engines.
- Resistance to discoloring and mechanical characteristics are increased by adding indium to gold denial alloys.
- $\bullet\,$  Indium is also used in nuclear reactor control rod alloys (e.g. Ag 80 In 15 Cd 5)
- A thin indium-tin oxide layer applied to the outer glass envelope of low pressure sodium lamps increases the operating temperature and its efficiency.
- In alkaline dry batteries indium is used as a substitute for mercury to prevent corrosion.

- Intermetallic indium-compounds are used as semiconductors, e.g. indium-gallium arsenide phosphide laser diodes emit light in the 1.27 1.6  $\mu$ m region whereas indium-gallium arsenide photodetectors have high responsivity at 1.3 and 1.55  $\mu$ m.
- Mirrors can be made by plating indium on metals or sputtering indium on glass, offering a better corrosion resistance than silver mirrors.
- Indium-tin oxide (ITO, 80% In<sub>2</sub>O<sub>3</sub>) is transparent to visible light but not for the infrared, in addition to possessing good electrical conductivity. Applications are: coatings on windshields for railway engines and airplanes for defogging, electrodes in liquid crystal displays and IR-reflecting coating in welding goggles.
- Indium phosphide (InP) is an advanced semiconductor material used for high frequency switching operations.

# Relevance in Life

Indium compounds are poorly absorbed when ingested and moderately so when inhaled, being stored mainly in muscle, skin, and bone. Ionic indium is concentrated in the kidneys, producing renal failure; colloidal indium is taken up by the reticuloendothelial system, causing damage to the liver and spleen.

Indium-radioisotope (In-111, In-114) compounds (e.g. indium trichloride and colloidal indium hydroxide) are used in the treatment of tumors and in organ scanning. [17]

# B: Thermophysical properties obtained by Pulse - heating

# Enthalpy

Table 13: Specific enthalpy results of indium, H in kJ·kg<sup>-1</sup>, polynomials taken from [38].

	$T_m = 429.8 \mathrm{K} [18]$	
	at.wt. = 114.818 [18]	
liquid	$H(T) = -64.0 + 0.390 \cdot T$	$2000{\rm K} < T < 5000{\rm K}$
	$c_p = 390 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 44.779 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	



Figure 13: Specific enthalpy of indium as a function of temperature.

# A: Basic survey

### The Element

Symbol:	Ir
Atomic number:	77
Group:	Transition metal
Atomic weight: [6]	192.217(3) u
Ground state electron configuration:	$[Xe]4f^{14}5d^{7}6s^{2}$
Crystal structure at $25^{\circ}$ C: [7]	Cubic fcc with $a = 3.839$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$22.562 \text{ g} \cdot \text{cm}^{-3}$
Melting point: [6]	$2446^{\circ}\mathrm{C}$
Boiling point: [6]	$4428^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.131 \mathrm{J}\cdot\mathrm{g}^{-1}\cdot\mathrm{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.10 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	165-198 (stable: 191, 193)

### Introduction

Iridium is a hard, white, brittle metal, neither ductile nor malleable. It belongs to the platinum family and the isotope 193 has the highest density of any element (at natural isotope-composition osmium has the highest density). Chemically it is very inert and even resistant to aqua regia, whereas vulnerable when exposed to molten salts like NaCl an NaCN. Furthermore it is the most corrosion-resistant metal known and will only oxidize at high temperatures. [9] [10]

# History

Iridium as well as its partner osmium were discovered by the English chemist Smithson Tennant (1761-1815) in 1803. The technique he used to separate iridium and osmium from crude platinum is the same as nowadays: He dissolved the minerals with aqua regia and analysed the shiny black residue. Iridium was given its name because Tennant observed that iridium dissolved in acid showed multiple colors, therefore *iris*, Greek for rainbow. [10] [9] Tennant, Smithson (1761-1815)

### Common Uses

Iridium is principally used as a hardening agent for platinum and to make it more durable. Applications are surgical pins or pivots, electro explosive devices, medical leads and electrodes, thermistors, catalytic applications, jewelry and electrical contacts. Further applications are: [9]

- In 1889, the International Prototype Meter and Kilogram mass were constructed from an alloy of 90 wt% platinum and 10 wt% iridium.
- Alloyed with osmium, it is used for tipping pens and compass bearings. [6]
- It is used to make special laboratory vessels, because iridium will not react with most chemical substances.
- A thorium-iridium alloy has been used in the radioisotope thermoelectric generators of unmanned spacecraft as encapsulation for the plutonium-238 fuel in the generator.
- Iridium-dioxide-based anodes are used for the production of persulfates, in electroplating and in hydrometallurgy for evolving oxygen. [11]
- An everyday usage of thorium-iridium alloys is in long life spark plugs.
- Iridium-Manganese-Chromium alloys are used as part of the read sensors in hard disc drives, replacing prior used platinum-manganese (PtMn) alloys [39]
- Used as electrodes in the chloralkali process.
- Osmium-iridium is used for compass bearings and for balances.
- Iridium crucibles are used for growing oxide mono crystals in the Czochralski technique. Single crystals such as gadolinium gallium garnet (GGG) and yttrium aluminium garnet (YAG) are used for computer memory devices and solid state lasers. [40]
- Ir-192 is used as a portable  $\gamma$ -ray source for radiographing pipelines, rigs, and other civil engineering structures. [40]
- The same isotope is used in radiation therapy treatment against cancer (→ brachytherapy, see below). For this purpose, fine wires or discs, 0.5 to 3.0 mm in diameter, with a thickness of 0.1 up to 3 mm are irradiated in a nuclear reactor. [40]
- Platinum iridium alloys are used as electrodes in pacemakers.[41]

### Relevance in Life

The concentration of iridium in the natural environment is extremely low and does not play any role in life. On the other hand, Ir-192 is used as a source of  $\gamma$ -radiation for the treatment of cancer in brachytherapy, applying irradiation at very close distances in the human body.[42]

# B: Thermophysical properties obtained by Pulse - heating

# Volume expansion

Table 14: Volume expansion results of iridium [43]. Density at 17 °C: 22420 kg  $\cdot m^{-3}$  [18].

	$T_m = 2719 \mathrm{K} [19]$	
solid	$V/V_0(T) = 0.999 + 1.768 \times 10^{-6} \cdot T$	
	$+9.571 \times 10^{-9} \cdot T^2$	$2000{\rm K} < T < 2719{\rm K}$
liquid	$V/V_0(T) = 0.814 + 1.187 \times 10^{-4} \cdot T$	$2719{\rm K} < T < 4000{\rm K}$



Figure 14: Volume expansion of iridium.

# Enthalpy

union n	JIII [44].	
	$T_m = 2719 \mathrm{K} [19]$	
	at.wt. = 192.217 [18]	
solid	$H(T) = -226.507 + 0.232 \cdot T$	$2300{\rm K} < T < 2719{\rm K}$
	$c_p = 232 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 44.594  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
liquio	$H(T) = -24.769 + 0.233 \cdot T$	$2719{\rm K} < T < 3550{\rm K}$
	$c_p = 233 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 44.787  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
	$H_{\rm s} = 404.3, H_{\rm l} = 608.8, \Delta H = 204.5$	

Table 15: Specific enthalpy results of iridium, H in kJ·kg<sup>-1</sup>, polynomials taken from [44].



Figure 15: Specific enthalpy of iridium as a function of temperature.

# Resistivity

Table 16: Electrical resistivity	results of in	ridium, $\rho$ in	$\mu\Omega \cdot m$ ,	polynomials
for $\rho_{\rm IG}$ taken from [44].				

110		
	$T_m = 2719 \mathrm{K} [19]$	
solid	$\rho_{\rm IG}(T) = -0.0228 + 2.453 \times 10^{-4} \cdot T$	$2000{\rm K} < T < 2719{\rm K}$
	$\rho(T) = -0.087 + 2.860 \times 10^{-4} \cdot T$	
liquid	$\rho_{\rm IG}(T) = 0.7791 + 2.515 \times 10^{-5} \cdot T$	$2719{\rm K} < T < 3550{\rm K}$
	$\rho(T) = 0.605 + 1.316 \times 10^{-4} \cdot T$	
	$\rho_{\rm IG,s} = 0.644,  \rho_{\rm IG,l} = 0.847$	
	$\Delta \rho_{\rm IG,s-l} = 0.203$	
	$\rho_{\rm s}=0.692,\rho_{\rm l}=0.963,\Delta\rho_{\rm s-l}=0.271$	



Figure 16: Electrical resistivity of iridium as a function of temperature. Dashed line: values including volume expansion.

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### 3.7 Iron

### A: Basic survey

#### The Element

Symbol: Atomic number: Group: Atomic weight: [6] Ground state electron configuration: Crystal structure at 25°C: [7] Allotropy<sup>3</sup>: [8]

Density at 20°C: [6] Melting point: [6] Boiling point: [6] Specific heat  $c_p$  at 25°C, 1 bar: [6] Molar heat  $C_p$  at 25°C, 1 bar: [6] Curie temperature: [9] Isotope range: [9] Fe 26Transition metal 55.845(2) u  $[Ar]3d^64s^2$ Cubic bcc with a = 2.8665 Å  $\alpha$ -Fe: bcc;  $\gamma$ -Fe: fcc;  $\delta$ -Fe: bcc Transition  $\alpha \to \gamma$  at 912°C Transition  $\gamma \rightarrow \delta$  at 1394°C  $7.874 \mathrm{g} \cdot \mathrm{cm}^{-3}$  $1538^{\circ}C$  $2861^{\circ}C$  $0.449 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$  $25.10 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  $769^{\circ}C$ 46-69 (stable: 54, 56, 57, 58)

#### Introduction

Pure iron is a silvery-white ferromagnetic and soft metal that is malleable and ductile, meaning it can easily be worked and hammered. At the same time, it is the only metal that can hardened by tempering. Mechanical properties like yield strength as well as tensile strength correlate mainly to interstitial impurities in its allotropic form.

Chemically, iron is quite reactive, given the number of compounds it is capable of forming with other elements. In aquous and moist air, oxidation ('rusting') occurs by the formation of a nonprotective and porous hydrated ferric-oxide film. The metal readily dissolves in several diluted strong mineral acids (e.g. HCl and  $H_2SO_4$ ), but is resistant to concentrated sulfuric and nitric acids. [11] [9]

<sup>&</sup>lt;sup>3</sup>There are two more phases of iron:  $\beta$ -Fe is the paramagnetic form of  $\alpha$ -Fe when heated above Curie temperature;  $\varepsilon$ -Fe is gained under high pressure (above 13 GPa), forming a hexagonal close-packed (hcp) structure.  $\varepsilon$ -Fe is of geophysical interest. [11]

# History

The first traces of worked iron were found in Mesopotamia, Asia Minor and Egypt, dating from 2700 to about 3000 BCE, mainly of meteoritic origin<sup>4</sup>. By the end of the Bronze Age in about 1500 BCE, iron-containing minerals were mainly forged, due to the difficulties of mining iron ores and the subsequent extraction of the metal, until the development of metallurgy around 1200 BCE. From the eastern Mediterranean countries as well as from China, the art of metallurgy spread around the then known world. With the fabrication of tools, vehicles, coins and weapons, the spread of civilization was enhanced. [9] [10]

The element's symbol derives from the Latin *ferrum*, itself possibly of Semitic origin. The English *iron* as well as the German *Eisen* originate from the Celtic *îsarno*, which in turn might have been derived from Indo-European *ayos*, meaning 'metal'. [45]

# Common Uses

Since iron is the most widely used metal, only a short abstract of applications can be given here, arranged in major categories:

- Cast irons have a wide field of applications in industry such as valves, pumps, brake drums and engine blocks. The major components are iron, carbon (3-5 wt%) and silicon (1-3 wt%), and additions of further alloying elements (< 0.1 wt%). *Class 30* iron belongs to the 'gray iron' subgroup, consisting of 3.40 wt% C, 2.38 wt% Si, 0.71 wt% Mn, 0.423 wt% P and 0.152 wt% S. [11] [15]
- Steel is the term for iron containing more than 0.15 wt% chemically bound carbon, subdivided in many groups: (*Plain*) carbon steel consists mainly of carbon with small amounts of Mn, e.g. AISI-SAE 1020 (Fe 0.18-0.23C 0.3-0.6Mn 0.04P(max) 0.05S(max)). Low-alloy steels contain specified amounts of alloying elements other than Mn, Cu, Si, S and P, such as Al, Co, Cr, Mo, Ti and W, modifying mechanical or physical properties in various degrees. [11]
- Stainless steel contains a certain amount of chromium (>12 wt%), resulting in an excellent corrosion resistance. Examples are *S34700* (Fe -18Cr -11Ni -2Mn -1Si -0.8Nb -0.08C), applied in airplane exhaust stacks, welded tank cars for chemicals and jet-engine parts, and *S41000* (Fe-12.5Cr-1Mn-1Si-0.15C-0.75Ni-0.04P-0.03S) as a general-purpose type applied in bushings, cutlery, mining machinery, rifle barrels, screws, valves and many more. [11]
- **High-strength low-alloy steels** (HSLA) are developments of the automotive industry intended as a replacement for low-carbon steels.

 $<sup>^4\</sup>mathrm{Verifiable}$  since iron meteorites consists of iron-nickel alloys with a nickel content between 4 and 20 wt%.

Improved mechanical properties are the prime aspect of these alloys, in some cases also corrosion resistance is an objective. High strength-to-weight ratio is another factor, utilized in door-intrusion beams as well as steering and suspension parts in automobiles, just as frames, booms and shovels. Structural elements utilize e.g. A715 (Fe 0.15C 1.65Mn 0.05Ti  $\leq 0.025P \leq 0.01$ Si  $\leq 0.035S$ , [46]), whereas pressure vessels can be made of A841 (Fe 0.2C 0.7-1.6Mn 0.03P 0.03S 0.15-0.5Si 0.25Cr 0.25Ni 0.08Mo 0.35Cu 0.06V 0.03Nb 0.02Al). [15] [11]

- Steels exceeding a yield strength of 1380 MPa are classified as ultrahigh-strength steels. SAE 4340 (0.38-0.43C 0.6-0.8Mn 0.035P 0.04S 0.15-0.35Si 1.65-2Ni 0.7-0.9Cr 0.2-0.3Mo) is one of them. Applications are body reinforcements (e.g. B-pillar) in automobiles or structural parts for aircrafts and missiles, as made of *Ladish D-6a* (Fe 0.42-0.48C 0.9-1.2Cr 0.6-0.9Mn 0.9-1.1Mo 0.4-0.7Ni 0.15-03Si 0.05-0.1V  $\leq$ 0.035P  $\leq$ 0.04S, [46]). [11] [15]
- Steels with special additions or hardened through certain techniques (e.g. quenching and tempering) are called **tool and machining steel**. Their properties include toughness, resistance to abrasion and thermal shock as well as strength at high temperatures. Additions of Cobalt increases hot hardness, Vanadium improves the forgeability. Examples are *T31501* (Fe-0.9C-1.2Mn-0.5W) for oil-hardening tool steel and *T41901* (Fe-2.3W-1.4Cr-0.75Si-0.48C-0.25Mn) for shock-resistant tool steels for pneumatic tooling parts, punches and bolts to mention a few. [11]
- Maraging steels are alloys of extra-low-carbon (< 0.03 wt%) and high nickel (18-22 wt%) content, with further additions of Co <12 wt%, Mo, Ti, Al and Cu. These alloys offer ultrahigh strength, enhanced fracture toughness and good corrosion resistance, widely used on landing gears and slat tracks. *M300* (Fe -18Ni -12Co -5Mo -0.6Ti -0.1Al -0.03C) and *M2000* (Fe-18.9Ni-4.1Mo-1.93Ti) are examples for this group. [47] [11]
- **Powder metallurgy** is another major process in high-performance tool steel production. Milling cutters, reamers, drills and broaching tools are products of this technique, utilizing alloys like *CPM Rex M4* (Fe 1.35C 4.25Cr 5.75W 4.5Mo 4V 0.06S), ASP 30 (Fe 1.28C 4.20Cr 6.40W 5.00Mo 3.10V 8.5Co) and *HAP 70* (2C 4Cr 12W 10Mo 4.5V 12Co). [15]

### Relevance in Life

Iron is a valuable metal for almost all organisms. Since 'free' iron catalyzes the formation of oxygen radicals that can damage cells and tissue, it is bound in specialized molecules. The role of iron in metabolism is a carefully regulated process, due to the elements biological functions covering oxygen transport, electron transfer and DNA synthesis, whereas the major part of body iron (60-70 wt%) is bound in the hemoglobinc complex, being part of the red blood cells. Excess as well as deficiency may affect health (e.g. anemia, organ failure) and can lead to death. [17]

# B: Thermophysical properties obtained by Pulse - heating

### Expansion

Table 17: Volume expansion results of Iron, polynomials converted from [48]. Density at  $20 \,^{\circ}$ C: 7874 kg·m<sup>-3</sup> [18].

· •	-	÷ ( )	
		$T_m = 1808 \mathrm{K} [49]$	
		rec. $T_m = 1811 \mathrm{K} [19]$	
	liquid	$V/V_0(T) = 0.8465 + 1.5119 \times 10^{-4} \cdot T$	$1808{\rm K} < T < 3000{\rm K}$



Figure 17: Volume expansion of Iron.

# Enthalpy

nom [00]	•	
	$T_m = 1808 \mathrm{K}  [49],  at.wt. = 55.845  [18]$	
	rec. $T_m = 1811 \mathrm{K} [19]$	
solid	$H(T) = -276.65 + 0.732 \cdot T$	$1420{\rm K} < T < 1790{\rm K}$
	$c_p = 732.0  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 40.878  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
liquid	$H(T) = -107.306 + 0.77 \cdot T$	$1830{\rm K} < T < 2370{\rm K}$
	$c_p = 770 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 43.001 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 1047, H_{\rm l} = 1285, \Delta H = 238$	

Table 18: Specific enthalpy results of Iron, H in kJ·kg<sup>-1</sup>, polynomials taken from [50].



Figure 18: Specific enthalpy of Iron as a function of temperature.

