

Table . 2 Abundance of the elements in the earth's crust, by weight

| | ppm | Relative abundance |
|----|------|--------------------|
| Ti | 6320 | 9 |
| Zr | 162 | 18 |
| Hf | 2.8 | 45 |

EXTRACTION AND USES

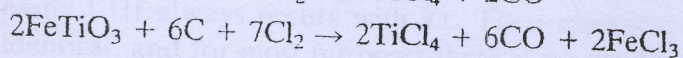
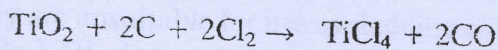
Ti has been called 'the wonder metal' because of its unique and useful properties. It is very hard, high melting (1667°C) and is stronger and much lighter than steel (densities Ti = 4.4 g cm⁻³, Fe = 7.87 g cm⁻³). However, even traces of non-metal impurities, for example H, C, N or O, make Ti, and also the other two metals Zr and Hf, brittle. Ti has better corrosion resistance than stainless steel. It is a better conductor of heat and electricity than the Sc group metals. Ti metal and alloys of Ti with Al are used extensively in the aircraft industry in jet and gas turbine engines, and in airframes. Supersonic aircraft like Concorde can use Al as the structural

Table . 3 Some physical properties

| Element | Covalent radius (Å) | Ionic radius M ⁴⁺ (Å) | Melting point (°C) | Boiling point (°C) | Density (g cm ⁻³) | Pauling's electro-negativity |
|---------|------------------------|--|-----------------------|-----------------------|----------------------------------|------------------------------|
| Ti | 1.32 | 0.605 | 1667 | 3285 | 4.50 | 1.5 |
| Zr | 1.45 | 0.72 | 1857 | 4200 | 6.51 | 1.4 |
| Hf | 1.44 | 0.71 | 2222 | 4450 | 13.28 | 1.3 |

skin (m.p. 660°C) by limiting the speed to Mach 2.2 (2.2 times the speed of sound). If and when SST (supersonic transport) planes are made which fly at three times the speed of sound, it is probable that they will be made of Ti (m.p. 1660°C). Ti is also used in marine equipment and in chemical plant. Small amounts of Ti alloyed with steel harden and toughen the steel. World production of Ti metal is almost 100 000 tonnes per year.

The metal is difficult to extract because of its high melting point and because it reacts readily with air, oxygen, nitrogen, and hydrogen at elevated temperatures. The oxide cannot be reduced by C or CO because it forms carbides. Since TiO₂ is very stable, the first stage is to form TiCl₄ by heating it with C and Cl₂ at 900°C.



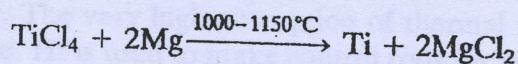
TiCl₄ is a liquid (b.p. 137°C) and is removed from FeCl₃ and other impurities by distillation. One of the following methods is then used.

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THE TITANIUM GROUP

Kroll process

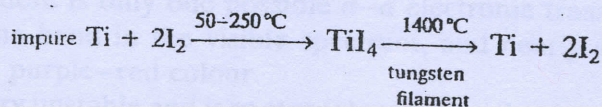
Originally Wilhelm Kroll produced Ti by reducing TiCl_4 with Ca in an electric furnace. Later Mg was used, and Imperial Metal Industries (IMI) use Na instead. At this temperature Ti is highly reactive and reacts readily with air or N_2 . It is therefore necessary to perform the reaction under an atmosphere of argon.



The MgCl_2 formed can be removed by leaching with water, or better with dilute HCl as this dissolves any excess Mg. Alternatively the MgCl_2 is removed by vacuum distillation. This leaves a sponge of Ti rather than a solid block. The Ti is converted to the massive form by melting in an electric arc under a high vacuum or an atmosphere of argon. The IMI process is almost the same. TiCl_4 is reduced by Na under an atmosphere of argon, and NaCl is leached out with water. The Ti is in the form of small granules. These can be fabricated into metal parts using 'powder forming' techniques and sintering in an inert atmosphere. The high fuel costs, the necessity to use argon, the cost of Mg or Na, and the need to reheat a second time all make Ti expensive. The high cost prevents its being more widely used. Zirconium is also produced by the Kroll process.

