Chem Factsheet

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Extraction of Metals

This Factsheet gives guidance on answering questions on topics related to the extraction of metals from their compounds.

The answers to questions are "best answers", however in some cases other answers will gain equal / partial credit. Common mistakes are also indicated so they can be avoided.

Before starting this Factsheet make sure you understand how to balance chemical equations and know the terms connected with oxidation and reduction including oxidation numbers.

1. Ores

An ore is any material from which a metal can be profitably extracted. It is usually a natural combination of minerals.

Many metals occur in the Earth's crust either as oxide ores or sulphide ores. Oxides ores include bauxite ($Al_2O_3.2H_2O$), haematite (Fe_2O_3), magnetite (Fe_3O_4), rutile (TiO_2) and pyrolusite (MnO_2). Sulphide ores include galena (PbS) and zinc blende (ZnS). These sulphide ores are roasted (heated strongly) in air to convert them to oxides before being reduced to the metal.

e.g. $2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$
and $2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$

The environmental problem of roasting sulphide ore is that sulphur dioxide is a by-product. However this can be used to manufacture sulphuric acid. Should SO_2 escape into the air sulphuric acid is again formed and falls as "acid rain".

Other ores include:
- malachite ($CuCO_3.Cu(OH)_2$)
- wolframite ($FeWO_4 + MnWO_4$) and
- scheelite ($CaWO_4$)

These are also converted to oxides before being reduced.

2. Metals are obtained by a Reduction Process

In all ores the metal atoms have a positive oxidation state (+n). e.g. The oxidation state of iron in Fe_2O_3 is +3.

Question 1: What are the oxidation states of:

1. Al in $Al_2O_3.2H_2O$;	2. Fe in Fe_3O_4;
3. Ti in TiO_2;	4. Mn in MnO_2;
5. Pb in PbS;	6. Zn in ZnS
7. Cu in $CuCO_3.Cu(OH)_2$);	8. W in $FeWO_4$;
9. W in $MnWO_4$;	10. W in $CaWO_4$.

To obtain the metal (M) the oxidation state has to be decreased to zero. Hence a reduction process is required;

$$\text{i.e. } M(+n) + ne^- \rightarrow M(0).$$

The electrons required for the reduction are supplied either by a chemical reducing agent such as carbon, hydrogen, sodium etc. or electrically, using electrolysis.

Whatever the reduction process, an essential condition to obtain the metal is a high temperature. Electrolytic reduction requires a high temperature since a molten electrolyte in essential because the ions must be mobile in order to move to the electrodes.

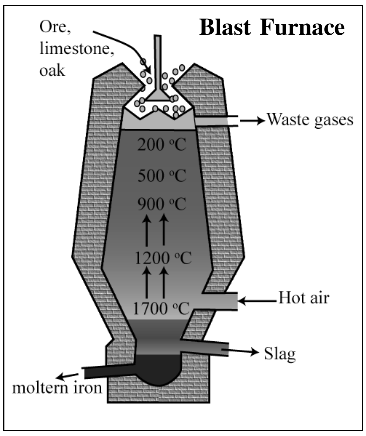
3. Reduction of Oxides

(a) Reduction of Oxide Ores by Carbon and Carbon Monoxide in a Furnace at High Temperatures in a Continuous Process

Carbon (coke from coal) and carbon monoxide (produced inside the furnace from coke and air) are the cheapest reducing agents and are used whenever they are effective and produce metal of suitable quality.

The initial reaction in the furnace is the very exothermic oxidation of carbon to carbon dioxide which produces a high temperature.

$C(s) + O_2(g) \rightarrow CO_2(g)$



This is followed by reduction of carbon dioxide by carbon to carbon monoxide.

$C(s) + CO_2(g) \rightarrow 2CO(g)$

The metal oxide can be reduced to the metal by either C or CO. The actual redox reaction occurring depends upon the particular metal oxide being reduced and the temperature in the furnace.