# Resistivity

h	$o_{\rm IG}$ take	n from [50], Volume expansion [48].	
		$T_m = 1808 \mathrm{K} [49]$	
		rec. $T_m = 1811 \mathrm{K} [19]$	
	solid	$\rho_{\rm IG}(T) = 0.591 + 6.594 \times 10^{-4} \cdot T$	
		$-1.648 \times 10^{-7} \cdot T^2$	$1250{\rm K} < T < 1790{\rm K}$
	liquid		$1830{\rm K} < T < 2370{\rm K}$
		$\rho(T) = 1.0274 + 2.2094 \times 10^{-4} \cdot T$	
		$\rho_{\rm IG,s} = 1.244,  \rho_{\rm IG,l} = 1.275$	
		$\Delta \rho_{\rm IG,s-l} = 0.031$	
		$ \rho_{\rm l} = 1.4269 $	

Table 19: Electrical resistivity results of Iron,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{IG}$  taken from [50], Volume expansion [48].



Figure 19: Electrical resistivity of Iron as a function of temperature. Dashed line: values including volume expansion.

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# A: Basic survey

### The Element

Symbol:	Pb
Atomic number:	82
Group:	Post-transition metals
Atomic weight: [6]	207.2(1) u
Ground state electron configuration:	$[Xe]4f^{14}5d^{10}6s^{1}6p^{2}$
Crystal structure at $25^{\circ}$ C: [7]	Cubic fcc with $a = 4.9508$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$11.35 \mathrm{g\cdot cm^{-3}}$
Melting point: [6]	$327.46^{\circ}\mathrm{C}$
Boiling point: [6]	$1749^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.130 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$26.84 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	181-215 (stable: 206-208)

## Introduction

Pure lead is a soft bluish-white metal which is highly dense, malleable and slightly formable as well as fusible. The metal oxidizes rapidly to a dull gray. It dissolves slowly in HCl as well as in corrosive and oxidizing environments (e.g. chromates, sulfates, carbonates) by forming a protective film of chlorides, oxides, carbonates or silicates, whereas in nitric acid it dissolves readily. Lead isotopes are the decay end products of naturally occurring radioactive elements. [16] [11]

# History

Mankind has used lead since ancient times - artifacts from the Bronze Age prove that. For example the Babylonians used lead plates used to write upon, in the Roman Empire and in Cyprus water piping was made from it. It was popular because of its softness and ductility, and because of the easiness of reducing it from its ore as well as its occurrence together with silver.

The Romans used lead and lead alloys quite multifariously: water supply via lead-lined pipes, pots, pans and containers were used for cooking and storage, sheets for roofing as well as lead shot for their catapults, but they were ignorant of its harmful, health-damaging properties. Later alchemists believed lead to be the oldest metal and associated it with the planet Saturn ( $\mathfrak{F}$ ). They tried to transform lead to gold.

The origin for the English *lead* is ambiguous ([45]), it may derive from the

Irish *luaide* of unknown origin, the Celtic *loud* or Sanskrite *loka* word for 'reddish', describing the red color of lead oxide (red lead). *Plumbum*, from which the symbol originates, was the word to describe<sup>5</sup> soft metals easy to smelt in Rome. [9] [10] [51]

# Common Uses

Though lead is toxic and avoided wherever possible, there are still applications where the metal can not be replaced without great effort:

The main consumption of refined lead (approx. 60 wt%) is by lead batteries such as automotive SLI- (starting, lighting, ignition), tractionand stationary batteries (secondary cells). These accumulators consists of lead oxide (PbO) coated electrode plates in an electrolyte of dilute sulfuric acid. [9]
 Applied ellege and L526220 (Db 1 55b 1 45Cd) L526220 (Db 1 65b)

Applied alloys are L52620 (Pb-1.5Sb-1.45Cd), L52630 (Pb-1.6Sb-0.1Sn-0.3As-0.02Se-0.005S) and L52905 (Pb -4Sb -0.3Sn -0.15As - 0.003S). [12]

- Sonorous crystal glass can be graduated into two types, whole crystal glass with at least 24 wt% lead oxide and semi-crystal glass, containing at least some degree of 10 wt% lead, potassium and zinc oxides. Refraction, brightness and weight are appreciated properties. Applications are in optics, cathode ray as well as fluorescent tubes, glass for radiation protection (X-ray) and light bulbs. E.g. lead glass with a content of 30 wt% PbO and 13 wt% K<sub>2</sub>O has an refractive index of 1.6, the density is 2.9 g/cm<sup>3</sup>. [9]
- Due to the metal's property of being impervious to water and its good corrosion resistance, lead was and is still used as sheathing material for power cables in the petrochemical industry and undersea, although in combination with aluminium foil and plastics. Used alloys are L52515 (Pb-0.2Sb-0.015As), L52520 (Pb-0.2Sb-0.4Sn) and L54030 (Pb-0.2Sn-0.075Cd) to metion a few.[51] [12]
- Lead is still present in ammunition for military and sporting purposes, like in the alloys L52560 (Pb-0.75Sb), L52725 (Pb-2.5Sb) and L53020 (Pb-5.0Sb-5.0Sn) for bullets, like L53235 (Pb-8Sb-0.0005Sn-1.25As) for hard shots and shot alloy L52815 ((Pb-3Sb-0.0005Sn(max)-0.6As). [12]
- Lead-base bearing alloys, also called lead-base babbitt metals, were long used as type metals before utilized for bearings. Used bearing alloys as used in internal-combustion engines are  $SAE \ 16$  (Pb-3.5Sb-4.5Sn-0.1Cu<sup>†</sup>-0.05As-0.1Bi<sup>†</sup>-0.005Zn<sup>†</sup>-0.005Al<sup>†</sup>-0.05Cd<sup>†</sup>),  $SAE \ 19$  (Pb-10Sn) and  $SAE \ 14^6$  (Pb-15Sb-10Sn -0.5Cu<sup>†</sup> -0.1Fe<sup>†</sup> -0.45As -0.1Bi<sup>†</sup>-0.005Zn<sup>†</sup>-0.005Zn<sup>†</sup>-0.005Al<sup>†</sup>-0.05Cd<sup>†</sup>), <sup>†</sup>... maximal content. [12]

 $<sup>^5\,</sup>Plumbum$  candidum or plumbum album was tin, plumbum nigrum was lead $^6{\rm also}$  Alloy 7 of ASTM B 23 alloys

- Red lead (Pb<sub>3</sub>O<sub>4</sub>), a brilliant orange-red water-insoluble dye, has long been one of the most important rust-inhibiting pigments used in primers and undercoats for the protection of steel structures, as well as in ceramic glazes and structures., [12] [16]
- Tin-lead solders are the most widely used, although restricted by the RoHS-regulation ([52]). Still, high melting temperature type solders (i.e. containing at least 85 wt% lead) are allowed, such as Pd-5Sn and Pd-10Sn, applied to seal cellular radiators for automobile, fill seams or dents and for coating and joining metals. General purpose solders like Pb-50Sn and Pb-35Sn however are no longer used. [12]
- High-lead tin bronzes, like *C93200* (Cu-7Sn-7Pb-3Zn) and *C93700* (Cu-10Sn-10Pb), are bearing alloys used where a softer metal is required at moderate loads and speeds. E.g. *C93200* is well suited for applications where lubrication may be deficient, whereas alloys with higher lead content, such as *C93800* (Cu-7Sn-15Pb) and *C94300* (Cu-5Sn-25Pb) find sufficient usage when high loads are accompanied with conditions where lubrication is poor or nonexistent. Examples are mining equipment like pumps, car bearings and stonecrushers, operating under corrosive and dusty conditions. [12]
- Lead and lead-alloy anodes are used for electrochemical applications, due to their corrosion resistance. Pure lead (>99.94 wt% Pb) is used in nickel electrowinning (electroextraction), lead-silver alloys (0.25-0.80 wt% Ag) for zinc and cobalt, and antimonial lead (2-6 wt% Sb, e.g. L52805 (Pb-3Sb)) for the electrowinning of cobalt and copper. [11]

### Relevance in Life

Lead and most of its inorganic compounds are poisonous (neurotoxins) when inhaled or ingested, as well as skin contact to lead alkalis. Organolead compounds like tetrabutyllead and tetraethyl lead are also absorbed through the skin. Gastrointestinal absorption of ingested lead in adults is about 10%, in children between 40-50 wt% due to their growing organs. It is about 30-50 wt% in adults when inhaled, mainly accumulating in blood, soft tissue and bones. Symptoms may include headaches, dizziness and insomnia. Lead toxicity mainly affects the hematopoietic system, the nervous system, the kidneys and the reproductive system. [51] [53]

# B: Thermophysical properties obtained by Pulse - heating

# Enthalpy

Table 20: Specific enthalpy results of lead, H in  $\rm kJ\cdot kg^{-1},$  polynomials taken from [54].

	$T_m = 600.6 \text{ K} [19], at.wt. = 207.2 [18]$	
liquid	$H(T) = -24.0 + 0.156 \cdot T$	$2000{\rm K} < T < 5000{\rm K}$
	$c_p = 156 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 32.3 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	



Figure 20: Specific enthalpy of lead as a function of temperature.

# A: Basic survey

### The Element

Symbol:	Мо
Atomic number:	42
Group:	Transition metal
Atomic weight: [6]	95.94(2) u
Ground state electron configuration:	$[Kr]4d^55s^1$
Crystal structure at $25^{\circ}$ C: [7]	Cubic bcc with $a = 3.147$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$10.22 \mathrm{g} \cdot \mathrm{cm}^{-3}$
Melting point: [6]	$2623^{\circ}\mathrm{C}$
Boiling point: [6]	$4639^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.251 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$24.06 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	86-110 (stable: 92, 94-98)

### Introduction

Molybdenum is a silvery white transition metal and relatively hard, malleable and ductile, but due to its high melting point, mostly formed by using powder metallurgy and sintering techniques. It oxidizes only at high temperatures, it is insoluble in acids and hydroxides at room temperature, resistant to atmospheric corrosion, acids and strong alkalis.

Molybdenite ore is very similar to graphite, and they have been mistaken for each other in the past. [10]

# History

The word  $Molybd\alpha na$  derives from the old Greek word molybdos, meaning 'lead', but also stood for lead gloss, lead ores and lead objects, later gradually for other blackening substances (like graphite), that could be used for writing. In Cronstedt's Mineralogy the mineral was called *molybdoena membranacea nitens* ('leaf-shaped and shining'). In German the mineral was called Wasser-Bley, falsely hinting at a lead content.

The credit for discovering molybdenum was given to Peter Jacob Hjelm (1746-1813), although Carl Wilhelm Scheele (1742-1786) did most of the preparatory work. Scheele researched molybdenite ( $MoS_2$ ) and was able to obtain the oxidic form, but not the pure element. At his suggestion, Hjelm reduced the oxide with carbon at the Laboratorium Chymicum in 1781 and called this new 'half metal' *molybdenum*. [9] [10]

Hjelm, Peter Jacob (1746-1813) Scheele, Carl Wilhelm (1742-1786)

# Common Uses

Its main use is as an additive to alloys (up to 8 wt%), which are widely used in industrial applications. These alloys offer high strength combined with high stiffness in high temperatures, good thermal conductivity, good resistance to abrasion and wear and minimal thermal expansion: [11]

- Molybdenum disulfide (MoS<sub>2</sub>) is a good lubricant, especially at high temperatures where normal lubricant oils quickly decompose.
- Sodium molybdate is used as an anodic corrosion inhibitor, effective against pitting corrosion, in a number of applications, such as in automobile anti-freeze products and in water cooling systems. [9]
- It is compatibile with many molten glass compositions, therefore used in handling equipment, tooling, and furnace constructions. The most common use for molybdenum is as electrodes for the melting of glass.
- Molybdenum disks are used as base plates and heat sinks for power transistors and silicon rectifiers. [13]
- Molybdenum clad with copper, known as Cu/Mo/Cu (or CMC), is a material whose properties can be tailored to the application at hand. Thereby, copper increases the thermal expansion coefficient of the composite, allowing a good match with ceramic substrate materials such as alumina (Al2O3) or beryllia (BeO).
- Molybdenum disilicide MoSi<sub>2</sub>, manufactured by powder metallurgy, is very durable in air even at very high temperatures (1900°C). Used as a resistance material in high-temperature furnaces ('Kanthal Super'). [9]
- Molybdenum is suitable as a catalyst because of its ability to change oxidation states (+6, +4, +5) for different redox reactions, e.g. *dehy-drosulfurization*, used to remove sulfur compounds from oil (recuction process). [9]
- *Molybdate Red* and *Molybdate Orange* are pigments used in paints, for coloring plastics (e.g. polyethylene) and coil coatings. [31]
- Important sputtering target material for electronic applications, mainly for codeposition of  $MoS_x$ , films from ultra-high-purity molybdenum and silicon targets. In integrated circuits, these films offer low parasitic capacitances and also low gate and interconnection propagation delays. [13]
- Radioisotope Mo-99, which decays into technetium-99 (Mo-99  $\rightarrow$  Tc-99m+ $\beta^- + \overline{\nu}_e \rightarrow$  Tc-99 +  $\gamma$ ), is given internally to cancer patients. Tc-99 is absorbed by the tissues of cancer patients and the emitted gamma radiation facilitates the imaging of the internal organs.

- Layers of molybdenum applied by thermal spraying offer extraordinary sliding properties and resistance to abrasion. Applications for this usage are in car engine parts like piston rings, selector forks and synchrorings. [31]
- The catalyst molybdenum hexacarbonyl is used among other things in the production of methanol from carbon and epoxidation monoxide. [31]

# Relevance in Life

Molybdenum is essential for the biological utilization of nitrogen, being a constituent of the enzyme *nitrogenase*, used to fix atmospheric nitrogen  $N_2$  into organic nitrogen by bacteria, as well as in *nitrate reductase*, responsible for the reduction of nitrate to nitrite in plants and microorganisms.

The adult's individual basic requirement of molybdenum is 25 mg per day and is met by nutrition (e.g. cereals). While a molybdenum deficiency syndrome has not been observed, too much molybdenum in the body induces copper deficiency. Further, copper toxicity in humans with Wilson's disease has been successfully cured with tetrathiomolybdate. [53] [17] [9]

# B: Thermophysical properties obtained by Pulse - heating

### Volume expansion

Table 21: Volume expansion results of molybdenum, polynomials converted from [55]. Density at 20 °C: 10220 kg·m<sup>-3</sup> [18].

	$T_m = 2895 \mathrm{K} [19]$	
liquid	$V/V_0(T) = 0.969 + 5.768 \times 10^{-5} \cdot T$	$2895{\rm K} < T < 5000{\rm K}$



Figure 21: Volume expansion of molybdenum.

# Enthalpy

Table 22: Specific enthalpy	results of molybdenum,	H in kJ·kg <sup>-1</sup> , polyno-
mials taken from $[56]$ .		

	$T_m = 2895 \mathrm{K}  [19],  at.wt. = 95.94  [18]$	
solid	$H(T) = -98.7046 + 0.3183 \cdot T$	
	$-3.8103 \times 10^{-5} \cdot T^2 + 1.5336 \times 10^{-8} \cdot T^3$	$480{\rm K} < T < 2480{\rm K}$
	$H(T) = -594.6586 + 0.5177 \cdot T$	$2480{\rm K} < T < 2895{\rm K}$
	$c_p = 517.7 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 49.668  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
liquid	$H(T) = -133.7498 + 0.4916 \cdot T$	$2895{\rm K} < T < 3600{\rm K}$
	$c_p = 491.6 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 47.164  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
	$H_{\rm s} = 904.6, H_{\rm l} = 1289.9, \Delta H = 385.3$	



Figure 22: Specific enthalpy of molybdenum as a function of temperature.

### Resistivity

	$T_m = 2895 \mathrm{K} [19]$	
solid	$\rho_{\rm IG}(T) = -0.0384 + 2.8436 \times 10^{-4} \cdot T$	
	$-1.0970 \times 10^{-8} \cdot T^2 + 3.6622 \times 10^{-12} \cdot T^3$	$400{\rm K} < T < 2895{\rm K}$
	$\rho(T) = -0.0342 + 2.6770 \times 10^{-4} \cdot T$	
	$+6.7741\times10^{-9}\cdot T^2 + 9.6354\times10^{-13}\cdot T^3$	
liquid	$\rho_{\rm IG}(T) = 0.9535 - 1.1498 \times 10^{-5} \cdot T$	$2895{\rm K} < T < 3600{\rm K}$
	$\rho(T) = 0.93106 + 3.95726 \times 10^{-5} \cdot T$	
	$\rho_{\rm IG,s} = 0.782, \ \rho_{\rm IG,l} = 0.910$	
	$\Delta  ho_{ m IG,s-l} = 0.128$	
	$\rho_{\rm s} = 0.821,  \rho_{\rm l} = 0.989,  \Delta \rho_{\rm s-l} = 0.168$	

Table 23: Electrical resistivity results of molybdenum,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{IG}$  and solid rho taken from [56], Expansion: s: [57] l: [55].



Figure 23: Electrical resistivity of molybdenum as a function of temperature. Dashed line: values including volume expansion.

# A: Basic survey

#### The Element

Symbol:	Ni
Atomic number:	28
Group:	Transition metal
Atomic weight: [6]	58.6934(2) u
Ground state electron configuration:	$[Ar]4s^23d^8$
Crystal structure at $25^{\circ}$ C: [7]	Cubic fcc with $a = 3.524$ Å
<b>Density at</b> $25^{\circ}$ C: [6]	$8.902 \mathrm{g\cdot cm^{-3}}$
Melting point: [6]	$1455^{\circ}C$
Boiling point: [6]	$2913^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.444 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$26.07 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Curie temperature: [9]	$354^{\circ}\mathrm{C}$
Isotope range: [9]	52-76 (stable: 58, 60, 61, 62,
	64)

### Introduction

Pure nickel is a dense and tough soft ferromagnetic metal with a silverywhite gloss. The conductivity of the metal for heat and electricity is fairly high, resistance to corrosion in moist air and water is evident at room temperature as well as resistance against concentrated alkaline solutions and molten alkalis. Eventually, diluted mineral acids (e.g. HCl) and nitric acid (HNO<sub>3</sub>) will dissolve it. [11]

### History

The element's name is believed to originate from medieval German miners, who mistook the niccolite (NiAs) mineral for copper ore. The inability to extract copper from that ores and superstitiousness made them give the mineral pejorative names *Nickel* and *Kupfer-Nickel*, subsequently. Nickel refers either to a malevolent dwarf called *Nicolaus* ([9] or to *Old Nick* himself ([10]), who transformed copper into worthless ore.