The van Arkel-de Boer method

Small amounts of very pure metal can be produced by this process. Impure Ti or Zr are heated in an evacuated vessel with I_2 . TiI_4 or ZrI_4 is formed, and volatilizes (thus separating it from any impurities). At atmospheric pressure TiI_4 melts at 150°C and boils at 377°C ; ZrI_4 melts at 499°C and boils at 600°C . Under reduced pressure, however, the boiling points are lower. The gaseous MI_4 is decomposed on a white hot tungsten filament. As more metal is deposited on the filament it conducts electricity better. Thus more electric current must be passed to keep it white hot.



Zr is produced on a much smaller scale than Ti. Zr is even more corrosion resistant than is Ti, and is used in chemical plants. Its most important use is to make the cladding (that is the casing) for UO_2 fuel in water cooled nuclear reactors. Its corrosion resistance, high melting point (1857°C) and low absorption of neutrons make it very suitable. (Of the metallic elements only Be and Mg have lower neutron absorption cross-sections than Zr. They are unsuitable for use as cladding as Be is brittle and Mg corrodes too easily.) Hf always occurs with Zr. Their chemical properties are almost identical, and for most purposes there is no need to separate them. However, Hf absorbs neutrons very strongly, and Zr used for cladding must be free from Hf.

The similarity in size of the ions makes separation exceedingly difficult.

The chromium group

Table .1 Electronic structures and oxidation states

| Element | | Electronic structure | Oxidation states* |
|------------|----|---|--|
| Chromium | Cr | [Ar] 3d ⁵ 4s ¹ | (-II) (-I) 0 (I) II III (IV) (V) VI |
| Molybdenum | Mo | [Kr] 4d ⁵ 5s ¹ | (-II) (-I) 0 I (II) III IV V VI |
| Tungsten | W | [Xe] 4f ¹⁴ 5d ⁴ 6s ² | (-II) (-I) 0 I (II) (III) IV V VI |

* The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type. Oxidation states that are unstable, or in doubt, are given in parentheses.

INTRODUCTION

Chromium metal is produced on a large scale, and is used extensively in ferrous and non-ferrous alloys, and for electroplating. The metals molybdenum and tungsten are produced in appreciable amounts. Sodium dichromate is also used in large amounts. CrO₃ and Cr₂O₃ are both used commercially.

Tungstate and molybdate ions both form extensive series of iso- and heteropolyacids. Chromium(II) acetate has an unusual structure with a quadruple bond. The lower halides MoX₂ and WX₂ form interesting cluster compounds based on the octahedral [M₆X₈]⁴⁺ metal cluster. Mo is important in nitrogen fixation.

ABUNDANCE, EXTRACTION AND USES

Chromium is the twenty-first most abundant element by weight in the earth's crust. This is about as common as chlorine. Molybdenum and tungsten are quite rare.

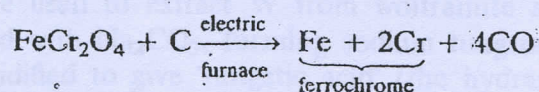
The only commercially important ore of Cr is chromite FeCr₂O₄. This is the chromium analogue of magnetite Fe₃O₄, which is better written as Fe^{II}Fe^{III}₂O₄. Chromite has a spinel structure. In this structure the O atoms are arranged in a cubic close-packed lattice with Fe^{II} in one eighth of the available tetrahedral holes and Cr^{III} in one quarter of the octahedral holes.

