Chromium

Discovered: In 1797 by L.N. Vauquelin as its oxide. He isolated it in 1798 by charcoal reduction of the oxide.

Name: From the Greek word *chroma*, meaning "color," because of the variety of colors its compounds display.

Occurrence: Moderate abundance. Its only important mineral is chromite ($FeCr_2O_4$) which is found principally in southern Africa (96% of known reserves), nations of the former USSR, and the Philippines.

Isolation:

$$FeCr_2O_4 + O_2 + \text{alkali} \longrightarrow Na_2Cr_2O_4 + \ldots$$

$$Na_2Cr_2O_4 + H_2O \longrightarrow Na_2Cr_2O_7 \text{ (need to balance)}$$

$$Na_2Cr_2O_7 + 2\,C \longrightarrow Cr_2O_3 + Na_2CO_3 + CO$$

$$Cr_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Cr$$

Natural Isotopes: ^{50}Cr (4.3%) ^{52}Cr (83.8%) ^{53}Cr (9.6%) ^{54}Cr (2.4%)

Cost of 1 gram, 1 mole: \$0.15, \$7.66

Physical and Chemical Properties:
- Shiny and silvery in color
- Soft and brittle
- High melting and boiling points
- Oxidation states from -2 to +6 are known
- Most stable oxidation state is +3
- Corrosion resistant

Reactions: Cr^{3+} forms thousands of complex ions that for the most part are 6-coordinate.

e.g. $Cr^{3+} + 6\,H_2O \longrightarrow Cr(H_2O)_6^{3+}$

The chromates and dichromates are important oxidizing agents. The half-reaction for dichromate oxidation is:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

Uses:
- Production of non-ferrous alloys
- Ornamental plating
- Green colored glass

Note: Compounds of Cr(VI) are known to be both toxic and potent carcinogens.

Cobalt

Discovered: First isolated by G. Brandt in 1735. It was identified as an element in 1780 by T.O. Bergman.

Name: From the German word *kobold* for "goblin" or "evil spirit." Several of the cobalt ores contain arsenic (*vide infra*) and the processing of them led to the formation of highly toxic, gaseous As_4O_6. The miners attributed this to evil spirits. Cobalt is also extremely similar to the Greek word *cobalos*, meaning "mine" but no connection is believed to exist between the two.

Occurrence: Moderate abundance. Over 200 minerals are known to contain cobalt. Important ones are: smaltite ($CoAs_4$), cobaltite (CoAsS), and linnaeite (Co_3S_4). These minerals almost always occur with nickel ores and frequently with copper, silver, and lead ores. Found in Africa and Canada, small reserves also exist in Australia and nations of the former USSR.

Isolation: Usually obtained as a by-product of iron or nickel production. The general ore is roasted to give a mixture of metals and oxides. Leaching with H_2SO_4 removes Cu and puts Fe and Co in solution. The iron is precipitated with lime and cobalt with NaOCl.

$$2\ Co^{2+} + OCl^- + 4\ OH^- + H_2O \longrightarrow 2\ Co(OH)_3 + Cl^-$$

Natural Isotopes: ^{59}Co (100%)

Cost of 1 gram, 1 mole: $0.36, $21.45

Physical and Chemical Properties:
Lustrous with a bluish, silvery color
Hard and brittle
2 allotropes
Ferromagnetic
Much less reactive than iron
Dissolves slowly in dilute mineral acids giving Co(II) in solution
Reacts, when heated, with halogens, B, C, P, As, S and O.
No binary Co hydride or nitride is known
Stable oxidation states range from -1 to +5 with +2 and +3 most common

Reactions: Like chromium, cobalt has an extensive coordination chemistry for the +3 oxidation state.