Examples of redox equations for the extraction of metals by C or CO.

(i) Iron : (in a Blast Furnace)
$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
and $Fe_3O_4 + 4C \rightarrow 3Fe + 4CO$

Note: the limestone ($CaCO_3$) is present to provide CaO by decomposition $CaCO_3 \rightarrow CaO + CO_2$

This reacts with silicon dioxide (sand) impurities in the iron ore forming calcium silicate ("slag") which is then easily removed because it floats on the molten iron product.

$CaO + SiO_2 \rightarrow CaSiO_3$

(ii) Manganese at 2000°C : $MnO_2 + C \rightarrow Mn + CO_2$

(iii) Copper at 2000°C : $CuO + C \rightarrow Cu + CO$

Question 2: Write balanced equations for the reductions of (a) CuO and (b) MnO_2 by CO gas.

Note: Malachite decomposes at the furnace temperature, giving copper(II) oxide. The latter then undergoes reduction:

$CuCO_3.Cu(OH)_2 \rightarrow 2CuO + CO_2 + H_2O$

Rem: sulphide ores are roasted in air to convert them to oxides. Hence, for zinc and lead :

$MO + C \rightarrow M + CO$
or $2MO + C \rightarrow 2M + CO_2$
or $MO + CO \rightarrow M + CO_2$

where "M" = Pb or Zn.

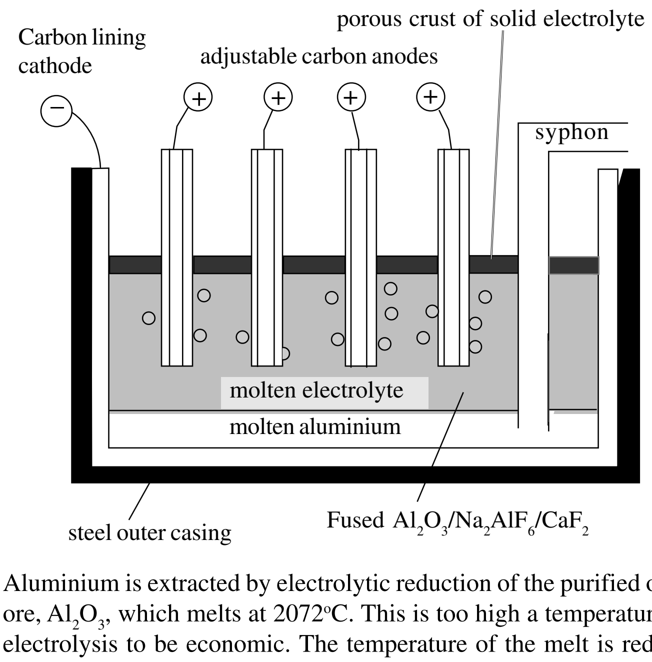
(b) Reduction of Tungsten(VI) Oxide by Hydrogen in a Furnace in a Continuous Process

Carbon will reduce tungsten(VI) oxide to tungsten but some of the tungsten produced will react with carbon to produce tungsten carbide (WC) that makes the tungsten brittle. Thus, more expensive hydrogen gas is used as the reducing agent to produce tungsten. No air must be present as H_2 / O_2 mixtures explode on ignition.

$WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g)$

Note: This process does not release toxic CO or the greenhouse gas, CO_2. However, it does not have a zero carbon footprint because of factors such as the energy requirements of extracting and transporting the ore and generating hydrogen gas.

(c) Reduction of Aluminium Oxide by Electricity in an Electrolytic Cell at High Temperature in a Continuous Process.



Aluminium is extracted by electrolytic reduction of the purified oxide ore, Al_2O_3, which melts at 2072°C. This is too high a temperature for electrolysis to be economic. The temperature of the melt is reduced by dissolving the Al_2O_3 in molten cryolite (Na_3AlF_6) at about 1000°C. This mixture is then electrolysed in a continuous process.