In 1751, Swedish chemist Axel Fredrik Cronstedt (1722-1756) researched a mineral found in a cobalt mine at Loos, Sweden. After ruling out cobalt he first thought of obtaining copper, but further examination led to the insight that a new element must have been discovered. Research on *Kupfer-Nickel* from Freiberg, Germany, lead to the same conclusion. Retaining the name from the German ore, the new element was labeled *nickel*. [9]

Cronstedt, Axel Fredrik (1722-1756)

### Common Uses

Although approximately 60 wt% of the annual nickel consumption accounts for the production of stainless steel, there are still other applications: nickel and its alloys (32.5-99.5 wt\% Ni) combine good corrosion resistance with extraordinary heat resistance in a wide temperature range.

- Commercially pure nickel and alloys with high nickel content are used in environments containing caustic alkaline hydroxides (NaOH, KOH, ...) or hydrogen halides (e.g. HF). Other applications are the food industry and the manufacture of springs for moderate operating temperatures. Examples for these alloys are *Duranickel® 301* (Ni 0.25Cu 0.6Fe 0.5Mn 0.3C 1Si 0.01S 4.00-4.75 Al 0.25-1Ti) and *Nickel 200* (Ni 0.25Cu 0.40Fe 0.35Mn 0.15C 0.35Si 0.01S). [11] [12]
- The corrosion resistance of nickel-copper alloys ('cupronickels') against reducing chemicals and sea water is outstanding, as is their excellent ductility. They are predominantly used in fastener applications in marine, aerospace, and chemical processing industry, and also in desalination plants. Applied alloys include, among others, *Monel*<sup>®</sup> *R-405* (Ni<sup>7</sup> 28-34Cu 2.5Fe 2Mn 0.3C 0.5Si 0.025-0.06S), *Monel*<sup>®</sup> *K-500* (Ni 27-33Cu 2Fe 1.5Mn 0.25C 0.5Si 0.01S 2.30-3.15 Al 0.35-0.85 Ti) and *Monel*<sup>®</sup> 400 (Ni 28-34Cu 2.5Fe 0.2Mn 0.3C 0.5Si 0.024S). Some special usages are gyroscope devices, anchor cables, propeller shafts in vessels, in valves and pumps and for sucker rods. [12] [11]
- Due to their superior resistance to HCl and other strongly reducing chemicals, nickel-molybdenum alloys such as *Hastelloy® B-2* (aka *Chlorimet 2*, Ni 1Co 1Cr 28Mo 2Fe 0.1Si 1Mn 0.02C 0.025P 0.01S, [58]) are encountered in connection with the handling and processing of hydrochloric acid. [11]
- Nickel alloyed with chromium exhibits high resistance to scaling at normal and increased temperatures, good high-temperature strength, and high electrical resistance. These alloys are utilized in heating elements and electrical shunts, such as *NiCr8020* (Ni 0.3Al 0.15C 15-21Cr 0.5Cu 1Fe 1Mn 0.5-2.0Si 1Co(max)) and *NiCr6015* (Ni 0.3Al 0.15C 14-19Cr 0.5Cu 19-25Fe 1Mn 0.5-2.0Si 1Co(max))<sup>8</sup> [13]
- Low-expansion alloys are in high demand in the lamp industry and electronics, where glass-to-metal seals in encapsulated components are particularly depending on nickel. Nickel-iron alloys such as *Invar* (aka *Alloy 36*, Fe 35-38Ni 0.5Cr 1Co 0.5Mo 0.1C 0.6Mn 0.35Si), *Alloy 42* (Fe 42Ni 0.5Cr 1Co 0.5Mo 0.15Al 0.05C 0.8Mn 0.3Si) and *Alloy 52*

<sup>&</sup>lt;sup>7</sup>Nickel always has a small content of cobalt, therefore unquoted <sup>8</sup>Single figures are maximal content declarations.

(Fe 50.5Ni 0.6Mn 0.3Si 0.05C 0.1Al 0.5Mg 0.025P 0.025S, [59]) satisfy these requirements, along with good thermal conductivity and low electrical resistance. *Invar*, possessing the lowest thermal expansion between 25 and 230 °C of any metal, is applied in the electronic industry for printed circuit boards, in combination with copper. With alumina, beryllia, and vitreous glass, *Alloy 42* is used because it best matches their thermal expansion coefficient. [12]

- Nickel-iron alloys with a content of 72-83 wt% nickel exhibit superior soft magnetic properties, and are used for magnetic shielding, medium-frequency transformers, chokes and relays. Heat treatment improves the permeability values, decreased Ni content (45-68 wt%) results in high saturation induction properties with a round hysteresis loop. These alloys are used for electrical measurement and leakage current protection in the 300 500 mA range. Ni48 (Fe 48Ni 0.25Cr 1Co 0.10Al 0.05C 0.80Si 0.30B) is one of these alloys. [13] [12]
- Superalloys used for critical components such as turbine discs are very special materials. Among others, mechanical strength and creep resistance at high temperatures are their distinctive features. Commonly used examples are *Inconel 706* (Ni-16Cr-2.9Nb-0.2Al-1.8Ti-40Fe-0.03C), *Waspaloy* (Ni-19.5Cr-13.5Co-4.3Mo -1.3Al -3Ti -0.08C -0.006B) and *Rene 95* (Ni-14Cr-8Co-3.5Mo-3.5Wb-3.5Al-2.5Ti-0.15C-0.010B-0.05Zr), to mention only a few. [35]

### Relevance in Life

Nickel's only life-supporting role in humans and mammals is its prevalence in the enzyme *urease*, a catalyst for the urea-ammonia decomposition. However, the element is important for microorganisms and plants. It appears to be an essential trace element, but a deficiency has never been observed. On the other hand, nickel acts as a carcinogen in humans and animals (respiratory tract cancer in particular), and nickel compounds seem to disturb DNA-protein interactions. Nickel allergy is well recognized, and testicular toxicity is observed. Acute nickel poisoning by inhalation or ingestion of nickel carbonyl or soluble nickel compounds may lead to headache, nausea, vomiting and pneumonia. [53] [17]

# B: Thermophysical properties obtained by Pulse - heating

# Volume expansion

Table 24: Volume expansion results of nickel [60]. Density at 25 °C: 8902 kg·m^{-3} [18].

	$T_m = 1728 \mathrm{K} [19]$	
solid	$V/V_0(T) = 1.000 - 6.604 \times 10^{-6} \cdot T$	
	$+2.738 \times 10^{-8} \cdot T^2$	$300{\rm K} < T < 1728{\rm K}$
liquid	$V/V_0(T) = 0.930 + 9.730 \times 10^{-5} \cdot T$	$1728{\rm K} < T < 2600{\rm K}$



Figure 24: Volume expansion of nickel.

# Enthalpy

Table 25:	Specific	enthalpy	results	of	Nickel,	Η	in	kJ·kg <sup>-</sup>	$^{-1},$	polynomials
taken from	n [50].									

	$T_m = 1728 \mathrm{K}  [19],  at.wt. = 58.6934  [18]$	
solid	$H(T) = -166.644 + 0.546 \cdot T$	
	$+2.394 \times 10^{-6} \cdot T^2$	$473{\rm K} < T < 1270{\rm K}$
	$H(T) = -272.961 + 0.634 \cdot T$	$1200{\rm K} < T < 1715{\rm K}$
	$c_p = 634.4  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 37.235 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
liquid	$H(T) = -151.913 + 0.720 \cdot T$	$1740{\rm K} < T < 2240{\rm K}$
	$c_p = 720.0 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 40.819 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 823, H_{\rm l} = 1092, \Delta H = 269$	



Figure 25: Specific enthalpy of nickel as a function of temperature.

# Resistivity

	$T_m = 1728 \mathrm{K} [19]$	
solid	$\rho_{\rm IG}(T) = -0.042 + 2.080 \times 10^{-4} \cdot T$	
	$+5.126 \times 10^{-7} \cdot T^2$	$473{ m K}{<}T<\!\!627{ m K}$
	$\rho(T) = -3.734 \times 10^{-2} + 1.857 \times 10^{-4} \cdot T$	
	$+5.411 \times 10^{-7} \cdot T^2$	
	$\rho_{\rm IG}(T) = -0.181 + 0.118 \times 10^{-2} \cdot T$	
	$-8.197 \times 10^{-7} \cdot T^2 + 2.351 \times 10^{-10} \cdot T^3$	$627 \mathrm{K} < T < 1270 \mathrm{K}$
	$\rho(T) = -0.181 + 0.118 \times 10^{-2} \cdot T$	
	$-8.145 \times 10^{-7} \cdot T^2 + 2.406 \times 10^{-10} \cdot T^3$	
	$\rho_{\rm IG}(T) = 0.094 + 3.764 \times 10^{-4} \cdot T$	
	$-5.644 \times 10^{-8} \cdot T^2$	$1300{\rm K} < T < 1715{\rm K}$
	$\rho(T) = 0.106 + 3.456 \times 10^{-4} \cdot T$	
	$-2.920 \times 10^{-8} \cdot T^2$	
liquid	$\rho_{\rm IG}(T) = 0.728 + 2.546 \times 10^{-5} \cdot T$	$1750 \mathrm{K} < T < 2200 \mathrm{K}$
_	$\rho(T) = 0.667 + 1.043 \times 10^{-4} \cdot T$	
	$\rho_{\rm IG,s} = 0.576,  \rho_{\rm IG,l} = 0.772$	
	$\Delta \rho_{\rm IG,s-l} = 0.196$	
	$\rho_{\rm s} = 0.616,  \rho_{\rm l} = 0.848,  \Delta \rho_{\rm s-l} = 0.232$	

Table 26: Electrical resistivity results of nickel,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{\rm IG}$  taken from [50].



Figure 26: Electrical resistivity of nickel as a function of temperature. Dashed line: values including volume expansion.

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### 3.11 Niobium

# A: Basic survey

### The Element

Symbol:	Nb
Atomic number:	41
Group:	Transition metal
Atomic weight: [6]	92.90638(2) u
Ground state electron configuration:	$[Kr]4d^45s^1$
Crystal structure at $25^{\circ}$ C: [7]	Cubic bcc with $a = 3.3004$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$8.57 \mathrm{g\cdot cm^{-3}}$
Melting point: [6]	$2477^{\circ}\mathrm{C}$
Boiling point: [6]	$4744^{\circ}C$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.265 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$24.60 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	83-110 (stable: 93)

#### Introduction

Niobium is a shiny white, soft, malleable and ductile metal, and takes on a bluish cast when exposed to air at room temperature for a long time. It is a chemically reactive metal that spontaneously forms a thin protective oxide layer of Nb<sub>2</sub>O<sub>5</sub> in an oxygen-containing environment. The metal starts to oxidize in air above 230 °C, so for processing, it must be placed in a protective atmosphere. It resists the action of most acids and possesses a strong inclination to form carbides. [11] [9]

### History

Charles Hatchett (1765-1847), an English chemist employed at the British Museum, was tasked to identify and list minerals from New England. One specimen attracted his interest - a black, heavy stone that gave a golden streak when scratched against porcelain. In 1801, Hatchett found that two-thirds of the mineral was a metal oxide with reactions different from any known oxide. He concluded that he had discovered a new element and gave the new element the name *Columbium*, with reference to its American origin. The mineral itself was named *Columbite* 

In 1802, Anders Gustaf Ekeberg (1767-1813) in Uppsala found the element *Tantalum* ( $\rightarrow$  **Tantalum**, page 108). Soon disputes arose because columbium and tantalum had great chemical similarity. For over forty years, chemists argued about the (non-)consilience of the two minerals as well as
about their name - columbium or tantalum. Until Heinrich Rose (1795-1864), a German analytical chemist, showed that in a Bavarian columbite specimen there were in fact two different metallic elements with great chemical similarity, the heavier one he called *Tantalum*, the lighter one *Niobium*, after *Niobe*, daughter of *Tantalus* and goddess of tears in Greek mythology. One naming problem had thus come to an end but another one had arisen - what should the lighter element be called? And further: are columbium and niobium not the same element? The second question was answered soon after, but the nomenclature was eventually decided in 1949 by the International Union of Pure and Applied Chemistry. [9]

Hatchett, Charles (1765-1847) Ekeberg, Anders Gustaf (1767-1813) Rose, Heinrich (1795-1864)

# Common Uses

Niobium is used extensively as an alloying element in carbon and alloy steels, in Ni- and Co-based superalloys, and in several nonferrous metals. They are used in high temperature applications, in the chemical-process industries and in corrosion engineering. Niobium alloys also exhibit a superconductive state at low temperatures.

Niobium's primary role in superalloys is via solid solution strengthening and precipitation hardening.

- The addition of niobium improves the high-temperature strength and high-temperature corrosion resistance of NiCr5O. [13]
- Alloy C-103 (Nb-10 Hf-1 Ti, medium strength, probably the best allaround alloy [61]) has been widely used for rocket components that require moderate strength at temperatures of about 1095 to 1370°C, preferably used in aerospace industry. [12]
- Nb-46.5Ti alloy is used as a low-temperature (transition temperature: 9 K) superconductor material. Superconducting magnets for magnetic resonance imaging machines employ the alloy in the superconducting composite wire, in which very fine filaments of the alloy (with thicknesses of  $< 1 \, \mu m$ ) are embedded in a copper matrix.

The more brittle niobium-tin (Nb3Sn) superconductor has a higher transition temperature (18.1 K) but its usage has been limited because of fabrication difficulties.

An Nb-55Ti alloy is used for fasteners (e.g. rivets) for aerospace structures. [12]

• Alloy Nb-1Zr is a low strength alloy (1 wt% niobium) for temperatures between 980 and 1205°C. It is used in nuclear applications because it has a low thermal neutron absorption cross section, good corrosion resistance, and good resistance to radiation damage. It is used extensively for liquid metal systems operating at temperatures from 980 to 1205°C. The Nb-1Zr alloy combines moderate strength with excellent

fabricability. As a result, it is used for parts in sodium vapor or magnesium vapor lamps.

Vapor deposited Nb-1Zr or niobium on the inside surface of stainless steel tubing improves the performance of the tubing in many chemical process applications without degrading the mechanical properties of the stainless steel. An intermediate layer of pure niobium under Nb-1Zr improves adherence to the steel substrate. [12] [61]

- Where high strength with low density is required, alloys C-129Y (Nb-10W-10Hf-.1Y) and Cb-752 (Nb-10W-2.5Zr) are used, formed into e.g. leading edges and nose caps for hypersonic flight vehicles, rocket nozzles, gas turbines, and guidance structures for reentry vehicles. [12] [61]
- Alloy C-3009 (Nb-3OHf-9W) is being evaluated for potential use in fasteners and gun barrels. [12]

# Relevance in Life

The mineral columbite is extremely insoluble in water and the concentration of dissolved niobium is very low. The element plays no role in biology. [9]

# B: Thermophysical properties obtained by Pulse - heating

#### Volume expansion

Table 27: Volume expansion results of niobium, polynomials taken from [62]. Density at  $20 \,^{\circ}$ C:  $8570 \, \text{kg} \cdot \text{m}^{-3}$  [18].

		$T_m = 2745 \mathrm{K}$	
ĺ	liquid	$V/V_0(T) = 0.963 - 2.5 \times 10^{-5} \cdot T$	
		$+3.14 \times 10^{-8} \cdot T^2 - 1.17 \times 10^{-12} \cdot T^3$	$2745{\rm K} < T < 6000{\rm K}$



Figure 27: Volume expansion of niobium.

# Enthalpy

	[].	
	$T_m = 2745 \mathrm{K}  [19]$	
	at.wt. = 92.90638 [18]	
solid	$H(T) = -82.451 + 0.280 \cdot T$	$473{\rm K} < T < 1573{\rm K}$
	$H(T) = -248.023 + 0.380 \cdot T$	$1790{\rm K} < T < 2745{\rm K}$
	$c_p = 380  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 35.304 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
liquid	$H(T) = -129.387 + 0.466 \cdot T$	$2745 < T < 3700 \mathrm{K}$
	$c_p = 466 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 43.294 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 795, H_{\rm l} = 1150, \Delta H = 355$	

Table 28: Specific enthalpy results of niobium, H in kJ·kg<sup>-1</sup>, polynomials taken from [63].



Figure 28: Specific enthalpy of niobium as a function of temperature.

# Resistivity

51	i mold taken nom [09].			
		$T_m = 2745 \mathrm{K}  [19]$		
	solid	$\rho_{\rm IG}(T) = 0.023 + 4.839 \times 10^{-4} \cdot T$		
		$-8.899 \times 10^{-8} \cdot T^2$	$473{\rm K} < T < 1573{\rm K}$	
		$\rho_{\rm IG}(T) = 0.199 + 2.441 \times 10^{-4} \cdot T$	$1790{\rm K} < T < 2745{\rm K}$	
	liquid	$\rho_{\rm IG}(T) = 0.972 + 5.527 \times 10^{-6} \cdot T$	$2745{\rm K} < T < 3700{\rm K}$	
		$\rho(T) = 0.6833 + 1.477 \times 10^{-4} \cdot T$		
		$ \rho_{\rm IG,s} = 0.87,  \rho_{\rm IG,l} = 0.99 $		
		$\Delta  ho_{ m IG,s-l} = 0.12$		
		$ \rho_{\rm l} = 1.089 $		

Table 29: Electrical resistivity results of niobium,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{\rm IG}$  taken from [63].



Figure 29: Electrical resistivity of niobium as a function of temperature. Dashed line: values including volume expansion.