$$Co(H_2O)_6^{3+} + 6\ NH_3 \xrightarrow[H_2O]{\Delta} Co(NH_3)_6^{3+} + 6\ H_2O$$

$$Co + X_2 \xrightarrow{\Delta} CoX_2\ (X = Cl \text{ or } Br)$$

$$2\ Co + O_2 \xrightarrow{\Delta} 2\ CoO \xrightarrow{650\ C^\circ} Co_3O_4$$

Uses: In blue pigments, dyes, and glasses
Co compounds are used as catalysts in hydrogenation, dehydrogenation, and hydroformylation reactions
High temperature alloys (30%)
Magnetic alloys (20%)
Electroplating (because of its inertness)
^{60}Co is used as a γ-ray source
Vitamin B_{12} is an organic molecule containing a Co(III) as an octahedral complex

Copper

Discovered: It has probably been in use since 5000 B.C.

Name: Both the name "copper" and *cuprum* (Latin) are derived from *aes cyprium* because the Romans first obtained their copper from the island of Cyprus.

Occurrence: It is found in moderate abundance. Some is found in elemental form. The principle copper containing minerals are chalcopyrite ($CuFeS_2$, *ca.* 50% of all copper deposits), chalcopyrite (Cu_2S), cuprite (Cu_2O), and malachite ($Cu_2CO_3(OH)_2$). Large deposits of these ores are found in North and South America, Africa, and nations of the former USSR.

Isolation: Most copper comes from the extraction of low grade (*ca.* ½ %) copper ores. After initial extraction cuprous sulfide is converted into copper by the following series of reactions that occur at 1400 ºC:

$$2\ Cu_2S + 3\ O_2 \xrightarrow{\Delta} 2\ Cu_2O + 2\ SO_2$$
$$2\ Cu_2O + Cu_2S \xrightarrow{\Delta} 6\ Cu + SO_2$$

Natural Isotopes: ^{63}Cu (69.1%) ^{65}Cu (30.9%)

Cost of 1 gram, 1 mole: $0.05, $3.00

Physical and Chemical Properties:
- Reddish color
- Good electrical (2^{nd} only to silver) and thermal conductor
- Soft and ductile
- Relatively low oxidation potentials (to +1 and +2)
- Fairly resistant to air oxidation because the oxide adheres strongly to the metal
- Forms numerous alloys
- Reacts with halogens and oxygen and sulfur at high temperatures
- Stable oxidation states range from +1 to +4 with +1 and +2 most stable

Reactions: $2\ Cu + O_2 \longrightarrow 2\ CuO$ (e.g. corrosion of copper such as on pennies)

$Cu + Sn \xrightarrow{\Delta}$ bronze

$Cu + Zn \xrightarrow{\Delta}$ brass

Uses:
- Coinage (in the USA, new pennies contain 2.5% Cu while, "silver" coins contain a majority of copper)
- Production of brass and bronze alloys
- Electrical conductance applications
- Copper sulfate is used as an agricultural poison
- Some shellfish use copper complexes in their oxygen transport systems

Iron

Discovered: Known since prehistoric times. Iron beads from around 4000 B.C. are known.

Name: Derived from an Anglo-Saxon word, *iren*, which means "holy metal," so named (from what I can tell) because it was used to make swords for the Crusades. *Fe*, the atomic symbol, is derived from the Latin word *ferrum* which is probably derived from an unknown Hebrew or Arabic word.

Occurrence: It is the Earth's second most abundant element in the crust and the most abundant element in the core. Common minerals include haematite (Fe_2O_3), magnetite (Fe_2O_4), limonite ($\sim 2Fe_2O_3 \cdot 3H_2O$), siderite ($FeCO_3$), and pyrite ($FeS_2$, "fool's gold"). It is common throughout the universe because one of its isotopes, ^{56}Fe, is the most stable nucleus and is produced in significant amounts when stars explode.