The half-equations are:

At cathode (-) : $Al^{3+}(l) + 3e^- \rightarrow Al(l)$

At anode (+) : $2O^{2-}(l) - 4e^- \rightarrow O_2(g)$

Overall equation for the electrolysis is : $Al_2O_3(l) \rightarrow 2Al(l) + 1½O_2(g)$

Question 3: Is the process occurring at the cathode an oxidation or a reduction. Explain.

Note In the presence of the O_2 product at such high temperatures, the graphite (carbon) anodes burns away.
e.g. $C(s) + O_2(g) \rightarrow CO_2(g)$ and must be periodically replaced.

Very large amounts of electrical energy are used to produce and maintain a molten electrolyte and decompose the Al_2O_3. Smelters tend to be located near hydro-electric power sources. However, electrolytic reduction is still cheaper than carbon reduction where the temperature required is much too high. Aluminium also forms aluminium carbide (Al_4C_3) in the presence of C which makes the metal brittle.

4. Extraction of Titanium

If carbon is used as the reducing agent for titanium oxide, the same problem occurs as for tungsten. i.e. titanium carbide formation makes the titanium brittle and hence unsuitable for engineering purposes such as turbine blades for jet engines.

The extraction of titanium involves two chemical reactions. The first step, which does not involve the reduction of the titanium compound, is the conversion of titanium(IV) oxide to titanium(IV) chloride by heating with coke and chlorine at high temperature.

$TiO_2 + 2C + Cl_2 \rightarrow TiCl_4 + 2CO$

This is an extraction and purification stage because the volatile $TiCl_4$ is distilled off and so separated from impurities present in the original ore.

Question 4: What type of structure and bonding must be present in $TiCl_4$? Explain.

The $TiCl_4$ is then reduced by either sodium or magnesium (both expensive and reactive metals) at high temperature in an atmosphere of argon in a batch process. An inert atmosphere is essential because at the high temperature used the sodium or magnesium would react with oxygen in the air.

The redox equations are :

$TiCl_4 + 4Na \rightarrow Ti + 4NaCl$
or $TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$

Note 1 It is not possible to obtain titanium by electrolysis of either TiO_2 or $TiCl_4$ as the bonding is covalent.

Note 2 Batch processes are used for low tonnage processes and have disadvantages over continuous processes in that they have to be started and stopped. Hence, when they are carried out at high temperatures, they have to be heated up and then allowed to cool down which is very wasteful of energy, along with the associated greenhouse emissions.

5. Solution Mining of Copper

The process involves spraying dilute sulphuric acid onto copper mining waste (or low grade ores can be used) in the presence of a bacterium (e.g. acidithiobacillus ferrooxidans) which results in a dilute solution of copper(II) ions being leached from the waste / ore. This is then reduced to copper using scrap iron, which is relatively cheap.

$Cu^{2+}(aq) + Fe(s) \rightarrow Fe^{2+}(aq) + Cu(s)$

This is an alternative process to the high temperature carbon reduction of copper oxide and it advantages include:

(i) Ambient temperatures are used and hence the cost of energy to achieve the high temperature used in carbon reduction of CuO is saved.

(ii) Carbon dioxide is not produced in this reduction process as it is in carbon reduction so the environment benefits as global warming is not facilitated.

Question 5: Why does this process come under the heading "biomining"?

6. Recycling Scrap Metals : Environmental and Economic aspects

Recycling is very important, especially for metals with a low crustal abundance as ores are a finite resource.

Recycling reduces the use of ores and saves the cost of exploration, mining (and hence mining waste) and extraction. However, it has its own environmental and economic problems in terms or collection, separation and reforming the metals into ingots.