#### 3.12 Palladium

#### A: Basic survey

#### The Element

Symbol:	Pd
Atomic number:	46
Group:	Transition metal
Atomic weight: [6]	106.42(1) u
Ground state electron configuration:	$[Kr]4d^{10}$
Crystal structure at $25^{\circ}$ C: [7]	Cubic fcc with $a = 3.8907$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$12.02 \text{ g} \cdot \text{cm}^{-3}$
Melting point: [6]	$1554.8^{\circ}\mathrm{C}$
Boiling point: [6]	$2963^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.246 \mathrm{J}\cdot\mathrm{g}^{-1}\cdot\mathrm{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.98 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	94,120 (stable: 102, 104-106,
	108, 110)

#### Introduction

Palladium is a steel-white, very ductile and malleable metal. Cold working increases its strength and hardness. It resists tarnishing in moist air, but when exposed to sulfur-contaminated environments, it tarnishes slightly. The metal is moderately vulnerable to most strongconcentrated mineral acids (e.g. HCl,  $H_2SO_4$ ) including aqua regia. However, palladium can absorb hydrogen up to 900 times its volume, diffusing out of it at a high rate when the metal is subsequently heated. [11]

#### History

William Hyde Wollaston (1776-1828), an English chemist, showed that naturally occurring platinum is an alloy of several metals. He dissolved natural platinum in aqua regia, filtered the black residue out and examined the filtrate. The addition of mercury cyanide formed a yellow precipitate (palladium cyanide  $Pd(CN)_2$ ). After heating of this cyanide, a metal other than platinum was obtained. In 1803, the new element was named by him after the asteroid *Pallas*, on her part named after *Pallas Athena*, Greek goddess of wisdom and heroic endeavour. [10] [9]

Wollaston, William Hyde (1776-1828)

# Common Uses

The main uses of palladium are in the electronics and electrical industries, in circuitry and in dental alloys. Further applications are catalysts in industry and automobiles, as well as in diffusion cells for the synthesis of hydrogen: [12] [9]

- Palladium and palladium-silver alloys are used as electrodes in multilayer ceramic capacitors (MLCC). Furthermore, the metal - and sometimes a Pd-Ni-alloy - is used in connector platings in consumer electronics.
- In the chemical industry, Pd as well as 60Pd-40Ag is used as a septum in hydrogen purification systems due to its selective transmission. Rh-Pt is used as catalyst for ammonia plus air to yield HNO<sub>3</sub> and for ammonia, air and methane to yield HCN, respectively.
- Apart from gold, palladium is the only metal that forms mixed crystals with silver without miscibility gaps. The Ag23Pd77 alloy, used for hydrogen diffusion membranes, features extremely high hydrogen permeability and high dimensional stability. [13]
- *White gold* is an alloy of gold decolorized by the addition of palladium.
- Palladium-rich alloys or pure palladium are mainly used nowadays in automobile catalytic converters.
- Palladium is used in chemical processes that require hydrogen exchange between two reactants, such as that which produces butadiene and cyclohexane, the raw materials for synthetic rubber and nylon. [64]
- Cancer therapy utilizes radioactive Pd-103 in brachytherapy in case of prostate and breast cancer. There, small seeds of the isotope are permanently implanted directly into the center of the tumor, releasing very low doses of radiation over the course of two months. [64]
- *DMC-100* (99.9% minimum palladium) is used in low current level operations like telephone relays and sensitive gauges. [65]
- The alloy Pd9.5Pt9.0Au32.5Ag is needed for conductor brushes and slide contacts. [12]
- AC and DC contacts, respectively, used in devices for high frequency operations utilise the alloy Pd26Ag2Ni. In DC circuits the material is paired with tungsten, when used as positive contact. [12]

# Relevance in Life

Metallic palladium is a skin sensitizer able to evoke allergic contact dermatitis. Palladium is not combustible except as fine powder or dust. Several of palladium's compounds are oxidizing agents, and some react violently with organic substances. [17]

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 30: Volume expansion results of palladium [43]. Density at 20 °C: 12020 kg·m^{-3} [18].

	$T_m = 1828 \mathrm{K} [19]$	
solid	$V/V_0(T) = 0.996 + 4.356 \times 10^{-5} \cdot T$	$1300{\rm K} < T < 1828{\rm K}$
liquid	$V/V_0(T) = 0.983 + 7.737 \times 10^{-5} \cdot T$	$1828{\rm K} < T < 3000{\rm K}$



Figure 30: Volume expansion of palladium.

# Enthalpy

Table 31: Specific enthalpy results of palladium, $H$ in kJ·kg <sup>-1</sup> , p	olynomials
taken from [66].	

	$T_m = 1828 \mathrm{K}  [19],  at.wt. = 106.42  [18]$	
solid	$H(T) = -95.8103 + 0.2854 \cdot T$	$1550{\rm K} < T < 1828{\rm K}$
	$c_p = 285.4 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 30.37  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
liquid	$H(T) = -55.5552 + 0.3507 \cdot T$	$1828{\rm K} < T < 2900{\rm K}$
	$c_p = 351  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 37.32 \mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$	
	$H_{\rm s} = 425.9, H_{\rm l} = 585.5, \Delta H = 159.6$	



Figure 31: Specific enthalpy of palladium as a function of temperature.

# Resistivity

Table 32: Electrical resistivity results of palladium,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{IG}$  taken from [66].

	$T_m = 1828 \mathrm{K} [19]$	
liquid		$1828{\rm K} < T < 2900{\rm K}$
	$\rho(T) = 0.777 + 2.058 \times 10^{-5} \cdot T$	
	$\rho_{\rm IG,s} = 0.461, \ \rho_{\rm IG,l} = 0.724$	
	$\Delta \rho_{\rm IG,s-l} = 0.263$	
	$\rho_{\rm s}=0.496,\rho_{\rm l}=0.814,\Delta\rho_{\rm sl}=0.318$	



Figure 32: Electrical resistivity of palladium as a function of temperature. Dashed line: values including volume expansion.

#### 3.13 Platinum

#### A: Basic survey

#### The Element

Symbol:	Pt
Atomic number:	78
Group:	Transition metal
Atomic weight: [6]	195.084(9) u
Ground state electron configuration:	$[Xe]4f^{14}5d^{9}6s^{1}$
Crystal structure at $25^{\circ}$ C: [7]	Cubic fcc with $a = 3.92942$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$21.45 \text{ g} \cdot \text{cm}^{-3}$
Melting point: [6]	$1768.2^{\circ}\mathrm{C}$
Boiling point: [6]	$3825^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.133 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.86 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	168-202 (stable: 192, 94-196,
	198)

#### Introduction

Pure platinum is a lustrous silvery-white metal of high density, ductile with low electrical resistivity and high thermal conductivity. The metal does not oxidize in air until reaching its melting point, resists corrosion by practically all chemicals at room temperature but readily dissolves in aqua regia. It neither corrodes nor tarnishes in air and is not affected by water, nevertheless can be easily corroded by some hot chemicals, e.g. molten oxides and hydroxides, concentrated sulfuric and phosphoric acids, liquid metals like lead, gold and copper. [11]

#### History

Archeological evidence shows that native platinum was known and used by the ancient Egyptians around 700 BCE, also that pre-Columbian natives of South America used platinum. In 1735 the Spanish astronomer Antonio de Ulloa (1716-1795) described a free metal he found in South America. The metal was heavier than gold, had a higher melting point, and was noncorrosive. He named it *platina*, the Spanish word for 'silver'.

In 1741 the element was rediscovered by the Englishman Charles Wood (1702-1774), found in ores of Columbian origin. Among others, Sir William Watson (1715-1787) researched the new element, but being aware of de Ulloa's descriptions. It became known as *white gold* (a term now used to

describe an Gold/Palladium alloy) as well as the *eighth metal*<sup>9</sup>. In 1752, a first detailed scientific description of the element was finally given by William Lewis. At the turn of the century, William Hyde Wollaston and Smithson Tennant formed a partnership to commercially exploit the production of platinum. For over 15 years they researched the platinum ores, over the course of which they discovered further platinum metals, Wollaston **Palladium** and **Rhodium** (page 76 and 96, respectively), Tennant **Iridium** (page 38) and **Osmium**. [9] [45]

de Ulloa, Antonio (1716-1795) Wood, Charles (1702-1774) Watson, William (1715-1787) Lewis, William (1706-1781) Wollaston, William Hyde (1776-1828) Tennant, Smithson (1761-1815)

#### Common Uses

Jewelry and 'three way' auto-catalysts are the principal uses of platinum, which fulfils a wide range of roles in the chemical industry: [67] [12]

- Ultra pure platinum is used as sensing element for resistance thermometers because of its stable and known resistance and high temperature coefficient (e.g. Pt 1000).
- In thermocouples, where stable temperature relations are required, the following combinations are used: 10Rh-Pt vs. Pt, 6Rh-Pt vs. 30Rh-Pt, 13Rh-Pt vs. Pt, 5Rh-Pt vs. 20Rh-Pt, Au-Pd vs. Rh-Pt, Au-Pd vs. Ir-Pt.
- Pure platinum is used in the glass and ceramics industry as tanks and crucibles for optical glass due to its noncontamination and insolubility.
- For bushings and valves for fiberglass, platinum alloys (e.g. 10Rh-Pt, 20Rh-Pt) are used.
- Corrosion and heat resistance requirements in laboratory ware are met by 0.6Ir-Pt and 3.5Rh-Pt alloys, e.g. platinum crucibles are used for calcination and weighing for gravimetric analysis.
- $\bullet$  Containers for high-temperature  $\mathrm{SO}_2$  are made of pure platinum as wall as Au-Pt alloys.
- Platinum and 5Ir-Pt offer corrosion resistance in chlorides and sulfates, applied as insoluble anodes for production of persulfates and perchlorates, and for electroplating.
- In jewelry, springs and housing-bottoms of wrist watches employ 15Ir-Pt, and 15Pd-Pt is applied in necklaces. Safety closures and pins are often made of 10Ir-Pt. [68]

 $<sup>^{9}\</sup>mathrm{The}$  seven metals Copper, Gold, Iron, Lead, Mercury, Silver and Tin have been known since ancient times.

- Au-Pd-Pt alloys are used for resistance wires and resistance films, whereas in resistors and potentiometers alloys like 8W-Pt, 5Mo-Pt and 10Ru-Pt are employed.
- Jet engine glow plugs utilize Rh-Pt alloys, some spark plug electrodes are made of thoriated Pt-4W.
- The drug *cisplatin* is built of a central platinum atom linked to two ammonia molecules and two chlorine atoms. The drug prevents the duplication of DNA during cell division and rapidly affects the division of cancer cells. It is applied in chemotherapy as an anti-tumor drug. [9]

# Relevance in Life

Fine platinum powder may explode if too close to an open flame. Because platinum is rather inert in its elemental metallic form, it is not poisonous to humans, but some of its compounds are, in particular its soluble salts which are toxic if inhaled or ingested. [10]

# B: Thermophysical properties obtained by Pulse - heating

# Volume expansion

Table 33: Volume expansion results of platinum [43]. Density at 20 °C: 21450 kg·m<sup>-3</sup> [18].

	$T_m = 2041.3 \mathrm{K} [19]$	
solid	$V/V_0(T) = 0.991 + 3.102 \times 10^{-5} \cdot T$	$1200{\rm K} < T < 2040{\rm K}$
liquid	$V/V_0(T) = 0.988 + 6.997 \times 10^{-5} \cdot T$	$2042{\rm K} < T < 3300{\rm K}$



Figure 33: Volume expansion of platinum.

# Enthalpy

	$T_m = 2041.3 \mathrm{K} [19]$	
	at.wt. = 195.078 [18]	
solid	$H(T) = -38.6891 + 0.1274 \cdot T$	
	$+1.3443 \times 10^{-5} \cdot T^2$	$473{\rm K} < T < 1573{\rm K}$
	$H(T) = -96.0750 + 0.180035 \cdot T$	$1700{\rm K} < T < 2040{\rm K}$
	$c_p = 180  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 35.114  \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
liquid	$H(T) = 1.63634 + 0.187235 \cdot T$	$2045 < T < 2830 \mathrm{K}$
	$c_p = 187 \mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$	
	$C_p = 36.48 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 271.6, H_{\rm l} = 384.0, \Delta H = 112.4$	

Table 34: Specific enthalpy results of platinum, H in kJ·kg<sup>-1</sup>, polynomials taken from [69].



Figure 34: Specific enthalpy of platinum as a function of temperature.

# Resistivity

101 / mong		
	$T_m = 2041.3 \mathrm{K}  [19]$	
solid	$\rho_{\rm IG}(T) = -0.0182 + 4.4636 \times 10^{-4} \cdot T$	
	$-6.955  imes 10^{-8} \cdot T^2$	$473{\rm K} < T < 1573{\rm K}$
	$\rho(T) = -0.024 + 4.540 \times 10^{-4} \cdot T$	
	$-6.401 \times 10^{-8} \cdot T^2$	
	$\rho_{\rm IG}(T) = 0.1545 + 2.2287 \times 10^{-4} \cdot T$	$1740{\rm K} < T < 2042{\rm K}$
	$\rho(T) = 0.128 + 2.518 \times 10^{-4} \cdot T$	
liquid	$\rho_{\rm IG}(T) = 0.8537 + 2.7129 \times 10^{-5} \cdot T$	$2042{\rm K} < T < 2900{\rm K}$
	$\rho(T) = 0.832 + 9.604 \times 10^{-5} \cdot T$	
	$\rho_{\rm IG,s} = 0.610, \ \rho_{\rm IG,l} = 0.909$	
	$\Delta \rho_{\rm IG,s-l} = 0.299$	
	$\rho_{\rm s}=0.642,\rho_{\rm l}=1.028,\Delta\rho_{\rm s-l}=0.386$	

Table 35: Electrical resistivity results of platinum,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{\rm IG}$  taken from [69].



Figure 35: Electrical resistivity of platinum as a function of temperature. Dashed line: values including volume expansion.

#### 3.14 Rhenium

#### A: Basic survey

#### The Element

Symbol:	Re
Atomic number:	75
Group:	Transition metal
Atomic weight: [6]	186.207(1) u
Ground state electron configuration:	$[Xe]4f^{14}5d^{5}6s^{2}$
Crystal structure at $25^{\circ}$ C: [7]	hcp with $a = 2.761$ Å
	and $c = 4.456$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$20.8 \text{ g} \cdot \text{cm}^{-3}$
Melting point: [6]	$3185^{\circ}C$
Boiling point: [6]	$5596^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.137 \mathrm{J}\cdot\mathrm{g}^{-1}\cdot\mathrm{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.48 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	160-192 (stable: $185, 187$ )

#### Introduction

Rhenium is a silvery or grayish-white metal with a metallic luster that tarnishes slowly in moist air but possesses good resistance against corrosion and oxidation. At room temperature, the metal reacts with alkalis, and it readily dissolves in concentrated nitric acid but is quite inert to aqua regia. Furthermore it reacts with boron, silicon, and phosphorus by forming stable salts. It does not form stable carbides. [11]

#### History

The element rhenium, known to belong to the manganese group (VIIB) under the Mendeleevian terminology called *dvi-manganese* - was not one of the elements discovered by accident: far from it! Still undiscovered at the beginning of the 1920s, German scientists Walter Noddack (1893-1960) and Ida Tacke-Noddack (1896-1978) tried to analyze the gap in the periodic system logically, calculating and predicting some of the element's chemical and physical properties.

Concentrating their research on columbite minerals and on platinum ores, their analysis showed that group 6 would be of particular interest (specifically tungsten and tungsten minerals) but not molybdenum - ironically, some molybdenum ores contain element 75 in considerable quantities.

In 1925, they investigated a gadolinite and highly enriched the content which

they already strongly suspected to be element No 75. Through X-ray investigation they were able to ascertain the discovery of the sought element, named *rhenium* after the river *Rhine*, 'Rhein' in German. [9] Noddack, Walter (1893-1960) Tacke-Noddack, Ida (1896-1978)

# Common Uses

Rhenium is added to tungsten- and molybdenum-based alloys to improve their properties at high temperatures as well as to nickel-based superalloys, mainly for ductility and strength. Another important use for the metal is as a catalyst.

- Thermocouples for tempertures up to 2300°C 2760°C for short term exposure are made from W5Re or W26Re wires. But they have to operate in protective gas atmospheres (e.g. hydrogen, inert gas) or in a vacuum. Other combinations are W/W26Re and W3Re/W25Re. [13] [70]
- Turbine blades in aircrafts employ nickel-based alloys with addition of 1-3 wt% rhenium because of its high strength and oxidation resistance, and due to the higher operating temperatures that can be achieved. Similar properties are obtained when coating gas turbine blades with MCrAlY alloys containing 1-20 wt% rhenium. [31]
- Molybdenum alloys become weldable after the addition of rhenium. Common used alloys are Mo41Re and Mo47.5Re - mostly used in the electronics, space, and nuclear industries. [71]
- Rotating X-ray anodes in computer tomography is one of the most important applications for tungsten-rhenium alloys, because the material is able to operate at higher electron currents and therefore shorter irradiation times as achieved. In this case the surface layer is made of W-(3-10)Re, while the body is either a Mo-W alloy, a Mo-Ti-Zr-O-C microalloy (TZM), or graphite. [13]
- Rhenium-Quartz-Halogen infrared lamps are primarily used in reaction tubes. About 90 wt% of the electric energy is converted into radiation, offering a color temperature of 3000 K and 3150 K, respectively. [71]
- Rhenium diboride (ReB<sub>2</sub>) is harder than diamond, synthesized by combining rhenium and boron powder at 1000°C over a long time. [72]
- Platinum-rhenium catalysts are used for hydrogenation of fine chemicals, hydrocracking and reforming in petrochemistry, and the disproportionation of alkenes. Furthermore, rhenium catalysts offer great resistance against nitrogen, phosphorus and sulfur. [11]

- Rhenium is used in rocket thrust chambers as well as in artificial satellites. A combination of iridium on the inner wall as oxidation protection and an outer cladding made of rhenium are used, sometimes substituted by carbon/carbon with an intermediate binding rhenium layer of 0.25 0.5 mm. [9]
- Rhenium wires are implemented in photoflash lamps used by photographers and thermistors, pure rhenium metal is utilized in filaments for mass spectroscopy and ion gauge. [11]
- The isotopes Re-186 and Re-188 are used for the diagnosis and treatment of leukemia when combined with monoclonal antibodies. [31]

# Relevance in Life

Rhenium is a very rare element and there is no evidence that it would play any biological role in humans or animals. Intoxication of people working in industries with either the metal or its most important compounds - perrhenic acid and ammonium perrhenate - has never been observed, whereas antitumor effects were shown in medical studies of rhenium carboxylates. [31]

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 36: Volume expansion results of rhenium, polynomials taken from [2]. Density at  $20 \,^{\circ}\text{C}$ :  $21020 \,\text{kg} \cdot \text{m}^{-3}$  [18].