Isolation: Iron was first smelted around 3000 B.C. in the Hittite empire. The iron ore is converted into iron by the following reactions:

$$3\ Fe_2O_3 + CO \xrightarrow{\Delta} 2\ Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \xrightarrow{\Delta} 3\ \text{"FeO"} + CO_2$$

$$C + CO_2 \xrightarrow{\Delta} 2\ CO$$

$$\text{"FeO"} + CO \xrightarrow{\Delta} Fe + CO_2$$

Natural Isotopes: ^{54}Fe (5.8%) ^{56}Fe (91.7%) ^{57}Fe (2.2%) ^{58}Fe (0.3%)

Cost of 1 gram, 1 mole: \$0.06, \$3.14

Physical and Chemical Properties:
- Silvery in color with a lustrous finish
- Relatively hard and brittle
- Ferromagnetic to 768 ºC
- Comparatively reactive
- Soluble (as Fe^{2+} in dilute mineral acids)
- Strong oxidizing acids passivate iron (through formation of an oxide coating)
- Oxidation states range from -2 to +6 with +2 and +3 the most common
- Pyrophoric when finely divided

Reactions:

$$4\ Fe + 3\ O_2 \longrightarrow 2\ Fe_2O_3 \quad \text{(rust)}$$

$$Fe + X_2 \longrightarrow FeX_2\ (X = Br \text{ or } I) \text{ or } FeX_3\ (X = F \text{ or } Cl)$$

$$Fe + 5\ CO \xrightarrow[\text{high P}]{200\ ^oC} Fe(CO)_5\ (l)$$

Uses: Steel (700 million tons annually worldwide in 1984)
Active site in Hemoglobin

Manganese

Discovered: In 1774 C.W. Scheele recognized a new element in the mineral pyrolusite (MnO_2). J.G. Gahn heated it with charcoal and oil to yield metallic manganese.

Name: Derived from the Latin word *magnes* meaning "magnet" for the magnetic properties of pyrolusite.

Occurrence: It is moderately abundant. It occurs in over 300 minerals of which about a dozen are important, e.g. pyrolusite (MnO_2), hausmannite (Mn_3O_4), rhodochrosite ($MnCO_3$) all are found in nations of the former USSR, Gabon, South Africa, Brazil, Australia, India, and China.

Isolation: a) Electrolysis of aqueous $MnSO_4$ solutions

b) $3\ MnO_2 + 4\ Al \xrightarrow{\Delta} 3\ Mn + 2\ Al_2O_3$

c) Mn used in steel alloys comes from the *in situ* reduction of MnO_2 in a blast furnace.

Natural Isotopes: ^{55}Mn (100%)

Cost of 1 gram, 1 mole: \$0.07, \$4.01

Physical and Chemical Properties:
Gray to white color
Hard and very brittle
Comparatively electropositive
Physical properties are similar to iron
Oxidation states range from -3 to +7 with high-spin, +2 most stable
Relatively active
i) Dissolves in dilute, non-oxidizing acids (Mn^{2+})
ii) Burns in O_2 when finely divided
iii) Slowly reacts with cold water
iv) Reacts with many non-metals at elevated temperatures
Pure metal exists in 4 allotropic forms

Reactions:
$Mn + 2\ H^+ \longrightarrow Mn^{2+}$
$3\ Mn + 2\ O_2 \longrightarrow Mn_3O_4$ (note that manganese is in 2 different oxidation states in this compound)
$2\ Mn(OH)_2 + O_2 \longrightarrow 2\ MnO_2 + 2\ H_2O$
$2\ Mn^{2+} + 5\ H_2O_2 \longrightarrow MnO_4^- + 6\ H^+ + 2\ H_2O$
Note the variety of oxidation states shown above.

Uses: Steel alloys (*ca.* 95%)
Oxidant ($KMnO_4$)
Dry cell batteries (MnO_2)
Colorizing agent in glass, bricks (MnO_2), and the gemstone amethyst (Mn^{2+})

Nickel

Discovered: In 1751 A.F. Cronstedt first isolated and named nickel.

Name: NiAs ore resembles Cu_2O (which was a desired mineral). Saxon miners attributed their inability to extract copper from it to the work of the devil (Old Nick's copper).