With respect to extraction, all reduction processes are expensive because they generally use high temperatures and this requires fuel. Titanium has the added expense of being a batch process and requires an expensive reducing agent (Na or Mg) and other expensive chemicals, especially chlorine. Aluminium requires expensive electricity for melting the electrolyte and for reduction of the Al_2O_3. Recycling however does involve the costs of collecting, sorting (this is relatively easy for iron as it is magnetic) and transporting the scrap to a site where the metal can be reprocessed. Recycling benefits the environment if the extraction method uses carbon either as a reducing agent or as electrodes, since CO and CO_2 is not emitted into the atmosphere and hence there is no contribution to global warming. Also, the CO is toxic before it is oxidised in air to CO_2. The recycling of zinc or lead, (i.e. metals extracted from sulphide ores) will also eliminate the roasting process which eventually results in acid rain.

Answers to Questions in Text

1. 1. Al(+3) 2. Fe(+2) and (+3) 3. Ti(+4) 4. Mn(+4)
   5. Pb(+2) 6. Zn(+2) 7. Cu(+2) 8. W(+6)
   9. W(+6) 10. W(+6)
2. (a) $CuO + CO \rightarrow Cu + CO_2$
   (b) $MnO_2 + 2CO \rightarrow Mn + 2CO_2$
3. Reduction since electrons are being added.
4. Molecular covalent since the compound is volatile, suggesting only intermolecular forces need to be broken during distillation.
5. This is because of the use of a living organism (a bacterium) in the extraction process.

Practice Questions

1. Reducing agents are used in the extraction of metals.
   (a) In terms of oxidation numbers, state the function of a reducing agent.
   (b) Write equations for the redox reactions that occur in which metals are produced industrially using the following reducing agents, (i) carbon, (ii) iron, (iii) hydrogen.
   (c) State, with reasons, two essential conditions which are required for the reduction of $TiCl_4$ by sodium.
   (d) Explain why it is desirable to recycle titanium but, as yet, very little occurs?

2. Iron is extracted from iron(III) oxide in a continuous process, whereas titanium is extracted from titanium(IV) oxide in a batch process.
   (a) Suggest why a high-temperature batch process is less energy-efficient than a high-temperature continuous process.
   (b) Write an overall equation for the reduction of iron(III) oxide.
   (c) (i) Write two equations to show how titanium is extracted from titanium(IV) oxide in a two-stage process.
   (ii) Use oxidation states to explain why titanium is not reduced in the first stage and why it in the second stage.
   (d) Give the major reason, other than its production is a batch process, why titanium is a more expensive metal than iron.
   (e) Give the major reason why aluminium is more expensive to extract than iron.

3 (a) The extraction of copper from an aqueous solution of copper(II) ions produced when dilute sulphuric acid reacts with copper ores in mine waste requires a reducing agent.
   (i) In terms of electrons, state what is meant by reduction and reducing agent.
   (ii) Write an equation with state symbols for the reaction between copper(II) ions and the reducing agent that is used industrially.
   (b) Copper can also be produced from the ore malachite ($CuCO_3.Cu(OH)_2$). The malachite is initially decomposed forming copper(II) oxide which is then reduced. Write two equations, the first for the decomposition of the copper carbonate of malachite and the second for the decomposition of copper hydroxide of malachite. Finally write an equation for the production of copper from copper oxide using a solid reducing agent.
   (c) Compare these two methods of obtaining copper in terms of energy used and global warming.

4. (a) Give the main reason why carbon reduction is not used to produce (i) aluminium, (ii) tungsten and (iii) titanium.
   (b) In the extraction of aluminium from aluminium oxide both cryolite and carbon are used.
   (i) Give one reason why cryolite is used.
   (ii) Write a half-equation for each of the electrode reactions and explain which half-equation involves reduction.
   (iii) Explain (including an equation) which electrode has to be periodically replaced.
   (c) Give the major reason why recycling of aluminium is economically viable.

5. The principle ore of the metal antimony (Sb) is stibnite (Sb_2S_3). Suggest the cheapest method of obtaining antimony from stibnite. Include in your answers experimental conditions, equations and environmental concerns.