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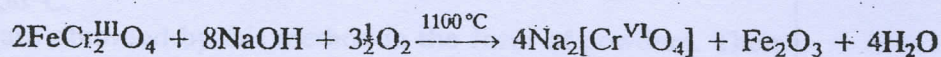
THE CHROMIUM GROUP

Chromite has a slight lustre and looks like pitch, with a brownish cast to the colour. It may be slightly magnetic. World production of chromite was 11.7 million tonnes in 1988, with a Cr content of 3.4 million tonnes. The largest sources of chromite ore are South Africa 36%, the USSR 28%, Turkey 7%, India 6.5%, Albania 6%, and Finland and Zimbabwe 5% each. Small amounts of crocoite PbCrO_4 and chrome ochre Cr_2O_3 are also mined.

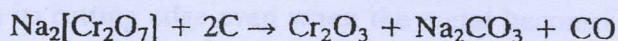
Chromium is produced in two forms: ferrochrome and pure Cr metal, depending on what it is to be used for. Ferrochrome is an alloy containing Fe, Cr and C. It is produced by reducing chromite with C. In 1988, 3.3 million tonnes of ferrochrome were produced. It is used to make many ferrous alloys, including stainless steel and hard 'chromium' steel.



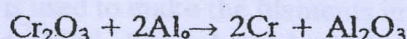
Several steps are required to obtain pure chromium. First chromite is fused with NaOH in air, when the Cr is oxidized to sodium chromate.



Fe_2O_3 is insoluble but sodium chromate is soluble. Thus the $\text{Na}_2[\text{CrO}_4]$ is removed by dissolving it in water, and is then acidified to give sodium dichromate. This is less soluble, and can be precipitated. The sodium dichromate is reduced to Cr_2O_3 by heating with C.



Finally Cr_2O_3 is reduced to the metal by Al or Si.



Since the metal is brittle, it is seldom used on its own. It is used to make non-ferrous alloys. Alternatively Cr_2O_3 is dissolved in H_2SO_4 , and deposited electrolytically on the surface of a metal. This both protects the metal from corrosion and gives it a shiny appearance.

Molybdenum occurs as the mineral molybdenite MoS_2 . World production of ores in 1988 had a molybdenum content of 92 000 tonnes. The largest sources are the USA 47%, Chile 15.5%, Canada 13.5% and the USSR 12.5%. Some MoS_2 is also obtained as a by-product from CuS ores.

Table 22.2 Abundance of the elements in the earth's crust, by weight

| | ppm | Relative abundance |
|----|-----|--------------------|
| Cr | 122 | 21 |
| Mo | 1.2 | 56 = |
| W | 1.2 | 56 = |

THE CHROMIUM GROUP

Table 22.3 Oxides and halides

| | Oxidation states | | | | |
|-------------------------|-------------------------|------------------------------------|-------------------------|-------------------------------------|------------------------|
| | (+II) | (+III) | (+IV) | (+V) | (+VI) |
| - | - | Cr₂O₃ | CrO₂ | - | CrO₃ |
| - | - | - | MoO₂ | Mo₂O₅ | MoO₃ |
| - | - | - | WO₂ | (W₂O₅) | WO₃ |
| CrF₂ | CrF₃ | CrF₄ | CrF₅ | (CrF₆) | - |
| CrCl₂ | CrCl₃ | CrCl₄ | - | - | - |
| CrBr₂ | CrBr₃ | CrBr₄ | - | - | - |
| CrI₂ | CrI₃ | CrI₄ | - | - | - |
| - | MoF₃ | MoF₄ | MoF₅ | MoF₆ | - |
| MoCl₂ | MoCl₃ | MoCl₄ | MoCl₅ | (MoCl₆) | - |
| MoBr₂ | MoBr₃ | MoBr₄ | - | - | - |
| MoI₂ | MoI₃ | MoI₄? | - | - | - |
| - | - | WF₄ | WF₅ | WF₆ | - |
| WCl₂ | WCl₃ | WCl₄ | WCl₅ | WCl₆ | - |
| WBr₂ | WBr₃ | WBr₄ | WBr₅ | WBr₆ | - |
| WI₂ | WI₃ | WI₄? | - | - | - |

The most stable oxidation states are bold, unstable are bracketed.

oxidation states become more stable and the lower states become less stable. A list of known oxides and halides is given in Table 22.3.