Occurrence: It is moderately abundant. Important ores: garnierite $(Ni,Mg)_6$, nickeliferrous limonite $(Fe,Ni)O(OH)_6 \bullet nH_2O$, pentlandite $(Ni,Fe)_9S_8$. The most important deposit in Canada.

Isolation: Very complicated. This one is not required.

Cost of 1 gram, 1 mole: $0.12, $6.75

Natural Isotopes: ^{58}Ni (68.3%) ^{60}Ni (26.1%) ^{61}Ni (1.1%) ^{62}Ni (3.6%) ^{64}Ni (0.9%)

Physical and Chemical Properties:
- Silvery, white in color
- Hard
- Ferromagnetic
- Does not corrode at room temperature
- Reacts with some non-metals, steam
- Soluble in dilute mineral acids
- Oxidation states from -1 to +4 with +2 most common
- High electrical and thermal conductivities
- Finely divided metal burns in air
- Atomic mass is smaller than that of the preceding element (Co) (58.7 amu *vs.* 58.9 amu)
- Nickel complexes tend to be either 4 coordinate tetrahedral complexes or 6 coordinate octahedral complexes.

Reactions:

$$Ni + 4\,CO \xrightarrow{50^oC} Ni(CO)_4 \quad \text{(a liquid at RT, very toxic)}$$

$$[Ni(H_2O)_6]Cl_2 + 6\,NH_3 \longrightarrow [Ni(NH_3)_6]Cl_2 + 6\,H_2O$$

Uses:
- Monel alloy (very corrosion resistant)
- Nichrome alloy (very low temperature coefficient of electrical resistance)
- Invar alloy (very small coefficient of expansion)
- Catalyst for the hydrogenation of unsaturated vegetable oils
- Storage batteries
- Coinage
- Alloy in alnico magnets (aluminum-nickel-cobalt alloy, get it?)
- Nickel steel
- Colors glass green

Scandium

Discovered: Oxide first isolated in 1879 by L.F. Nilsen. Pure element was first isolated in 1937 from the electrolysis of a mixture of KCl/NaCl/$ScCl_3$, at 700 ºC by Fischer, Brunger, and Grieneisen.

Name: From the oxide, Sc_2O_3, called *scandia* for the location of the ore.

Occurrence: Rare element and widely distributed. It's only rich mineral is thortveitite ($Sc_2Si_2O_7$) which is found in Norway.

Isolation: As a by-product of uranium processing (contains *ca.* 0.02% Sc_2O_3)

Cost of 1 gram, 1 mole: $164, $7,350

Natural Isotopes: ^{55}Sc (100%)

Physical and Chemical Properties:
Soft, silvery white metal
Moderately electropositive
Unexpectedly high melting and boiling points (compared to calcium)
Reacts with most non-metals at elevated temperatures
Only chemically important oxidation state is + 3
Complexing properties similar to aluminum
Chemistry anomalous compared to the other transition metals. Its chemistry is closer to that of the main group metals.

Reactions:

$$4\ Sc + 3\ O_2 \longrightarrow 2\ Sc_2O_3$$

$$2\ Sc + 3\ F_2 \longrightarrow 2\ ScF_3$$

$$ScF_3 + 3\ NaF \longrightarrow Na_3[ScF_6]$$

Uses: The oxide is used in the production of high intensity lights

Titanium

Discovered: By William Gregor of England in 1791 in TiO_2. First isolated by J.J. Berzelius in 1825, but not made pure until 1910 by Mathew Hunter.

Name: Named by a German chemist, M.H. Klaproth, in 1795 after the *Titans*, people of Greek mythology that were children of Heaven and Earth, condemned to live amongst the hidden fires of the earth.

Occurrence: It is abundant. Two most significant minerals are ilmenite (Canada, U.S., Australia, Scandinavia, Malaysia) and rutile (Australia).