Answers and Mark Schemes

General Points:

A. In structured questions don't write out the question before the answer. Just give the answer. In longer questions, make it clear which part of the question is being answered.

B. Only give the number of examples required in the question. e.g. more than one equation can be given for the reduction of Fe_2O_3, only give one if that is what the question wants.

C. Don't provide state symbols unless they are required.

D. When answering a question on an environmental / economic aspect make sure you give a main reason and not a minor one.

1. (a) To decrease the oxidation state of an atom. *(1)*
   (b) (i) See 3 (a), (ii) See 5, (iii) See 3 (b). *((1) for species ; (1) for balance.) x 2*
   (c) High temperature *(1)* for a rapid / suitable rate of reaction. *(1)* An argon (inert) atmosphere *(1)* to prevent sodium / magnesium reacting with the air / oxygen in the air. *(1)*
   (d) Ti is expensive to produce *(1)* especially since sodium is expensive (or Mg). *(1)* Large carbon footprint in terms of energy production *(1)*. However, most Ti is used for long-lasting purposes (e.g. medical implants) making very little available for recycling *(1)*.

2. (a) Each batch involves starting and stopping. *(1)* On stopping, energy is lost and has to be replaced before the next batch of reactants can be reacted. *(1)*
   (b) $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$
   or $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
   or $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$.
   (1) for species ; (1) for balance.)
   (c) (i) See 4. *(4)*.
   (ii) In stage 1 the oxidation state of Ti is +4 in both TiO_2 and $TiCl_4$. In stage 2 the oxidation state is changes from +4 ($TiCl_4$) to 0 (Ti). Decreases in oxidation state is reduction. *(1 + 1 mark for each ox. st.)*
   (d) The reductant (Na or Mg)/Cl_2 is expensive to make. *(1)*.
   (e) Electrolysis requires a lot of expensive electricity. *(1)*

3. (a) (i) Gain of electrons. *(1)* Electron donor. *(1)*
   (ii) $Cu^{2+}_{(aq)} + Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + Cu_{(s)}$ *(2)*
   (b) $CuCO_3 \rightarrow CuO + CO_2$ *(1)*
   and $Cu(OH)_2 \rightarrow CuO + H_2O$ *(1)*.
   $2CuO + C \rightarrow 2Cu + CO_2$ or See 3 (a) (iii). *(2)*.
   (c) Carbon reduction needs much more energy since a high temperature is needed. *(1)*. Carbon reduction produces carbon dioxide, a greenhouse gas. *(1)*

4. (a) (i) The temperature needed is too high. *(1)*
   (ii) WC forms which makes W brittle. *(1)*
   (iii) TiC forms which makes Ti brittle. *(1)*

   (b) (i) Lowers the melting point (of the electrolyte). *(1)*
   (ii) $Al^{3+} + 3e^- \rightarrow Al$. *(1)* Reduction as electrons are gained / oxidation state decreases. *(1)*
   $2O^{2-} \rightarrow O_2 + 4e^-$ / $O^{2-} \rightarrow ½O_2 + 2e^-$. *(1)*
   (iii) The positive electrode / anode *(1)* burns in/reacts with the oxygen. *(1)* e.g. $C + O_2 \rightarrow CO_2$. *(1)*
   (c) Saves energy / electricity (used to reduce the Al_2O_3). *(1)*

5. Roast the ore in air *(1)* to convert the sulphide to the oxide *(1)*.
   $2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2$ *(2)*
   Reduce the arsenic(III) oxide with carbon (1) at high temperature. *(1)*
   $Sb_2O_3 + 3C \rightarrow 2Sb + 3CO$ or $2Sb_2O_3 + 3C \rightarrow 4Sb + 3CO_2$ *(2)*
   The roasting can release sulphur dioxide in to the air which can produce acid rain. *(1)*
   Carbon reduction produces carbon dioxide which adds to global warming. *(1)*

Acknowledgements: *This Factsheet was researched and written by Bob Adam.*
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