GENERAL PROPERTIES

The metals are hard and have very high melting points and low volatility (Table 22.4). The melting point of W is the next highest to carbon.

Cr is unreactive or passive at low temperatures because it is protected by a surface coating of oxide, thus resembling Ti and V in previous groups. It is because of this passive behaviour that Cr is extensively used for electroplating onto iron and other metals to prevent corrosion. Cr dissolves

Table 22.4 Some physical properties

| | Covalent radius (Å) | Ionic radius (Å) | | Melting point (°C) | Boiling point (°C) | Density (g cm ⁻³) | Pauling's electronegativity |
|----|---------------------|--|-----------------|--------------------|--------------------|-------------------------------|-----------------------------|
| | | M ²⁺ | M ³⁺ | | | | |
| Cr | 1.17 | 0.80 ^h 0.73 ^l | 0.615 | 1900 | 2690 | 7.14 | 1.6 |
| Mo | 1.29 | - | 0.69 | 2620 | 4650 | 10.28 | 1.8 |
| W | 1.30 | - | - | 3380 | 5500 | 19.3 | 1.7 |

h = high spin value, l = low spin radius.

The same problem is encountered in separating the lanthanide elements (see Chapter 29). Zr and Hf are separated by solvent extraction of their nitrates into tri-n-butyl phosphate or thiocyanates into methylisobutyl ketone. Alternatively the elements can be separated by ion exchange of an alcoholic solution of the tetrachlorides on silica gel columns. On eluting the column with an alcohol/HCl mixture, the Zr comes off first.

Zr is also used to make alloys with steel, and a Zr/Nb alloy is an important superconductor. The very high absorption of thermal neutrons by Hf is turned to good use. Hf is used to make control rods for regulating the free neutron levels in the nuclear reactors used in submarines.

OXIDATION STATES

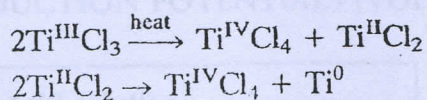
The most common and most stable oxidation state for all the elements is (+IV). Anhydrous compounds such as TiCl_4 are covalent and the molecules are tetrahedral in the gaseous state. Most of the halides retain their tetrahedral structure in the solid. TiF_4 has the largest electronegativity difference and is the most likely compound to be ionic. It is a volatile white powder, which sublimates at 284°C – not behaviour typical of an ionic salt. Its crystal structure is a polymeric F bridged structure in which each Ti is octahedrally surrounded by six F atoms.

In the oxidation state (+IV) the elements have a d^0 configuration with no unpaired electrons: hence their compounds are typically white or colourless and diamagnetic.

Ti^{4+} ions do not exist in solution but oxoions are formed instead. The titanyl ion TiO^{2+} is found in solution but it usually polymerizes in crystalline salts.

The oxidation state (+III) is reducing, and Ti^{3+} ions are more strongly reducing than Sn^{2+} . They are reasonably stable, and exist as solids and in solution. Since the M^{3+} ions have a d^1 configuration they have one unpaired electron and are paramagnetic. The magnetic moments of their compounds are close to the spin only value of 1.73 Bohr magnetons. With only one d electron, there is only one possible $d-d$ electronic transition: hence there is only one band in the visible spectrum, and nearly all the compounds are a pale purple-red colour.