	$T_m = 3458 \mathrm{K}$ [73]	
solid	$V/V_0(T) = 0.995 + 1.688 \times 10^{-5} \cdot T$	$1500{\rm K} < T < 3458{\rm K}$
liquid	$V/V_0(T) = 0.650 + 1.271 \times 10^{-4} \cdot T$	$3458{\rm K} < T < 4500{\rm K}$



Figure 36: Volume expansion of rhenium.

# Enthalpy

anon noi	[-]-	
	$T_m = 3458 \mathrm{K} [73]$	
	at.wt. = 186.207 [18]	
solid	$H(T) = -140.202 + 0.186 \cdot T$	$2500{\rm K} < T < 3458{\rm K}$
	$c_p = 186  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 34.635  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
liquid	$H(T) = -363.634 + 0.283 \cdot T$	$3458{\rm K} < T < 5000{\rm K}$
	$c_p = 283  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 52.697  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
	$H_{\rm s} = 503.0, H_{\rm l} = 615.0, \Delta H = 112$	

Table 37: Specific enthalpy results of rhenium, H in kJ·kg<sup>-1</sup>, polynomials taken from [2].



Figure 37: Specific enthalpy of rhenium as a function of temperature.

# Resistivity

$T_m = 3458 \mathrm{K} [73]$	
	$2000{\rm K} < T < 3458{\rm K}$
$-5.650 \times 10^{-8} \cdot T^2$	
$-2.915 \times 10^{-7} \cdot T^2$	$3458{\rm K} < T < 3880{\rm K}$
$\rho(T) = -3.682 + 2.5428 \times 10^{-3} \cdot T$	
$-3.235 \times 10^{-7} \cdot T^2$	
$\rho_{\rm IG}(T) = 1.859 - 3.001 \times 10^{-4} \cdot T$	
$+3.019 \times 10^{-8} \cdot T^2$	$3880{\rm K} < T < 4500{\rm K}$
$\rho(T) = 1.520 - 1.753 \times 10^{-4} \cdot T$	
$+3.150 \times 10^{-8} \cdot T^2$	
$\rho_{\rm IG,s} = 1.139,  \rho_{\rm IG,l} = 1.139$	
$\Delta \rho_{\rm IG,s-l} = 0$	
$\rho_{\rm s} = 1.200, \ \rho_{\rm l} = 1.243, \ \Delta \rho_{\rm s-l} = 0.043$	
	$\begin{split} \rho_{\rm IG}(T) &= 0.354 + 4.229 \times 10^{-4} \cdot T \\ &- 5.665 \times 10^{-8} \cdot T^2 \\ \rho(T) &= 0.338 + 4.446 \times 10^{-4} \cdot T \\ &- 5.650 \times 10^{-8} \cdot T^2 \\ \rho_{\rm IG}(T) &= -2.843 + 2.160 \times 10^{-3} \cdot T \\ &- 2.915 \times 10^{-7} \cdot T^2 \\ \rho(T) &= -3.682 + 2.5428 \times 10^{-3} \cdot T \\ &- 3.235 \times 10^{-7} \cdot T^2 \\ \rho_{\rm IG}(T) &= 1.859 - 3.001 \times 10^{-4} \cdot T \\ &+ 3.019 \times 10^{-8} \cdot T^2 \\ \rho(T) &= 1.520 - 1.753 \times 10^{-4} \cdot T \\ &+ 3.150 \times 10^{-8} \cdot T^2 \\ \rho_{\rm IG,s} &= 1.139, \rho_{\rm IG,l} = 1.139 \\ &\Delta \rho_{\rm IG,s-l} &= 0 \end{split}$

Table 38: Electrical resistivity results of rhenium,  $\rho$  in  $\mu\Omega$ ·m, polynomials taken from [2].



Figure 38: Electrical resistivity of rhenium as a function of temperature. Dashed line: values including volume expansion.

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# A: Basic survey

#### The Element

Symbol:	Rh
Atomic number:	45
Group:	Transition metal
Atomic weight: [6]	102.90550(2) u
Ground state electron configuration:	$[Kr]4d^85s^1$
Crystal structure at 25°C: [7]	Cubic fcc with $a = 3.8034$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$12.41 \text{ g} \cdot \text{cm}^{-3}$
Melting point: [6]	$1964^{\circ}\mathrm{C}$
Boiling point: [6]	$3695^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.243 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$24.98 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	94-117 (stable: 103)

## Introduction

Rhodium is a hard and silvery-white metal, fairly ductile when heated and its melting point is high. The metal is corrosion resistant against most strong mineral acids as well as to hot aqua regia up to 100°C. Moreover, it is also oxidation resistant in air at high temperatures, turning red in its oxidic form upon heating but returning to the elementary form at higher temperatures. Furthermore, it absorbs oxygen upon melting, releasing it upon solidification. [11]

## History

The English chemist William Hyde Wollaston (1776-1828) discovered the element palladium in the residue of dissolved platinum ore in aqua regia in 1803. In the same year, further investigations of the solution showed another metal was present, after partially neutralizing with sodium hydroxide and precipitating platinum with ammonium chloride ( $\rightarrow$  **Platinum**, page 82) and palladium with mercury cyanide ( $\rightarrow$  **Palladium**, page 76), subsequently. He added hydrochloric acid to the separated remaining solution and dried it. He tried to dissolve the residue in alcohol, but a beautiful dark-red powder remained undissolved - a double chloride of sodium and a new element.

Because of the rose color of its salts, Wollaston named the new element *rhodium*, after the Greek word *rhodon* meaning 'rose'. [9] [10] Wollaston, William Hyde (1776-1828)

# Common Uses

The most important usages for rhodium are as an additive in alloys to increase strength and high temperature durability as well as corrosion protection, and as a component of industrial catalytic systems.

- Thin coatings of rhodium, formed via electroplating, are used as protection against scratches and tarnishing. In these application, its high and uniform reflectivity in UV as well as IR ranges are exploited. Applied for silverware, jewelry, optical instruments, mirrors, and reflectors in lighting devices. [10] [12]
- In the production of nitric acid, Pt10Rh is used as a catalyst for the oxidation of ammonia. [12]
- The chemical industry uses rhodium as catalyst for the manufacture of acetic acid and for the hydroformylation of alkenes [67]
- Pt10Rh is the most common used Pt-Rh alloy. In the glass industry it is used for feeder dies and for handling glasses of high melting point, and is also employed for rayon spinnerettes. [12]
- The alloys Pt10Rh, Pt20Rh and Pt40Rh are utilized as windings in high-temperature furnaces (up to 1800°C) that operate under oxidizing atmospheres. [12]
- Standard thermocouples are commonly made of Pt10Rh versus Pt (Type S), employed for the temperature range from 630.74 °C to 1064.43 °C (gold point). Other configurations are Pt13Rh/Pt (Type R) and Pt30Rh/Pt6Rh (Type B). Unlike the above mentioned ones, iridium-rhodium thermocouples (Ir40Rh/Ir, Ir50Rh/Ir and Ir60Rh/Ir) are only recommended for operation in inert atmospheres and in vacuum. [12]
- Crucibles are made of Pt3.5Rh alloy, offering little weight-loss at high temperatures. [12]
- Bushings made of ZGS<sup>10</sup> platinum-rhodium are used in the fabrication of continuous filament glass fiber. The material is resistant to creep-induced sagging. [12]
- Excellent gray filters are gained by thin coatings of rhodium on glass via vacuum deposition. [8]

# Relevance in Life

Rhodium metal powder and dust are inflammable in air. Skin irritations may occur through contact with a number of its compounds. [10]

 $<sup>^{10}{\</sup>rm ZGS}$  (Zirconia Grain Stabilized) is a form of platinum, resistant to grain growth, contamination and deformation at high temperatures. [74]

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 39: Volume expansion results of rhodium, polynomials taken from [75]. Density at 20°C:  $12423 \text{ kg} \cdot \text{m}^{-3}$ [76].

-	$T_m = 2236 \mathrm{K} [19]$	
solid	$V/V_0(T) = 0.943 + 5.994 \times 10^{-5} \cdot T$	$1400{\rm K} < T < 2236{\rm K}$
liquid	$V/V_0(T) = 0.893 + 1.055 \times 10^{-4} \cdot T$	$2236{\rm K} < T < 3500{\rm K}$



Figure 39: Volume expansion of rhodium.

# Enthalpy

li moni [	••].	
	$T_m = 2236 \mathrm{K} [19]$	
	at.wt. = 102.9055 [18]	
solid	$H(T) = -486.154 + 0.523 \cdot T$	$1900{\rm K} < T < 2236{\rm K}$
	$C_p = 53.820 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
liquid	$H(T) = -98.980 + 0.448 \cdot T$	$2236{\rm K} < T < 3150{\rm K}$
	$C_p = 46.102 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 683, H_{\rm l} = 903, \Delta H = 220$	
	solid	$\begin{array}{c c} at.wt. = 102.9055 \ [18] \\ \hline solid & H(T) = -486.154 + 0.523 \cdot T \\ c_p = 523 \ \mathrm{J\cdot kg^{-1} \cdot K^{-1}} \\ \hline C_p = 53.820 \ \mathrm{J\cdot mol^{-1} \cdot K^{-1}} \\ \hline liquid & H(T) = -98.980 + 0.448 \cdot T \\ c_p = 448 \ \mathrm{J\cdot kg^{-1} \cdot K^{-1}} \\ \hline C_p = 46.102 \ \mathrm{J\cdot mol^{-1} \cdot K^{-1}} \end{array}$

Table 40: Specific enthalpy results of rhodium, H in kJ·kg<sup>-1</sup>, polynomials taken from [75].



Figure 40: Specific enthalpy of rhodium as a function of temperature.

# Resistivity

Table 41:	Electrical	resistivity	$\operatorname{results}$	of rhodium	, $\rho$ in	$\mu\Omega \cdot m$ ,	polynomials
taken from	n [75].						

	$T_m = 2236 \mathrm{K} [19]$	
solid	$\rho_{\rm IG}(T) = -0.126 + 3.085 \times 10^{-4} \cdot T$	$1950{\rm K} < T < 2236{\rm K}$
	$\rho(T) = -0.202 + 3.617 \times 10^{-4} \cdot T$	
liquid	$\rho_{\rm IG}(T) = 0.635 + 6.975 \times 10^{-5} \cdot T$	$2236{\rm K} < T < 3150{\rm K}$
	$\rho(T) = 0.516 + 1.680 \times 10^{-4} \cdot T$	
	$\rho_{\rm IG,s} = 0.564,  \rho_{\rm IG,l} = 0.791$	
	$\Delta \rho_{\rm IG,s-l} = 0.227$	
	$\rho_{\rm s}=0.607,\rho_{\rm l}=0.892,\Delta\rho_{\rm sl}=0.285$	



Figure 41: Electrical resistivity of rhodium as a function of temperature. Dashed line: values including volume expansion.

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3.16 Silver

# A: Basic survey

#### The Element

Symbol:	Ag
Atomic number:	47
Group:	Transition metal
Atomic weight: [6]	107.8682(2) u
Ground state electron configuration:	$[Kr]4d^{10}5s^{1}$
Crystal structure at 25°C: [7]	Cubic fcc with $a = 4.0853$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$10.50 \mathrm{g} \cdot \mathrm{cm}^{-3}$
Melting point: [6]	$961.78^{\circ}\mathrm{C}$
Boiling point: [6]	$2162^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.235 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.350 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	94-128 (stable: 107, 109)

### Introduction

Silver is a soft, ductile and malleable metal with white metallic brilliance, which can be highly polished. Because of its white shine alchemists related silver to the moon, symbolized by  $\mathfrak{D}$ . Its chemical symbol (Ag) refers to the Latin word for silver, *argentum*. The word 'silver' itself derives from the Anglo-Saxon word *siolfor*.

In comparison to gold silver is somewhat harder, and can therefore be formed by swaging, rolling, drawing through a die and other processes. It is insoluble in water, but dissolves in hot concentrated acids. Freshly exposed silver displays a mirror-like gloss that subsequently blurs as a result of a reaction with hydrogen sulfide in the air, forming silver sulfide (AgS). [21] [10]

## History

Silver was - along with gold and copper - one of the first metals used by humans (about 5000 BCE), since it could be found in its elementary form. Over six thousand year old jewelry and burial objects were found in tombs, marking the time when humans learned how to extract the metal out of its ore. Descriptions of the refining process as well as the use for jewelry were found in ancient Egyptian writings and in the Old Testament. During that time, silver was more precious than gold because of the difficulties of finding it in its natural state as well as extracting it from its ores.

The Anatolian region is considered one of the first major sources of mined

silver, serving the Western cultures flourishing in the Near East, Crete, and Greece. Concentrated efforts to mine silver began some time after 3000 BCE. For the upcoming Greek civilization, the mines of Laurium near Athens became the leading center of production. In addition, Spanish mines became a critically important source of silver, first for the Carthaginians, thereafter for the Romans.

With the discovery of the 'New World', the silver production expanded significantly, most notably after the development of the mercury amalgamation process. Later on, better technologies permitted a more effective mining and tabbing of newly discovered deposits. [77]

# Common Uses

The market for silver is divided into three main parts: industrial and decorative uses, photography, and jewelry/silverware. Together they represent more then 95 wt% of annual silver consumption. Because of its unique properties, the range of possibilities in application is wide; strong dependencies exists because of the fact that substitution of silver in most applications is restricted. [77]

• Because of its reflective brilliance, beauty and tarnish resistance, silver was used early for jewelry and later on for silverware. Mixed with copper, the annealed metal was used for cutlery, bowls and decorative items.

Note: Sterling silver consists of  $92.5\,\rm wt\%$  silver (or 925 fineness, meaning 925%) and  $7.5\,\rm wt\%$  copper.

- Silver-copper-gold-alloys are very important in jewelry, they cover a wide range of hardness and color. [13]
- In photography, silver is used in the form of silver nitrate and silver halides.
- Silver-electroplated steel ball bearings offer greater load carrying capacity and fatigue strength compared to any other type, especially used in continuous, heavy-duty applications such as in jet engines.
- Silver facilitates the joining of materials, utilized in the brazing and soldering process, producing leak-tight, corrosion-resistant and smooth joints, combining high tensile strength, ductility and thermal conductivity.

Caused by the Restriction of Hazardous Substances (RoHS) legislation, the substitution of tin/lead (63:37 wt%) solder through a combination of silver, tin and copper solder was boosted.

• In electronics, the field of application ranges from silver membrane switches in buttons, e.g. telephones and keybords, over printed circuit boards to create electrical pathways as well as in RFID tags, and coatings for CDs and DVDs.

- The alloy Ag80Cd5In15 has been used to control nuclear reactors. It combines a high thermal neutron capture cross section with high thermal conductivity, mechanical stability, and good corrosion resistance in hot water. [13]
- The high hydrogen permeability of silver-palladium-alloys (e.g. Ag23 -Pd77) makes them a suitable material for hydrogen diffusion membranes.
- Silver-lead-gold alloys are used in the noble-metal recycling process as lead shaft furnaces.
- Silver-based dental alloys are made of silver amalgam and contain minor amounts of tin, copper, and zinc for hardening reasons (e.g. Ag 33, Hg 52, Sn 12, Cu 2, Zn <1).

# Relevance in Life

Silver has no essential function in biology and its compounds have a very low toxicity, acute as well as chronic. Silver ions prevent bacteria and algae buildup, so it is used in water purification systems. Because of its very low toxicity, silver replaces traditional methods for germ killing (which used harmful chemicals like chlorine and bromine). It is also used for woundtreatment, as for example in topical gels or impregnated into bandages. [9]

# B: Thermophysical properties obtained by Pulse - heating

# Volume expansion

Table 42: Volume expansion results of silver [60]. Density at 20 °C: 10500 kg  $\cdot m^{-3}$  [18].

	$T_m = 1234.93 \mathrm{K} [26]$	
liquid	$V/V_0(T) = 1.002 + 4.736 \times 10^{-5} \cdot T$	$1234{\rm K} < T < 2000{\rm K}$



Figure 42: Volume expansion of silver.

# Enthalpy

	$T_m = 1234.93 \mathrm{K}  [26]$	
	at.wt. = 107.8682 [18]	
solid	$H(T) = 17.2367 + 0.1656 \cdot T$	$1000{\rm K} < T < 1234{\rm K}$
	$c_p = 165.6  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 17.863  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
liquid	$H(T) = 2.5807 + 0.2598 \cdot T$	$1234 < T < 2000 \mathrm{K}$
	$c_p = 259.8 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$	
	$C_p = 28.024 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 221.6, H_{\rm l} = 323.2, \Delta H = 101.6$	

Table 43: Specific enthalpy results of silver, H in kJ·kg<sup>-1</sup>, polynomials taken from [78].



Figure 43: Specific enthalpy of silver as a function of temperature.
## Resistivity

molg taken nom [10].			
	$T_m = 1234.93 \mathrm{K}  [26]$		
solid	$ \rho_{\rm IG}(T) = -2.9415 \times 10^{-3} $		
	$+7.2481 \times 10^{-5} \cdot T$	$1100{\rm K} < T < 1234{\rm K}$	
liquid	$\rho_{\rm IG}(T) = 0.0554 + 8.3336 \times 10^{-5} \cdot T$	$1234{\rm K} < T < 1950{\rm K}$	
	$\rho(T) = 4.592 \times 10^{-2} + 9.856 \times 10^{-5} \cdot T$		
	$\rho_{\rm IG,s} = 0.0865, \ \rho_{\rm IG,l} = 0.1582$		
	$\Delta \rho_{ m IG,s-l} = 0.0717$		
	$\rho_{\rm s}=0.090$ , $\rho_{\rm l}=0.168,\Delta\rho_{\rm s-l}=0.078$		

Table 44: Electrical resistivity results of silver,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{\rm IG}$  taken from [78].



Figure 44: Electrical resistivity of silver as a function of temperature. Dashed line: values including volume expansion.