Isolation: This method was developed by Wilhelm Kroll in 1932 in Luxemburg.

$$2\ FeTiO_3 + 7\ Cl_2 + 6\ C \longrightarrow 2\ TiCl_4 + 2\ FeCl_3 + 6\ CO$$
$$TiCl_4 + 2\ Mg \longrightarrow Ti + 2\ MgCl_2$$

Cost of 1 gram, 1 mole: $0.21, $9.96

Natural Isotopes: ^{46}Ti (7.9%) ^{47}Ti (7.3%) ^{48}Ti (73.9%) ^{49}Ti (5.5%) ^{50}Ti (5.3%)

Physical and Chemical Properties:
- Lustrous, silvery metal
- High melting and boiling points
- Not especially good conductor relative to other metals
- Low density
- Very resistant to corrosion
- Relatively unreactive at normal temperatures
- Oxidation states range from -1 to +4, except -1. +4 is the most significant
- Burns in N_2 at high temperatures

Reactions: $Ti + 2\ Cl_2 \xrightarrow{\Delta} TiCl_4$ (mp = -23 ºC !)

$TiCl_4 + 2\ H_2O \longrightarrow TiO_2 + 4\ HCl$ (smoke screens for ships in WW II)

Uses: Form high strength construction alloys
Low density ("lightweight"), high temperature alloys for aircraft
TiO_2 is the principle pigment in white paint. It replaced $Pb(OH)_2 \bullet 2PbCO_3$ and $2PbSO_4 \bullet PbO$ in that role when many commercial uses of lead were phased out in the 1970s.

Uranium

Discovered: M.H. Klaproth identified it as a component of pitchblende in 1789. It is believed that B. Peligot first isolated uranium metal in 1841.

Name: It was named after the planet *Uranus* by Klaproth because the planet had been discovered shortly before he discovered uranium. Uranus was the god of the heavens in Greek mythology.

Occurrence: It is fairly abundant (more so than tin). Its most important minerals include: pitchblende or uraninite (U_3O_8) and carnotite ($K_2(UO_2)(VO_4)_2 \cdot 3H_2O$). Principle sources are the U.S., Canada, South Africa, and Australia.

Isolation:

$$\text{ore} \xrightarrow{\Delta} \xrightarrow{H_2SO_4} UO_2^{2+} \xrightarrow{300\ ^oC} UO_3 \xrightarrow[H_2]{700\ ^oC} UO_2$$

$$UO_2 + 4\,HF \xrightarrow{\Delta} UF_4 \xrightarrow[Mg]{700\ ^oC} U + 2\,MgF_2$$

Cost for 1 gram, 1 mole: $5.88, $281

Natural Isotopes: ^{234}U (0.0054%) ^{235}U (0.71%) ^{238}U (99.28%)

Physical and Chemical Properties:

Radioactive (^{234}U, $t_{½} = 2.5 \times 10^5$ yr)
(^{235}U, $t_{½} = 7.1 \times 10^8$ yr)
(^{238}U, $t_{½} = 4.5 \times 10^9$ yr)
Very dense (19.1 g/cm^3)
Silvery white color
Ductile and malleable
Pyrophoric when finely divided
Soluble in acids
Last naturally occurring element
Electropositive
Tarnishes rapidly in air
Oxidation states of +3 to +6 are known with +4 most stable
Toxic (beyond its radioactivity)

Reactions:

$$2\,U + 3\,H_2 \xrightarrow{250\ ^oC} 2\,UH_3$$

$$^{238}U + {}^1n \longrightarrow {}^{239}U \xrightarrow[23\ min]{-\beta} {}^{239}Np \xrightarrow[2.3\ days]{-\beta} {}^{239}Pu$$

$$UCl_6 + 2\,H_2O \longrightarrow UO_2Cl_2 + 4\,HCl$$

Uses: Electrical power generation fuel (1 lb U ≅ 1500 lb coal)
Used in inertial guidance devices, gyro compasses, counter weights for aircraft control surfaces, as ballast for missile reentry vehicles, and to generate high energy X-rays
Photographic toner ($U(NO_3)_3$)
Uranium salts are used as yellow glass colorants
Alloy with titanium is used in armor piercing shells

Vanadium

Discovered: By A.M. del Rio in 1801 and named it *erythronium* but he withdrew his claim after someone else incorrectly suggested that his results were in error. In 1830, N.G. Sefstrom rediscovered the element and gave it its current name.