The (+II) state is very unstable and is so strongly reducing that it reduces water. Thus few compounds are known and these exist only in the solid state. The (0), (-I) and (-II) states are found in the dipyriddy complexes $[\text{Ti}^0(\text{dipy})_3]$, $\text{Li}[\text{Ti}^{-1}(\text{dipy})_3]^{3.5}$ tetrahydrofuran and $\text{Li}_2[\text{Ti}^{-II}(\text{dipy})_3]^5$ tetrahydrofuran. The lower oxidation states tend to disproportionate.



SIZE

The covalent and ionic radii increase normally from Ti to Zr, but Zr and Hf are almost identical in size. The reason why Hf does not show the expected

7- Catalytic Properties

Many transition metals and their compounds have catalytic properties.

For example

V_2O_5 : converts SO_2 to SO_3 in the contact process for making H_2SO_4 .

MnO_2 : catalyst for decomposition of $KClO_3$ to give O_2 .

Pd : catalyst for hydrogenation (e.g phenol to cyclohexanone) and many others.

In some cases the transition metals with their variable valency may form unstable intermediate compounds and in other cases they provide a suitable reaction surface.

8- Nonstoichiometry

Many transition elements form nonstoichiometric compounds. These are compounds of indefinite structure and proportions. For example, in iron(II) oxide FeO the ratio of $Fe : O$ is not exactly 1 : 1, but analysis shows that the formula varies between $Fe_{0.94}O$ and $Fe_{0.84}O$. Vanadium and selenium also form a series of nonstoichiometric compounds.

Nonstoichiometry is shown particularly among transition metal compounds of the group VI elements (O, S, Se and Te). It is mostly due to the variable valency of the transition elements, for example when Cu is precipitated by H_2S the analysis of the precipitate proves the presence of a mixture of CuS and Cu_2S .

9- Magnetic Properties

There are three types of magnetism:

Paramagnetism

When a substance is placed in an external magnetic field of strength H , the intensity of the magnetic field in the substance may be greater than or less than the applied field H . If the field in the substance is greater

than H , the substance is said to be **paramagnetic**. In this case, it is easier for magnetic lines of force to travel through the substance than through the vacuum. Thus paramagnetic materials (when are free to move) attract line of force and will move from a weaker to a stronger part of the field. Paramagnetism arises as a result of unpaired electron spins in the atom.

Diamagnetism

If the magnetic field in the substance is less than the applied field H , the substance is said to be **diamagnetic**. Diamagnetic materials tend to repel lines of force. It is harder for magnetic lines of force to travel through diamagnetic materials than through a vacuum, and such materials tend to move from a stronger to a weaker part of magnetic field when hold freely. In diamagnetic compounds all the electrons are paired and their spins are cancelled. The paramagnetic effect is much larger than the diamagnetic effect.

Ferromagnetism

Ferromagnetism can be regarded as a special case of paramagnetism in which the moments on individual atoms become aligned and all points in the same direction. When this happens the magnetic susceptibility is greatly enhanced compared with that it would be if all the moments behaved independently. Alignment occurs when materials are magnetized. This phenomenon is largely present in case of Fe, Co and Ni, so these elements can form permanent magnets. Ferromagnetic property is found in several of the transition metals and their compounds. It is also possible to get **antiferromagnetism** by pairing the moments on adjacent atoms which point in opposite directions. This gives a magnetic moment less than would be expected for an array of independent ions. Since, ferromagnetism and antiferromagnetism depend on orientation, they disappear in solution.

- ii- Going down the group of transition elements, the higher oxidation states become increasingly more stable than the lower ones.

Knowing these trends is useful to comparisons of the strength of oxidizing agents. For example, in the first row of transition elements, the horizontal trend suggests that Ni^{3+} has a greater tendency to become Ni^{2+} than Fe^{3+} has to become Fe^{2+} . In since these species are functioning as oxidizing agent, we conclude that Ni^{3+} is a stronger oxidizing agent than Fe^{3+} .

We can also make vertical comparisons. For example for the MnO_4^- and ReO_4^- , since high oxidation states become more stable going down, so ReO_4^- should be a weaker oxidizing agent than MnO_4^- .