# A: Basic survey

#### The Element

Symbol:	Та
Atomic number:	73
Group:	Transition metal
Atomic weight: [6]	180.94788(2) u
Ground state electron configuration:	$[Xe]4f^{14}5d^{3}6s^{2}$
Crystal structure at $25^{\circ}$ C: [7]	Cubic bcc with $a = 3.3013$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$16.4 \mathrm{g} \cdot \mathrm{cm}^{-3}$
Melting point: [6]	$3017^{\circ}C$
Boiling point: [6]	$5458^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.140 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.36 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	156-186 (stable: 181)

## Introduction

Tantalum of high purity is a very soft metal of grayish-blue color, that is dense, ductile and malleable and can therefore be fabricated easily. Traces of interstitial impurities such as carbon, hydrogen, nitrogen and oxygen harden the metal significantly. The metal is chemically inert to most chemicals (inorganic and organic) at medium temperatures, protected by a tantalum pentoxide ( $Ta_2O_5$ ) passivating film. [11]

## History

Swedish chemist Anders Gustaf Ekeberg<sup>11</sup> (1767-1813) examined a sample from a feldspar quarry. On this occasion he discovered a mineral with a new and at the time unknown element. In 1802 he isolated its oxidic compound and after recognizing its nearly absolute resistance to acids, he named the element *tantalum*, after King Tantalus of Lydia, son of Zeus in Greek mythology, condemned to eternal suffering from hunger and thirst in Hades. [... relating to the fact that the oxide of this metal is incapable of feeding itself even in the middle of a surplus of acid].

Four years later, Charles Hatchett isolated niobium - or as he named it, columbium. The subsequent quarrels over tantalum and columbium are

<sup>&</sup>lt;sup>11</sup>Ekeberg is also remembered for teaching chemistry to Jöns Jacob Berzelius and for his determination to rid Swedish chemistry from the phlogiston theory (i.e., all flammable materials supposedly contain a substance - phlogiston - which is released during combustion, an idea similar to the aether theory.)

described in chapter 3.11 **Niobium**, page 70. But in the 1840s Ekeberg was finally given credit for the discovery. [9]

 Ekeberg, Anders Gustaf (1767-1813) Hatchett, Charles (1765-1847) Berzelius, Jöns Jakob<br/> (1779-1848)

## Common Uses

- A major quantity of tantalum is used in the production of electronic components, mainly tantalum capacitors. There tantalum metal powder as well as dielectric  $Ta_2O_5$  are used in the fabrication of capacitors. [31]
- In air- and spacecrafts, alloys like Ta-8W-2Hf (*T-111*) and Ta-9.6W-2.4Hf-0.01C (*T-222*) are utilized in nozzles, as combustion chambers' inner cladding as well as for the hull of rockets. Good machining and high-temperature properties are prime factors for their usage. [13]
- Because of their nontoxicity and compatibility with tissue, tantalum is used in surgery in the form of small balls or wires. They are applied as markers for controlling the position or function in organs, bones or implants by X-rays. Its bioinertness is also taken advantage of in clips for rapid occlusion of vessels. [31]
- Tantalum nitride (TaN) films are used as diffusion barriers in semiconductor technology and as a protective coating against moisture. [31]
- Tantalates find application in the form of lithium tantalate (LiTaO<sub>3</sub>) single crystal wafers in the production of surface acoustic wave (SAW) filters for HF applications. In combination with lithium niobate it is used for making waveguides, frequency doublers and optical switches. Diagnostic medicine uses yttrium tantalate (YTaO<sub>3</sub>) as a phosphor for the amplification of X-rays in order to reduce the dose of radiation necessary. [31]
- Superalloys are another important sector of usages for tantalum. Alloy *PWA 1480* is a nickel-based alloy (Ni-10Cr-5Co-4W-12Ta-5.0All 1.5Ti), used for turbine blades and vane parts. [15]
- Tantalum-tungsten alloys are widely used in the chemical industry, due to the metal costs in the form of claddings and coatings. Ta-2.5W is used for for heat exchangers, linings for towers, valves, and tubing, Ta-7.5W is a typical powder metallurgy product, cold drawn into wire for springs and elastic parts, made to persist under severe acid exposure. Ta-10W is utilized in aerospace application, functional in temperatures up to 2480°C, such as rocket engine extension skirts, hot gas metering valves and fasteners. [12]

• Tantalum carbides (TaC, Ta<sub>2</sub>C) are chemically very stable, and are mostly combined with WC-Co cemented carbides. Up to 15 wt% tantalum carbides improve performance characteristics of cutting tools, generally improving resistance to shock, wear and oxidation as well as high-temperature hardness. [79]

## Relevance in Life

Tantalum plays no biological role, is neither toxic nor has any other effect on the human body, but one study exists linking tantalum to local sarcomas. [17]

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 45: Volume expansion results of tantalum, polynomials taken from [80]. Density at 20 °C: 16654 kg·m<sup>-3</sup> [18].

	$T_m = 3270 \mathrm{K} [80]$	
solid	$V/V_0(T) = -1.3393 + 2.4883 \times 10^{-3} \cdot T$	
	$-0.86945 \times 10^{-6} \cdot T^2 + 0.1026 \times 10^{-9} \cdot T^3$	$2750{\rm K} < T < 3250{\rm K}$
liquid	$V/V_0(T) = 0.95634 + 5.6199 \times 10^{-5} \cdot T$	
	$-2.6656 \times 10^{-9} \cdot T^2 + 3.7798 \times 10^{-13} \cdot T^3$	$3300{\rm K} < T < 5000{\rm K}$



Figure 45: Volume expansion of tantalum.

## Enthalpy

0011011 11 01		
	$T_m = 3270 \mathrm{K} [80]$	
	at.wt. = 180.9479 [18]	
solid	$H(T) = -255.9 + 0.2429 \cdot T$	$2500{\rm K} < T < 3270{\rm K}$
	$c_p = 242.9  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
	$C_p = 43.952 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
liquid	$H(T) = -26.32 + 0.226 \cdot T$	$3270{\rm K} < T < 5000{\rm K}$
	$c_p = 226 \mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$	
	$C_p = 40.895 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 538.4, H_{\rm l} = 712.7, \Delta H = 147.3$	

Table 46: Specific enthalpy results of tantalum, H in kJ·kg<sup>-1</sup>, polynomials taken from [81].



Figure 46: Specific enthalpy of tantalum as a function of temperature.

## Resistivity

10	for mold taken from [01].			
		$T_m = 3270 \mathrm{K} [80]$		
ſ	solid	$\rho_{\rm IG}(T) = 0.2307 + 2.7007 \times 10^{-4} \cdot T$	$2500{\rm K} < T < 3270{\rm K}$	
		$\rho(T) = 0.098 + 3.394 \times 10^{-4} \cdot T$	$2750{\rm K}{<}T < 3250{\rm K}{}$	
	liquid	$\rho_{\rm IG}(T) = 1.3401 - 6.243 \times 10^{-5} \cdot T$		
		$+5.503 \times 10^{-9} \cdot T^2$	$3300{\rm K} < T < 5000{\rm K}$	
		$\rho(T) = 1.19622 + 4.40644 \times 10^{-5} \cdot T$		
ſ		$\rho_{\rm IG,s} = 1.114, \ \rho_{\rm IG,l} = 1.195$		
		$\Delta \rho_{\rm IG,s-l} = 0.081$		
ſ		$\rho_{\rm s} = 1.212, \ \rho_{\rm l} = 1.344, \ \Delta \rho_{\rm s-l} = 0.132$		

Table 47: Electrical resistivity results of tantalum,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{\rm IG}$  taken from [81].



Figure 47: Electrical resistivity of tantalum as a function of temperature. Dashed line: values including volume expansion.

# A: Basic survey

#### The Element

```
Symbol:
                                                         Ti
Atomic number:
                                                         22
                                                         Metal
Group:
                                                         47.867(1) u
Atomic weight: [6]
                                                         [Xe]4f^{14}5d^{10}6s^{2}6p^{1}
Ground state electron configuration:
Crystal structure at 25^{\circ}C: [7]
                                                         hcp with a = 2.9508 Å
                                                           and c = 4.6855 Å
Allotropy: [8]
                                                         \alpha-Ti: hcp; \beta-Ti: bcc
                                                         Transition \alpha \rightarrow \beta at 882.5°C
                                                        4.51 \text{ g} \cdot \text{cm}^{-3}
Density at 20^{\circ}C: [6]
Melting point: [6]
                                                         1668^{\circ}C
Boiling point: [6]
                                                         3287^{\circ}C
Specific heat c_p at 25°C, 1 bar: [6]
                                                         0.523 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}
                                                         25.060 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
Molar heat C_p at 25°C, 1 bar: [6]
Isotope range: [9]
                                                         39-57 (stable: 46-50)
```

# Introduction

Titanium is a light but hard paramagnetic metal with a silvery-gray luster. The metal is ductile when interstitial alloying elements (i.e. H, C, N and O) are missing. Titanium is neither a good conductor of heat nor of electricity. The liquid phase near the melting point is highly corrosive and reactive toward most materials, so contamination always occurs. Pure titanium is highly chemically reactive, but forms an impenetrable and adherent protective oxide layer of *rutile* (TiO<sub>2</sub>) in oxygenic environment. The metal dissolves, among others, in hydrogen fluoride and hot strong mineral acids like HCl and  $H_2SO_4$ . [11]

# History

William Gregor (1761-1817), a vicar in Cornwall, England, was a passionate mineralogist. One day in 1791 he discovered a black sand<sup>12</sup>, analyzed it and identified the material as a compound of magnetite and an unknown material he was able to reduce to its oxidic form, a red powder. Based on the location, he named the material *menachanite* and published his results. Independently, German chemist Martin Heinrich Klaproth (1743-1817) in

 $<sup>^{12}</sup>$ Today's  $ilmenite, \, {\rm FeTiO_3}$ 

1795 prepared the same oxide from Hungarian rutile. He decided to give it a name independent from its origin or properties, so he chose *titanium*, meaning 'Earth' in Latin. The term is also related to the Titans of the Greek mythology. The Titans were children of Uranos<sup>13</sup> and Gaia, the earth goddess. [10] [9] [11]

Gregor, William (1761-1817) Klaproth, Martin Heinrich (1743-1817)

#### Common Uses

The most common use of titanium is in alloys with other metals, utilizing its lightness, strength and corrosion resistance. The field of application is wide, so only a short overview can be given:

- Titanium oxide (TiO<sub>2</sub>) is a white pigment of high refractive index and opacity used for paints, plastics, fine paper and glazes on porcelain. In electronics, TiO<sub>2</sub> is applied as a light-sensitive semiconductor in the near UV range. The property to absorb UV radiation and its non-toxicity are also employed in cosmetic powders, soaps, toothpaste and in other products of the cosmetic industry. [9] [16]
- Titanium with its protective oxide layer is bioinert, i.e., no metal ions are dissolved in biological environments. Implants (for example in jaws, teeth), pins for bone fixture as well as surgical instruments are for this reason made of titanium or the alloy Ti-6Al-4V ( $\alpha + \beta$ , Timetal<sup>®</sup> 6-4). Another aspect is its non-magnetic property, enabling MRI. [9]
- The before mentioned alloy Ti-6Al-4V is by far the most commonly used  $\alpha + \beta$  titanium alloy. Major applications of these alloys are aircraft structural parts and rotating and non-rotating parts in aeroengines. Parts like booster case, fan disk, compressor spool, tail plug and fan vane frame of the GE-90 aero-engine used for the Boeing 777 are made of this alloy. Restrictions on usability are imposed only by means of the maximum operating temperature of about 400°C, with creep resistance reaching up to 325°C. [82] [11]
- Commercially pure (CP) titanium<sup>14</sup> features excellent corrosion resistance, preferably used for process equipment in the chemical and petrochemical industries, e.g heat exchangers, surface condensers and pressure vessels. *Ti-0.2Pd* (Ti 0.25O(max) 0.30Fe(max) 0.12-0.25Pd, Grade 7), *Ti-0.05Pd* (Ti 0.18O(max) 0.20Fe(max) 0.04-0.08Pd, Grade 17), *Ti-0.1Ru* (Ti 0.18O(max) 0.20Fe(max) 0.08-0.14Ru, Grade 27) belong also to this type. [82]

 $<sup>^{13}\,</sup>Uranos$  is the Roman version of the Greek god of the sky, after whom he also named another element he had discovered in 1789: *uranium* - named after the planet *Uranus* in first place, which in turn bears the deity's name.

 $<sup>^{14}</sup>$  Pure  $\alpha$  titanium with maximum traces of oxygen (0.18-0.4) and iron (0.2-0.5), Grade 1-4, typical values of C and N are 0.08-0.10 and 0.03-0.05, respectively. All figures represent wt.%. [82]

- $\alpha$  titanium alloys, such as Ti-0.3Mo-0.9Ni, Ti-3Al-2.5V, Ti-3Al-2.5V-0.05Pd, Ti-3Al-2.5V-0.1Ru and Ti-5Al-2.5Sn, exhibit excellent corrosion and oxidation behaviour as well as deformability. They have the same field of application as CP titanium. A further use (e.g. of Ti-5Al-2.5Sn) is in cryogenic tanks for spacecrafts. [83] [82]
- Ti-10V-2Fe-3Al (β, Timetal<sup>®</sup> 10-2-3) is an alloy that combines ductility, strength, fracture toughness and high cycle fatigue strength. Typically critical aircraft structures are forged from this material, a practical example is the landing gear truck beams for the Boeing 777. [47] [11]
- High temperature alloys employed in engines are near  $\alpha$  alloys like  $IMI \ 834$  (Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.3Si-0.05C), Ti-6242 (Ti-6Al-2Sn-4Zr-2Mo-0.08Si),  $Timetal^{\textcircled{R}} \ 834$  (Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C) and  $Timetal^{\textcircled{R}} \ 1100^{-15}$  (Ti-6Al-2.7Sn-4Zr-0.4Mo-0.45Si). They can operate in a range of 500 600°C, offering tensile strength, creep resistance and fracture toughness. Applications include blades and disks in the compressor section (high pressure stages,  $T > 350^{\circ}$ C) of aero-engines. [47] [11] [82]
- Ti-15-3 (Ti-15V-3Cr-3Sn-3Al) is like the above mentioned  $Timetal^{\textcircled{B}}$ 10-2-3 (Ti-10-2-3) also another  $\beta$  titanium alloy, but a heavily stabilized one. The alloy is used for the fabrication of nut clips and springs - low modulus of elasticity and relatively high yield stress are its prime properties. *Beta 21S* (Ti-15Mo-2.7Nb-3Al-0.2Si) is another alloy of this category, offering excellent resistance against oxidation. Used for nacelle structure parts like exhaust plugs and nozzles. [82]
- $\gamma$  alloys (titanium aluminides) such as Ti-48Al-2Cr-2Nb and Ti-47Al-2Mn-2Nb+0.8vol%B are of selective use, e.g. turbocharger rotors, exhaust valves and low pressure turbine blades in aero-engines. Creep strength is appropriate up to 750°C (max), and surface stability is at a height. [82]
- Nb-47Ti alloy is a low temperature (4.2 K), high current superconductor (110 A at 5 T, [84]), assembled as filaments (diameter less than 30  $\mu$ m, [85]) in a copper matrix. Applications are magnets for MRI, NMR, particle accelerators, electric power conditioning, minesweeping and ore separation. [82]

## Relevance in Life

Titanium is not an essential element, neither for humans nor for animals, it is non-toxic, as are its compounds. Its protective oxide layer is biocompatible, therefore it is used for implants, fixtures as well as for surgical

 $<sup>^{15}\</sup>mathrm{According}$  to [82], this alloy is no longer available on the market.

instruments. Exposure and inhalation of larger quantities of  $\rm TiO_2$  can cause lung fibrosis. [17]

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 48: Volume expansion results of titanium [60]. Density at 20 °C: 4540  $\rm kg\cdot m^{-3}$  [18].

	$T_m = 1943 \mathrm{K} [19]$	
liquid	$V/V_0(T) = 0.938 + 6.108 \times 10^{-5} \cdot T$	$1943{\rm K} < T < 3000{\rm K}$



Figure 48: Volume expansion of titanium.

## Enthalpy

tallen nom [00] but have been corrected where necessary.			
	$T_m = 1943 \mathrm{K}  [19]$		
	at.wt. = 47.867 [18]		
solid	$H(T) = -187.758 + 0.607 \cdot T$	$473{\rm K} < T < 880{\rm K}$	
	$H(T) = 358.284 - 0.639 \cdot T$		
	$+7.134 \times 10^{-4} \cdot T^2$	$880{\rm K} < T < 1090{\rm K}$	
	$H(T) = -2917.626 + 5.127 \cdot T$		
	$-1.820 \times 10^{-3} \cdot T^2$	$1090{\rm K} < T < 1250{\rm K}$	
	$H(T) = -62.831 + 0.568 \cdot T$	$1250{\rm K} < T < 1370{\rm K}$	
	H(T) = -769.969 + T	$1700{\rm K} < T < 1943{\rm K}$	
	$c_p = 1000  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$		
	$C_p = 47.867  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$		
liquid	$\hat{H(T)} = -608.296 + 1.043 \cdot T$	$1943{\rm K} < T < 2500{\rm K}$	
	$c_p = 1043  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$		
	$C_p = 49.925 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$		
	$H_{\rm s} = 1173, H_{\rm l} = 1418, \Delta H = 245$		

Table 49: Specific enthalpy results of titanium, H in kJ·kg<sup>-1</sup>, polynomials are taken from [63] but have been corrected where necessary.



Figure 49: Specific enthalpy of titanium as a function of temperature. Dotted line: temperature of the  $\alpha \rightarrow \beta$  transformation (1166) [86].