Name: From *Vanadis*, the Scandinavian goddess of beauty because its compounds come in a variety of colors.

Occurrence: It is moderately abundant and is widely distributed in nature. Common minerals: patronite (VS_4), vanadinate ($(Pb_5(VO_4)_3Cl)_2$ = $PbCl_2 \cdot 3Pb_3(VO_4)_2$), carnotite ($K(UO_2)(VO_4) \cdot 3/2H_2O$). Venezuelan crude oil. Chief exporters: U.S., nations of the former USSR, China, and South Africa.

Isolation:

carnotite + NaCl $\xrightarrow{850^oC}$ $NaVO_3$ + . . .

$\downarrow$ pH = 2-3 H_2SO_4

V $\xleftarrow{\text{reduction}}$ V_2O_5 $\xleftarrow{500^oC}$ a polyvanadate

Cost of 1 gram, 1 mole: $2.56, $130

Natural Isotopes: ^{50}V (0.24%) ^{51}V (99.76%)

Physical and Chemical Properties:
- Shiny, silvery appearance
- Soft and ductile
- Highest melting point, boiling point, and enthalpy of atomization of the first-row transition metals
- Last first-row transition metal in which its *d*-electrons don't enter the inert core and whose group oxidation state (+5) is not highly oxidizing
- Corrosion resistant
- VO^{2+} is possibly the most stable diatomic ion
- Has stable oxidation states ranging from +5 to -1 with +4 the most stable

Reactions:

$V_2O_5 + 6\ OH^- \longrightarrow 2\ VO_4^{3-} + 3\ H_2O$

$V_2O_5 + 2\ H_3O^+ \longrightarrow 2\ VO^{2+} + 3\ H_2O$

$V + 2\ Cl_2 \longrightarrow VCl_4$

$VCl_4 + 6\ H_2O \longrightarrow VO(H_2O)_5^{2+} + 2\ H^+ + 4\ Cl^-$

Uses: Alloy in steel to yield strong, high temperature performance
Mordant in dyeing (V_2O_5)
V_2O_5 is used as a catalyst in the contact process for the production of H_2SO_4

Zinc

Discovered: First isolated by the 13th century in India. Early brass (*ca.* 1400 B.C.) was made with out isolating the zinc. Rediscovered in Europe by Marggraf in 1746.

Name: The origin of the name is not certain but it appears to be derived from the German word *Zinke* meaning "spike" or "tooth" referring to the shape of the metal when it crystallizes.

Occurrence: It is relatively non-abundant. It's major minerals include zinc blende (sphalerite, ZnS), calamine (silicate), and smithsonite ($ZnCO_3$). Large deposits are found in Canada, the USA, and Australia.

Isolation: Most Zn is derived from ZnS ore. The method is not important.

Natural Isotopes: ^{64}Zn (48.9%) ^{66}Zn (27.8%) ^{67}Zn (4.1%) ^{68}Zn (18.6%)

Cost for 1 gram, 1 mole: $0.04, $2.35

Physical and Chemical Properties:
- Low melting and boiling points
- Silvery solid with a bluish tint when freshly made
- Brittle at room temperature
- Only chemically important oxidation state is +2
- Alloys with a variety of other metals
- Chemically similar to the alkaline earth metals

Reactions:

$$Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2$$

$$Zn + 2\,OH^- \longrightarrow ZnO_2^{2-} + H_2$$

Uses:
- Anti-corrosion coating (galvanizing)
- Carbon-zinc batteries
- Brass (alloy with copper)
- ZnO has a wide variety of uses (incl. paints, cosmetics, plastics, textiles and pharmaceuticals)