3-Ionization Energy (IE)

In contrast to the wide range of chemical properties of the *d*-block elements, the lanthanides show remarkable similarities in chemical properties. This is due to the fact that the *4f* subshell, which is the only partially filled, is buried beneath the outer *5d* and *6s* subshells and does not interact with the outer valence electrons. Consequently, the chemistry of lanthanides is mainly due to the +3 oxidation state and difference in behavior depends only on difference in ionic size.

Values of Ionization Energy of transition elements are tabulated

The actinide elements exhibit greater variation in oxidation numbers than lanthanides. For example, uranium forms compounds in the +3, +4, +5 and +6 oxidation states, this is due to the fact that *5f* orbitals of the actinide lie farther toward the outer parts of the atom than the *4f* orbitals of the lanthanides.

2-Atomic and Ionic Radii

The horizontal and vertical trends in atomic size can be briefly reviewed as: " As we move across a given transition series, there is a gradual

decrease in atomic radius". This is because the 3d-electrons which are added to the atom shield the outer 4s electrons quite well from the increasing nuclear charge and as a result, the effective nuclear charge exerted by the outer electrons rises only slowly. Therefore, only a small size decrease occurs.

Vertically, we find a rather large increase in size among the d-block elements going from period 4 to period 5. However, between period 5 and 6 there is only a very small size increase and in some cases non at all. This is due to the lanthanide contraction that occurs across the lanthanide series and just cancels the size increase that would be expected as we go from period 5 to period 6. It is worthy to mention that many chemical and physical properties can be correlate with the variation in atomic and ionic radii as we will see below.

3- Ionization Energy (IE)

As mentioned above, the gradual decrease in size along the period is associated with an increase in effective charge which is also accompanied by an increase in the ionization energy. In other words, as we proceed across the period from left to right, it becomes more difficult to oxidize the elements. On the other hand, the ionization energy generally decreases as we proceed down the group which is parallel to the increase in size.

Values of ionization energy of transition elements are intermediate between those of the s- and p-block elements. This would suggest that the transition elements are less electropositive than group I and II and may form either ionic or covalent bonds depending on the conditions. Generally, the lower valent states are ionic and the higher valent states are covalent.

4- Density

The atomic volumes of the transition elements are low compared with elements in the neighboring groups I and II. This is a result of the

decrease in atomic radii observed in transition elements. Consequently, the density of transition metals are high. Practically all have density greater than 5g cm^{-3} except Sc and Ti; 3g cm^{-3} and 4.5g cm^{-3} respectively. The two elements with the highest densities are osmium (22.57g cm^{-3}) and iridium (22.61g cm^{-3}).

5- Melting and Boiling Points

The melting and boiling points of the transition elements are generally very high due to the strong metallic bonds. They typically melt above 1000°C , some elements melt above 3000°C for example Ta; 3000°C , W; 3410°C and Re; 3180°C . There are few exceptions as in the case of La and Ag (920 and 961°C respectively). Other notable exceptions are Zn, Cd and Hg the latter is liquid at room temperature. These three elements behave atypically because the d-shell is complete and d-electrons do not participate in metallic bonding.

6- Colour

Many ionic and covalent compounds of the transition elements are coloured. In contrast compounds of the s- and p-block elements are almost colourless. Colour arises from absorption of radiation in the visible region of spectra, the transmitted light is coloured with the complementary colour to the colour of the light absorbed. Absorption in the visible and UV regions is caused by electronic transition from lower to higher energy levels and is called electronic spectra.

In free isolated gaseous ion the five d orbitals are degenerate i.e they are identical in energy. In real life situation the ion will be surrounded by solvent molecule if it is in solution, by other ligands if it is in complex or by other ions if it is in crystal lattice. In such cases the surrounding groups affect the energy of some d orbitals more than others and the d orbitals are not degenerate but form two groups of orbitals of different