## Resistivity

	$T_m = 1943 \mathrm{K}  [19]$	
solid	$\rho_{\rm IG}(T) = -0.382 + 3.070 \times 10^{-3} \cdot T$	
	$-1.098 \times 10^{-6} \cdot T^2$	$473 \mathrm{K} < T < 1130 \mathrm{K}$
	$\rho_{\rm IG}(T) = 50.11699 - 0.10947 \cdot T$	
	$+8.21216 \times 10^{-5} \cdot T^2$	
	$-2.05115 \times 10^{-8} \cdot T^3$	$1130 \mathrm{K} < T < 1340 \mathrm{K}$
	$\rho_{\rm IG}(T) = 1.282 + 1.850 \times 10^{-4} \cdot T$	$1640 \mathrm{K} < T < 1943 \mathrm{K}$
liquid	$\rho_{\rm IG}(T) = 1.794 - 7.830 \times 10^{-5} \cdot T$	$1943{\rm K} < T < 2500{\rm K}$
	$\rho(T) = 1.7063 + 1.483 \times 10^{-5} \cdot T$	
	$\rho_{\rm IG,s} = 1.641,  \rho_{\rm IG,l} = 1.642$	
	$\Delta \rho_{\mathrm{IG,s-l}} = 0.001$	
	$ ho_{ m l} = 1.735$	

Table 50: Electrical resistivity results of titanium,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{IG}$  are taken from [63] but have been corrected where necessary.



Figure 50: Electrical resistivity of titanium as a function of temperature. Dotted line: temperature of the  $\alpha \rightarrow \beta$  transformation (1166) [86]. Dashed line: values including volume expansion.

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# A: Basic survey

#### The Element

Symbol:	W
Atomic number:	74
Group:	Transition metal
Atomic weight: [6]	183.84(1)
Ground state electron configuration:	$[Xe]4f^{14}5d^46s^2$
Crystal structure at $25^{\circ}$ C: [7]	Cubic bcc with $a = 3.1652$ Å
<b>Density at</b> $20^{\circ}$ C: [6]	$19.3 \mathrm{g\cdot cm^{-3}}$
Melting point: [6]	$3422^{\circ}\mathrm{C}$
Boiling point: [6]	$5555^{\circ}\mathrm{C}$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.132 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$24.27 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	158-190 (stable: 180, 182,
	186)

## Introduction

Tungsten of high purity is a rather soft and ductile metal that can be cut, forged, drawn, and extruded. Its color varies from steel-gray to a white shine like tin. Traces of interstitial impurities (e.g. oxygen or carbon) result in considerable hardness and brittleness which the metal is known for. Its high melting point and the lowest vapor pressure at T > 1650 °C as well as its highest tensile strength and creep resistance at high temperatures are welcome properties for very-high-temperature vacuum furnaces and arc lamp electrodes.

Corrosion resistance to most chemicals is excellent; it is attacked by concentrated strong mineral acids (e.g. nitric acid, aqua regia) and aerated molten salts (e.g. KOH,  $Na_2CO_3$ ) slightly but dissolves in a molten mixture of NaNO<sub>3</sub> and NaOH. [11] [9]

## History

The origin of the German name for tungsten, *Wolfram*, goes way back to the  $16^{\text{th}}$  century. While melting tin ores<sup>16</sup>, smelters observed that sometimes instead of slag covering the molten tin, a foam<sup>17</sup> appeared, loaded with tin dropplets, resulting in less tin recovery. Superstitiousness caused them to make a wolf in the ore - who ate the tin - responsible, therefore the foam

<sup>&</sup>lt;sup>16</sup>Ideal metallurgical reaction:  $SnO_2 + 2 C \rightarrow Sn_{lig.} + 2 CO$ 

 $<sup>^{17}</sup>$ Foam occurs when the tin ore contains *wolframite*, (Fe,Mn)WO<sub>4</sub>.

was believed to be the foam of that wolf, Wolf Rahm in German.

In 1751, Swedish scientist Axel Fredrik Cronstedt ( $\rightarrow$  Nickel, page 62) researched a mineral containing lime and an unknown earth, and called it *tungsten*, from the Swedish *tung sten* meaning 'heavy stone'. The mineral is today known as *scheelite* (CaWO<sub>4</sub>), named in honor of Carl W. Scheele who analyzed the mineral in 1781.

Finally, two Spanish brothers Juan José (1755-1796) and Fausto d'Elhuyar (1756-1833) discovered in 1783, that *scheelite* and *worframite* contained the identical oxidic form of tungsten and thereafter isolated the metallic form, although not its pure form. They also named the metal *wolfromium*. Depending on the particular national scientific community, either 'tungsten' or 'wolfram' were used. In the 19<sup>th</sup> century, Berzelsius finally recommended wolfram and accordingly the symbol W, as it still remains. But the different names were too well established in the different countries' usage to allow for standardization of the naming to 'wolfram', which was last attempted by the INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY in 1960. [9] [10]

d'Elhuyar, Juan José (1755-1796) d'Elhuyar, Fausto (1756-1833) Cronstedt, Axel Fredrik (1722-1756) Scheele, Carl Wilhelm (1742-1786) Berzelius, Jöns Jakob (1779-1848)

## Common Uses

The major usage of tungsten is as hard metal, or cemented carbide, a powder metallurgy product (60 wt% and more relating to consumption). Graphite and tungsten are melted together to form a eutectic mixture of WC and W<sub>2</sub>C. This brittle material is ground and then bonded with molten cobalt, resulting in a hard, tough and wear-resistant product. It is utilized as tool material for wire drawing, mining and stone cutting as well as gas, oil and water drilling. Other known uses are in engineering machinery such as drilling and turning. [11] [9]

Further applications are:

- In lighting application, filaments in incandescent lamps are mainly made of non-sag tungsten (NS-W, also called doped tungsten), whereas special shock and vibration-resistant lamps utilize W-ThO<sub>2</sub> or W-Re wires. In high-intensity discharge lamps, electrodes made of coated NS-W, W-ThO<sub>2</sub>, NS-W-ThO<sub>2</sub> and W-La<sub>2</sub>O<sub>3</sub> are employed. [87]
- The linear thermal expansion coefficient of tungsten is about the same as that of borosilicate glass, therefore it can be utilized in glass-to-metal seals. [11]
- In microelectronic production, W-10Ti is used as a sputtering target for devices like DRAM. [13]
- Tungsten heavy metal are two-phase tungsten alloys, either magnetic W-Ni-Fe (1-7 wt% Ni, 0.8-3 wt% Fe,0-4 wt% Mo) or nonmagnetic W-

Ni-Cu (1-7 wt% Ni, 0.5-3 wt% Cu, 0-7 wt% Fe). Produced by powder metallurgy, the materials' modulus of elasticity is high, as well as its electrical and thermal conductivity. They find their uses in radiation shielding due to their good absorption properties for  $\gamma$ - and X-rays. [13]

- Compounds of tungsten and sulfur (WS<sub>2</sub>) as well as of tungsten and selenium (WSe<sub>2</sub>) are used as oil-soluble lubricants, where WS<sub>2</sub> can be used under extreme conditions (pressure, temperature, vacuum). WS<sub>2</sub> is also utilized as catalyst for the desulfurization of mineral oil. [31]
- Welding electrodes, employed for inert gas welding (TIG) and plasma welding, consist of W, W-ThO<sub>2</sub>, W-La<sub>2</sub>O<sub>3</sub> and W-ZrO<sub>2</sub>. [87]
- Tungsten-tantalum alloys combine corrosion resistance and elasticity properties of tantalum with advanced strength and strength at high-temperatures. E.g., tantalum alloys with 7-8 wt% tungsten are used for springs operating in strongly corrosive environments. [13]
- Tungsten thermocouples, exercisable up to 2600 °C, used in combustion chambers of turbine engines or reactors and high-temperature furnaces mostly use W-5Re/W-26Re and W-3Re/W-25Re combinations. [87]
- Tungsten has a wide range of catalytic applications: Colloidal WO<sub>3</sub> is used for the photocatalytic reduction of organic compounds, W<sub>29</sub>O<sub>58</sub> catalyzes among others hydrogenation, hydroxylation and epoxydation, the reformation of n-heptane as well as the formation of hydrogen from water utilize WC. [31]
- Tungsten-copper and tungsten-silver composites are also called 'pseudoalloys', since their mutual solubility is practically nonexistent. They are used for circuit breakers, resistance welding electrodes and as electrodes for electrical discharge machining. [87]
- Tungsten bronzes are  $M_xWO_3$ -compounds of (alkali) metal cations M (e.g. H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>), x between 0 and 1. They are used as colored pigments, catalysts for  $CO_x$  oxidation in fuel cells and as electrochromic coating for glasses, the property varying from transparent to reflecting depending on the applied voltage. [31]

# Relevance in Life

Tungsten and its compounds are generally non-toxic and play practically no biological role. However, some compounds like tungsten hexafluoride (WF<sub>6</sub>) are poisonous. Anaerobic bacteria, especially *clostridium*, use the element to assist redox reactions (e.g.  $CO_2$  fixation). [9] [31]

# B: Thermophysical properties obtained by Pulse - heating

Volume expansion

Table 51: Volume expansion results of tungsten, polynomials taken from [88]. Density at 20 °C: 19300 kg·m<sup>-3</sup> [18].

	$T_m = 3687 \mathrm{K} [19]$	
liquid	$V/V_0(T) = 0.95062 + 6.344 \times 10^{-5} \cdot T$	$3680{\rm K} < T < 5000{\rm K}$
	$V/V_0(T) = 1.34989 - 1.0333 \times 10^{-4} \cdot T$	
	$+1.73957 \times 10^{-8} \cdot T^2$	$5000{\rm K} < T < 9000{\rm K}$



Figure 51: Volume expansion of tungsten.

## Enthalpy

ion n	L	1-	
		$T_m = 3687 \mathrm{K} [19]$	
		at.wt. = 183.84 [18]	
so	lid	$H(T) = -39.272 + 0.133 \cdot T$	
		$+4.195 \times 10^{-6} \cdot T^2$	$423{\rm K} < T < 1723{\rm K}$
		$H(T) = 83.342 + 0.011 \cdot T$	
		$+3.576 \times 10^{-5} \cdot T^2$	$2300{\rm K} < T < 3687{\rm K}$
liq	uid	$H(T) = -97.894 + 0.279 \cdot T$	$3687{\rm K} < T < 5400{\rm K}$
		$c_p = 279  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	
		$C_p = 51.291  \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	
		$H_{\rm s} = 610,  H_{\rm l} = 931,  \Delta H = 321$	

Table 52: Specific enthalpy results of tungsten, H in kJ·kg<sup>-1</sup>, polynomials taken from [63].



Figure 52: Specific enthalpy of tungsten as a function of temperature.

## Resistivity

LU.	or mold taken from [05], vorume consideration. [00].			
		$T_m = 3687 \mathrm{K} [19]$		
	solid	$\rho_{\rm IG}(T) = -0.021 + 2.467 \times 10^{-4} \cdot T$		
		$+1.201 \times 10^{-8} \cdot T^2$	$423{\rm K} < T < 1723{\rm K}$	
		$\rho_{\rm IG}(T) = -0.059 + 3.166 \times 10^{-4} \cdot T$	$2390{\rm K} < T < 3687{\rm K}$	
	liquid	$\rho_{\rm IG}(T) = 1.833 - 2.573 \times 10^{-4} \cdot T$		
		$+2.169 \times 10^{-8} \cdot T^2$	$3687{\rm K} < T < 5400{\rm K}$	
		$\rho(T) = 2.313 - 4.585 \times 10^{-4} \cdot T$		
		$+5.65 \times 10^{-8} \cdot T^2$		
		$\rho_{\rm IG,s} = 1.10,  \rho_{\rm IG,l} = 1.18$		
		$\Delta \rho_{\rm IG,s-l} = 0.08$		
		$ \rho_{\rm l} = 1.39 $		

Table 53: Electrical resistivity results of tungsten,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{IG}$  taken from [63], volume consideration: [88].



Figure 53: Electrical resistivity of tungsten as a function of temperature. Dashed line: values including volume expansion.

# A: Basic survey

#### The Element

Symbol:	V
Atomic number:	23
Group:	Transition metal
Atomic weight: [6]	50.9415(1)
Ground state electron configuration:	$[Ar]3d^34s^2$
Crystal structure at $25^{\circ}$ C: [7]	Cubic bcc with $a = 3.03$ Å
<b>Density at</b> 18.7°C: [6]	$6.0 \mathrm{g} \cdot \mathrm{cm}^{-3}$
Melting point: [6]	$1910^{\circ}\mathrm{C}$
Boiling point: [6]	$3407^{\circ}C$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.489 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$24.89 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	43-60 (stable: 51)

## Introduction

Vanadium is a soft and ductile metal with a silvery whitish-gray color. While its corrosion resistance against bromine water, alkalis and salt water is good, it dissolves in aqua regia and hydrobromic acid. Above 660 °C the metal starts to oxidate. About 90% of vanadium consumption is related to metallurgy; its compounds find applications as catalysts in the chemical industry. [11] [9]

## History

Andrés Manuel del Rio (1764-1849), of Spanish origin, who was well connected to the great scientists of that time (Lavoisier, von Humboldt) became a professor at the mining college *Real Seminario de Mineria* in Mexico City in 1973. By researching a lead containing mineral known as *Plomo pardo de Zimapán* (vanadinite), he discovered a further component of an unknown element. It resembled the resently discovered element chromium, so he first named it *pan-chromium* but later changed to *erythronium*, from the Greek word for red, *erythros*. Still he was not absolutely sure of his discovery. Later published results of investigations of chromium misleadingly made him believe his metal was indeed chromium.

Nils Gabriel Sefström (1787-1845), a Swedish doctor, was also a competent geologist and mineralogist. This quality made him the manager of a mining and metallurgical school in Falun in 1922. While studying a cold, brittleness-free iron bar made of a less pure iron ore in 1830, he discovered a metal resembling chromium and uranium and declared it to be a new element - *vandium*. The name is derived from *Vanadis*, goddess of youth and beauty in Scandinavian mythology, and was chosen because vanadium compounds have beautiful colors. [9] [10] [11]

del Rio, Andrés Manuel (1764-1849) Sefström, Nils Gabriel (1787-1845) von Humboldt, Alexander (1769-1859) Lavoisier, Antoine (1743-1794)

## Common Uses

As mentioned before, metallurgy consumes about 90% of vanadium production, due to its structural strength ( $\beta$  stabilizer).

- The addition of vanadium improves the properties of titanium. Ti -Al6 -V4 is the most important alloy to mention, mainly used as a wrought alloy and casting alloy in airframe construction for loadbearing components and fixing devices. Additional applications include jet engine blades. Other alloys of similar strength are TiAl3V2.5, TiV15Cr3Sn3Al3, Ti -V10 -Fe2 -Al3 and TiAl6V6Sn2. [13]
- 2V-49Co-49Fe (also known as *Vanadium Permendur*, 2V-Permendur, Supermendur) is a soft magnetic alloy, usually cold rolled to a thickness of 0.64 to 0.15 mm. Used for various lamination configurations for rotors, stators and transformers. [12]
- 6150 chromium-vanadium steel (Fe -0.52C -0.84Mn -0.023P -0.025S -1.03Cr -0.23V) is an alloy used for springs utilized in environments of demanding temperatures (e.g. valve springs) as well as for gears, crankshafts, wrenches and rams. [15] [89]
- Vanadium pentoxide  $(V_2O_5)$ , a yellow-brown to orange solid, is used as catalyst among others in the production of sulfuric acid (contact process). Further applications are as a developer for photos, as textile and ceramics dyestuff. It is used in the production of artificial rubber. When applied on glass it acts as a UV filter. [10]
- Vanadium dioxide (VO<sub>2</sub>) functions as an IR filter when applied on glass. [42]
- ZrCMn and ZrVFe alloys are used as gettering materials for gas purification and for improving vacuums. The content of vanadium is up to 30%. [13]
- *CPM 10V* (Fe 2.45C 5.25Cr 1.3Mo 9.75V 0.07S) is a highly wear resistant cold-work tool steel, manufactured through *powder metallurgy*. The alloy finds application as punches and dies for cold-forming and stamping operations, tools for compacting powder metal as well as for wood working and rolls for roll-forming. [15]

- The intermetallic phase ZrV<sub>2</sub>, partially substituted by Ni, Cr, Ti or Mn, is used as electrode material in metal hydride/nickel hydroxide batteries. [13]
- Vanadium-gallium alloys (V<sub>3</sub>Ga) as well as vanadium-niobium alloys and vanadium-hafnium/zirconium alloys posses good superconducting properties. [13]

## Relevance in Life

Vanadium powder and dust, as well as most of its oxidic compounds are explosive when exposed to heat and air. They are toxic when inhaled. Poisoning occurs when vanadium chloride compounds are ingested. Skin contact leads to strong irritation.

Vanadium is essential for certain bacteria and microorganisms as well for mammals, but as far as we know not for humans. In the body it is widely distributed, mainly in bone, kidney, liver, and spleen. The effects of insulin are enhanced by vanadium compounds. Carcinogenic activity has been shown though inhalation of vanadium pentoxide (in mice), therefore the metal was classified by the IARC<sup>18</sup> as a possible carcinogen. [17] [10]

 $<sup>^{18}\</sup>mathrm{IARC}...\mathrm{International}$  Agency for Research on Cancer

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 54: Volume expansion results of vanadium [43]. Density at 18.7 °C: 6110 kg·m^{-3} [18].

	$T_m = 2199 \mathrm{K}, \mathrm{rec.:}  T_m = 2201 \mathrm{K} [90]$	
solid	$V/V_0(T) = 0.990 + 3.137 \times 10^{-5} \cdot T$	
	$+1.262 \times 10^{-9} \cdot T^2$	$1200{\rm K} < T < 2199{\rm K}$
liquid	$V/V_0(T) = 0.910 + 7.727 \times 10^{-5} \cdot T$	$2199{\rm K} < T < 2900{\rm K}$



Figure 54: Volume expansion of vanadium.

## Enthalpy

union no.	[0]]	
	$T_m = 2199 \mathrm{K}, \mathrm{rec.:}  T_m = 2201 \mathrm{K} [90]$	
	at.wt. = 50.942 [18]	
solid	$H(T) = -833.711 + 0.932 \cdot T$	$1800{\rm K} < T < 2199{\rm K}$
	$c_p = 932 \mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$	
	$C_p = 47.478 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
liquid	$H(T) = -503.525 + 0.964 \cdot T$	$2199{\rm K} < T < 2900{\rm K}$
	$c_p = 964 \mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$	
	$C_p = 49.108 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	
	$H_{\rm s} = 1210, H_{\rm l} = 1616, \Delta H = 406$	

Table 55: Specific enthalpy results of vanadium, H in kJ·kg<sup>-1</sup>, polynomials taken from [91].



Figure 55: Specific enthalpy of vanadium as a function of temperature.

## Resistivity

ior mong		
	$T_m = 2199 \mathrm{K}, \mathrm{rec.:}  T_m = 2201 \mathrm{K} [90]$	
solid	$\rho_{\rm IG}(T) = -0.22754 + 0.112 \times 10^{-2} \cdot T$	
	$-2.15791 \times 10^{-7} \cdot T^2$	$1800{\rm K} < T < 2199{\rm K}$
	$\rho(T) = -0.280 + 0.118 \times 10^{-2} \cdot T$	
	$-2.174 \times 10^{-7} \cdot T^2$	
liquid	$\rho_{\rm IG}(T) = 1.486 - 2.305 \times 10^{-4} \cdot T$	
	$+5.188 \times 10^{-8} \cdot T^2$	$2199{\rm K} < T < 2900{\rm K}$
	$\rho(T) = 1.418 - 1.730 \times 10^{-4} \cdot T$	
	$+6.012 \times 10^{-8} \cdot T^2$	
	$\rho_{\rm IG,s} = 1.195, \ \rho_{\rm IG,l} = 1.230$	
	$\Delta \rho_{\rm IG,s-l} = 0.035$	
	$\rho_{\rm s}=1.269,\rho_{\rm l}=1.328,\Delta\rho_{\rm s-l}=0.059$	

Table 56: Electrical resistivity results of vanadium,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{IG}$  taken from [91].



Figure 56: Electrical resistivity of vanadium as a function of temperature. Dashed line: values including volume expansion.

3.21 Zinc

## A: Basic survey

#### The Element

Symbol:	Zn
Atomic number:	30
Group:	Transition metal
Atomic weight: [6]	65.409(4) u
Ground state electron configuration:	$[Ar]3d^{10}4s^2$
Crystal structure at 25°C: [7]	hcp with $a = 2.6649$ Å
	and $c = 4.9468$ Å
<b>Density at</b> $25^{\circ}$ C: [6]	$7.134 \mathrm{g}\cdot\mathrm{cm}^{-3}$
Melting point: [6]	$419.53^{\circ}\mathrm{C}$
Boiling point: [6]	$907^{\circ}C$
Specific heat $c_p$ at 25°C, 1 bar: [6]	$0.388 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$
Molar heat $C_p$ at 25°C, 1 bar: [6]	$25.390 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Isotope range: [9]	57-81 (stable: 64, 66-68)

#### Introduction

Pure zinc is a hard, dense metal with a bluish-white hue. Tarnishing occurs in moist but not in dry air. In a natural environment its corrosion resistance is rather high due to a hard oxide coating, but it is vulnerable to strong mineral and organic acids. The metal is malleable and can be machined in every imaginable way, e.g. rolled and die-cast. [10]

#### History

Since about 3000 years ago, zinc containing minerals have been used just in brass as an alloying part to copper ( $\rightarrow$  **Copper**, page 16). Some evidence shows that around 500 CE, metallic zinc was melted in India by heating calamine (ZnCO<sub>3</sub>), later on also in China. Since zinc has always been mixed with other metals (e.g. lead, antimony, bismuth), the pure metal was not discovered for a long time. Around 1616 Paracelsus (Theophrastus Bombastus von Hohenheim, 1493-1541) described a new metal he called zinc (in German: Zink), derived from the Greek word zink, meaning 'prong' or 'point' - since metallic zinc crystals have a needle-like appearance. Andreas Sigismund Marggraf (1709-1782), German analytical chemist, isolated and identified metallic zinc in 1746 by heating calamine with charcoal. [10] [21]

# Common Uses

In about three quarters of the known applications of zinc, its metallic form prevails. The remaining quarter uses zinc in compounds for paint and in fertilizers in agriculture. The main field of application for this metal is in coatings on steel and sometimes aluminium. An overview of further uses is given here:

- Hot-dip galvanizing, electrodeposition of a zinc layer  $(86 150 \ \mu m)$  generally achieved in an aqueous electrolyte at a temperature from 440 to 465°C. Through a diffusion processes a layer of iron-zinc alloy is formed on the steel surface, offering an excellent basis for the zinc coating. Best results are achieved by using steel with less than 0.15 wt% carbon. [11] [16] Some special zinc alloys have been developed, e.g. *Sendzimir galvanizing*: Zinc containing 0.05-0.3 wt% Pb and 0.15-0.35 wt% Al, *Zincalume*: Zinc alloy with 55 wt% Al and 1.0 wt% Si, or for galvanizing Si containing steel: Zinc containing 0.05 wt% Al, 0.008 wt% Mg, 0.15 wt% Sn [13]
- Zinc alloys are used for (pressure) die casting and gravity casting production of automotive equipment, household appliances, tools and more. The alloys used are GD-ZnAl4Cu1  $(Z410)^{19}$ , G-ZnAl4Cu3 (Z430) and GK-ZnAl8Cu1 (ZA8), to mention a few. [13]
- Slush casting alloys, for example used in the production of table lamp bases, are Z34510 (Zn 4.5-5.0Al 0.2-0.3Cu max(0.005Cd 0.1Fe 0.007Pd 0.005Sn) and Z30500 (Zn 5.25-5.75Al max(0.1Cu 0.005Cd 0.1Fe 0.007Pd 0.005Sn) [12]
- Ductile alloys like Zn-Al-Mg (e.g. ca. 0.01 wt% Al, ca. 0.05 wt% Mg) are used for the etched plates in the graphic letterpress printing process. [13]
- ZA-8 (Zn 8Al 1Cu 0.02Mg) is a high strength alloy, formed by pressure die castings and gravity castings. Applications include agricultural equipment, domestic and garden appliances, electronic and electrical fittings and automobiles, to mention a few. ZA-12 (Zn 11Al 1Cu 0.025Mg) is similar in ZA-8, but used in bearings and bushings for heavy duty applications at low speed.[12]
- For brass (copper-zinc-alloy) see page 17, uses of **copper**.
- Batteries, primary and secondary, often use zinc as anodes. Primary cells like Alkaline (Zn/MnO2 KOH as electrolyte) are popular general-purpose batteries, whereas zinc/silver oxide (Zn/Ag<sub>2</sub>O KOH as electrolyte) are used for hearing aids, clocks and watches and in larger sizes in missiles and space applications. Secondary

<sup>&</sup>lt;sup>19</sup>The commercial designation is given in brackets.

(rechargeable) cells are used for space flight applications and in underwater equipment in the form of silver oxide/zinc storage batteries  $(Zn/Ag_2O/Ag, KOH)$  or as zinc chlorine cells (inert electrodes, ZnCl<sub>2</sub> as electrolyte) for stationary energy storages. [92]

• Zinc hydrosulphite (ZnS<sub>2</sub>O<sub>4</sub>) is used in the textile and paper industries as a bleaching agent, and is also applied to bleach sugar and glue. [92]

## Relevance in Life

Zinc is essential for life since it is a component of more than 300 enzymes ([17]) for the metabolism: [9]

- Important for replication of the genetic codes of DNA and RNA.
- Zinc contributes to the preparation of insulin in the pancreas.
- Zinc deficiency affects wound healing and leads to loss of hair.
- Zinc is essential for nerve conduction, a deficiency among other things affects the ability to taste (hypogeusia).
- For children, delayed mental development may be caused by zinc deficiency, as well as retarded growth.
- Zinc's role in protein synthesis is an important aspect during pregnancy and for newborns. Recommended daily intake for adults is 11 mg, for babies 6 mg (i.e. 1.5 mg per kg body weight).
- Cadmium, lead and arsenic affect the regulation of zinc; on the other hand zinc can counteract toxic effects of Cd. [17]
- Inhalation of freshly formed zinc fume (e.g. during welding) may lead to *metal-fume fever*. [17]

# B: Thermophysical properties obtained by Pulse - heating

## Volume expansion

Table 57: Volume expansion results of zinc, polynomials converted from [93] and [94]. Density at 20 °C: 7133 kg·m<sup>-3</sup> [18].

	$T_m = 692.677 \mathrm{K} [26]$	
liquid	$V/V_0(H) = 1.218 - 5.347 \times 10^{-4} \cdot H$	
	$+2.571 \times 10^{-6} \cdot H^2$	$300 < H < 650  \rm kJ\cdot  kg^{-1}$



Figure 57: Volume expansion of zinc as a function of enthalpy.

## Resistivity

Table 58: El	ectrical resistivity	<sup>r</sup> results of zinc,	$\rho$ in $\mu\Omega$ ·m,	polynomials taken
from $[93]$ and	d [94].			

	$T_m = 692.677 \mathrm{K} [26]$	
liquid	$ \rho_{\rm IG}(H) = 0.54171 - 0.104 \times 10^{-2} \cdot H $	
	$+1.174 \times 10^{-6} \cdot H^2$	$300 < H < 650  \mathrm{kJ} \cdot  \mathrm{kg}^{-1}$
	$\rho(H) = 0.88648 - 0.252 \times 10^{-2} \cdot H$	
	$+3.362  imes 10^{-6} \cdot H^2$	
	$\rho_{\rm IG,l} = 0.344$	
	$\rho_{\rm l} = 0.445$	



Figure 58: Electrical resistivity of zinc as a function of enthalpy. Dashed line: values including volume expansion.

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## A: Basic survey

#### The Element

```
Symbol:
                                                         \mathbf{Zr}
Atomic number:
                                                         40
Group:
                                                         Transition metal
Atomic weight: [6]
                                                         91.224(2) u
                                                         [Kr]4d^25s^2
Ground state electron configuration:
Crystal structure at 25^{\circ}C: [7]
                                                         hcp with a = 3.232 Å
                                                           and c = 5.147 Å
                                                         \alpha-Zr: hcp; \beta-Zr: bcc
Allotropy: [8]
                                                         Transition \alpha \rightarrow \beta at 862°C
                                                         6.52 \text{ g} \cdot \text{cm}^{-3}
Density at 20^{\circ}C: [6]
Melting point: [6]
                                                         1855^{\circ}C
Boiling point: [6]
                                                         4409^{\circ}C
                                                         0.278 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}
Specific heat c_p at 25°C, 1 bar: [6]
                                                         25.36~\mathrm{J}\cdot\mathrm{mol^{-1}}\cdot\mathrm{K^{-1}}
Molar heat C_p at 25°C, 1 bar: [6]
Isotope range: [9]
                                                         81-105 (stable: 90-92, 94)
```

## Introduction

Zirconium as a metal has a grayish shine, is hard, ductile and malleable. Its chemical inertness results from its tough and adherent protective oxide layer (*zirconia*,  $ZrO_2$ ). This layer is formed spontaneously in an oxygen-containing environment, is impenetrable as well as self-healing, and as a result protects the base metal.

The metal offers very good corrosion resistance to most strong mineral and organic acids, some molten salts and strong alkalis, but dissolves in hydrofluoric acid (HF), chlorides like iron chloride (FeCl<sub>3</sub>) and aqua regia. Furthermore, wet chlorine gas attacks the metal strongly. [9] [11]

## History

Minerals containing zirconium (e.g. *jargon*, *hyacinth*, *jacinth*) were known in ancient times. Until the late 18th century, zirconium minerals were mainly used in jewelry because of their beauty. It was 1789, when the German analytical chemist Martin Heinrich Klaproth (1743-1817) discovered a new element - more precisely its oxide - in *hyacinth*<sup>20</sup>. He named it

 $<sup>^{20}</sup>$  Klaproth's analysis showed a combination of  $70\,\rm wt\%~ZrO_2$  and  $25\,\rm wt\%~SiO_2$  for the mineral *jacinth*, mined in Ceylon (Sri Lanka) [9]

Zirkonerde (zirconium earth), derived from the Persian name for the mineral, Zargün, meaning 'gold-colored'.

The impure metal was first isolated by Swedish chemist Jöns Jakob Berzelius (1779-1848) in 1824 but not until 1914 was the pure metal gained. Its high-purity form was finally achieved by Van Arkel and de Boer in 1925. [9] [11]

Klaproth, Martin Heinrich (1743-1817) Berzelius, Jöns Jakob (1779-1848) van Arkel, Anton Eduard (1893-1976) de Boer, Jan Hendrik (1899-1971)

## Common Uses

By combining good corrosion resistance and mechanical properties, zirconium and its alloys offer a wide range of applications:

- In nuclear reactor appliances, the metal's major use is in structure components.  $Zircaloy^{\ensuremath{\mathbb{R}}}2$  (Zr 1.5Sn 0.14Fe 0.1Cr 0.05Ni),  $Zircaloy^{\ensuremath{\mathbb{R}}}4$  (Zr 1.5Sn 0.22Fe 0.1Cr <0.004Ni) and Zr-2.5Nb (Zr <0.02Sn <0.08Fe <0.02Cr <0.007Ni 2.5Nb) are the materials from which container tubes for nuclear fuel pellets are made of. Low cross section for thermal neutrons (0.18 barn), resistance against damage caused by radiation, and good ductility are especially advantageous here. [11]
- Zirconium powder is used in vacuum tubes as a getter for oxygen due to its affinity for that element. The same characteristic is used in photoflash bulbs or explosive primers. [11]
- Zircadyne<sup>®</sup> alloys (e.g. Zircadyne<sup>®</sup> 702 (Zr+Hf 99.2 wt%min with Hf 4.5 wt%max, Fe+Cr 0.20 wt%max, also H, N, C, O), Zircadyne<sup>®</sup> 705 (Zr+Hf 97.2wt.%min with Hf 4.5 wt%max, Fe+Cr 0.2 wt%max, Nb 2.0-3.0 wt% also H, N, C, O) [11]) are used as structural material in the chemical processing industry, utilizing its corrosion resistance and the appearance of being non-toxic and bio-compatible: [61]
  - Stripper and drying columns are built depending on the media they can be used for, e.g.  $Zircadyne^{\ensuremath{\mathbb{R}}}$  702 finds usage in the most attacking environments like H<sub>2</sub>SO<sub>4</sub> (> 55 wt%), whereas  $Zircadyne^{\ensuremath{\mathbb{R}}}$  705 offers better performance when used with less aggressive substances.
  - In pressure and reactor vessels, the steel shell is lined with  $Zirca-dyne^{\textcircled{R}}$  metals as corrosion protection.
  - Its lightness compared to stainless alloys and its corrosion resistance make very thin Zircadyne<sup>®</sup> metals appropriate for light, durable and structural packaging.
- A standard material used in ultrasonic transducers is lead zirconate titanate (PZT), utilizing the piezoelectric properties of this component. Further applications are piezoelectric ceramics used for gas fur-

nace igniters, microphones as well as record-player crystals, and for ultrasound imaging in materials testing and in medicine. [9]

- The alloy C15000 (zirconium copper) consists of 99.8 wt% Cu+Ag and 0.1-0.2 wt% Zr. Applications, among others, include resistance welding tips and electrodes, circuit breaker switches, commutators and welding wheels. [95]
- Zircon (ZrSiO<sub>4</sub>) finds major use in refractories, ceramic opacification and foundry sands: [31]
  - In decorative ceramics, milled zircon is used as opacifier for porcelain enamels and for tile glazes, utilizing its high refractive index to yield an opaquely white glaze.
  - Fused zircon and AZS (aluminium-zircon-silica) refractories are used in the glass industry for its high resistance to molten glass.
  - The steel industry utilizes zircon in form of ladles and continuous casting nozzles.
  - Aluminium-zircon (AZ) is used as an abrasive for grinding of steel and steel alloys.

## Relevance in Life

Zirconium is not an essential element for humans. The toxicity of the element is low. [9]
# B: Thermophysical properties obtained by Pulse - heating

#### Volume expansion

Table 59: Volume expansion results of zirconium [60]. Density at 20 °C: 6506 kg·m^{-3} [18].

	$T_m = 2127 \mathrm{K} [19]$	
	$V/V_0(T) = 0.984 + 2.861 \times 10^{-6} \cdot T$	
liquid	$V/V_0(T) = 0.920 + 5.944 \times 10^{-5} \cdot T$	$2127{\rm K} < T < 4000{\rm K}$



Figure 59: Volume expansion of zirconium.

### Enthalpy

taken nom [50].				
	$T_m = 2125 \mathrm{K} \ [97], \mathrm{rec.:} \ T_m = 2127 \ [19]$			
	at.wt. = 91.224 [18]			
solid	$H(T) = -239.3 + 0.4319 \cdot T$	$1775{ m K} < T < 2090{ m K}$		
	$c_p = 431.9  \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$			
	$C_p = 39.400 \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$			
liquid	$H(T) = -230.1 + 0.4963 \cdot T$	$2220{\rm K} < T < 3430{\rm K}$		
	$c_p = 496.3 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$			
	$C_p = 45.274 \mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$			
	$H_{\rm s} = 678.6, H_{\rm l} = 824.6, \Delta H = 146.0$			

Table 60: Specific enthalpy results of zirconium, H in kJ·kg<sup>-1</sup>, polynomials taken from [96].



Figure 60: Specific enthalpy of zirconium as a function of temperature.

#### Resistivity

10	for mold taken from [50].						
		$T_m = 2127$ [19]					
	solid	$\rho_{\rm IG}(T) = 0.8656 + 2.146 \times 10^{-4} \cdot T$	$1660{\rm K} < T < 2115{\rm K}$				
		$\rho(T) = 0.830 + 2.592 \times 10^{-4} \cdot T$					
	liquid	$\rho_{\rm IG}(T) = 1.3695 + 4.735 \times 10^{-6} \cdot T$	$2155{\rm K} < T < 3500{\rm K}$				
		$\rho(T) = 1.258 + 8.735 \times 10^{-5} \cdot T$					
		$\rho_{\rm IG,s} = 1.319,  \rho_{\rm IG,l} = 1.380$					
		$\Delta \rho_{\rm IG,s-l} = 0.061$					
		$\rho_{\rm s}=1.378,\rho_{\rm l}=1.446,\Delta\rho_{\rm s-l}=0.068$					

Table 61: Electrical resistivity results of zirconium,  $\rho$  in  $\mu\Omega$ ·m, polynomials for  $rho_{IG}$  taken from [96].



Figure 61: Electrical resistivity of zirconium as a function of temperature. Dashed lines: values including volume expansion.

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