Unit 10

Metallurgy

This unit online, with its interactives:
science-playground.com/s/10a10

Pick up a lump of hematite, the commonest ore of iron, and it looks like nothing much: a heavy, rust-red rock that leaves a red streak on paper. Yet seven tenths of its mass is iron. Every steel rod in the pillars of a new house, every nail, every karahi started as rock like this, and the iron was got out of it in a tower as tall as a ten-storey building, burning day and night for years without being let go cold.

Gold is the opposite. It is found as gold, shining in river sand, and it stays shining for thousands of years. No single acid in the laboratory can dissolve it. But mix two acids, each of which leaves it alone, and the gold disappears. This unit is about how metals are got out of their ores, how iron is made in a blast furnace, and how five metals we use every day, iron, copper, aluminium, silver and gold, behave and react.



Figure 10.1 *Hematite ore in a rock face in England, a coin for scale. Hematite, Fe_2O_3, is the main ore of iron. Ground to a powder, it is red: the same red as rust, which is also an oxide of iron.*
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10.1 Metallurgy

Introduction

A few unreactive metals, such as gold, platinum and sometimes silver and copper, are found in the ground as the metal itself: they are found **native** (in the free state). Most metals are too reactive for that. Over millions of years they have joined with oxygen, sulphur, carbon dioxide or water, and are found as compounds in rocks: they are found in the **combined state**.

A few words you will need, all from Grade 10 Science:

- A **mineral** is a substance found naturally in the Earth's crust, with a definite composition. Hematite (Fe_2O_3), bauxite ($Al_2O_3 \cdot 2H_2O$) and copper pyrites ($CuFeS_2$) are minerals.
- An **ore** is a mineral from which a metal can be extracted **easily and profitably**. Every ore is a mineral, but not every mineral is an ore: clay contains aluminium, but getting aluminium out of clay costs far too much, so clay is not an ore of aluminium; bauxite is.
- **Gangue** is the unwanted rock, sand and earth mixed with the ore as it comes out of the mine.
- A **flux** is a substance added to the furnace to join with the gangue and make a liquid that is easy to remove. Limestone is the flux in a blast furnace.
- **Slag** is that liquid waste: the flux joined with the gangue. It floats on the molten metal and is run off.

Metallurgy is the process of extracting a metal from its ore and purifying it for use. More widely, it is the whole science and technology of metals: getting them out of their ores, purifying them, and making them into useful alloys.

The steps of metallurgy

No two metals are extracted in exactly the same way, and not every metal needs every step (gold, found native, needs no roasting or reduction), but the main steps are these (Grade 10 Science draws them as a flowchart):

1. **Crushing and grinding (pulverization).** Big lumps of ore are broken in crushers and ground to a powder in ball mills. A powder has a huge surface, so every later step goes faster.
2. **Concentration (ore dressing).** The gangue is removed, so that more of what is left is ore. It is done by **gravity separation** (washing away the lighter gangue with water, for heavy ores like hematite), **magnetic separation** (for magnetic ores like magnetite), or **froth flotation** (for sulphide ores like copper pyrites, which stick to oily bubbles while the sand sinks).
3. **Roasting or calcination.** The concentrated ore is changed into the metal's oxide, which is the easiest form to reduce. **Roasting** heats it strongly in plenty of air, for sulphide ores: $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$. **Calcination** heats it strongly with little or no air, for carbonate and hydrated ores: $ZnCO_3 \rightarrow ZnO + CO_2$. Both also drive off water and burn off impurities such as sulphur and arsenic as gases.

4. **Reduction.** Oxygen is taken away from the oxide to leave the metal. Metals in the middle of the reactivity series (zinc, iron, lead, copper) are reduced by heating with carbon or carbon monoxide; done hot enough to melt the metal, this is called **smelting**. Very reactive metals (sodium, magnesium, aluminium) hold oxygen too tightly for carbon, and are got by **electrolysis** of their molten compounds.
5. **Refining.** The impure metal is purified, for example by distillation (zinc, mercury) or by electro-refining (copper).

Check 1

Why is clay not called an ore of aluminium, even though it contains aluminium?

a clay has no aluminium compounds
b aluminium can't be extracted from clay easily and profitably
c clay is not a mineral
d aluminium in clay is native

WORKED EXAMPLE

How much iron is in each ore?

Find the percentage of iron by mass in (i) hematite, Fe_2O_3, and (ii) magnetite, Fe_3O_4. (Fe = 56, O = 16)

Answer

(i) Molar mass of $Fe_2O_3 = 2 \times 56 + 3 \times 16 = 112 + 48 = 160$ g/mol.

$$\%\ \text{Fe} = \frac{112}{160} \times 100\% = 70\%$$

(ii) Molar mass of $Fe_3O_4 = 3 \times 56 + 4 \times 16 = 168 + 64 = 232$ g/mol.

$$\%\ \text{Fe} = \frac{168}{232} \times 100\% = 72.4\%$$

Hematite is 70% iron, magnetite 72.4%. Real ores are mixed with gangue, so a rock from the mine has less.

YOUR TURN

Siderite

Siderite is iron(II) carbonate, $FeCO_3$. What percentage of it is iron? (Fe = 56, C = 12, O = 16)

Answer

Molar mass = $56 + 12 + 3 \times 16 = 116$ g/mol. Iron: $56 \div 116 \times 100\% =$ **48.3%**. That is one reason siderite is a poorer ore than hematite.

10.2 Extraction of iron

The ores of iron

Ore	Chemical name	Formula	Iron by mass
Hematite	iron(III) oxide (ferric oxide)	Fe_2O_3	70%
Magnetite	iron(II,III) oxide (ferrosoferric oxide)	Fe_3O_4	72%
Limonite	hydrated iron(III) oxide	$2Fe_2O_3{\cdot}3H_2O$	60%
Siderite	iron(II) carbonate	$FeCO_3$	48%
Iron pyrites	iron disulphide	FeS_2	47%

Iron is extracted mainly from **hematite**, and also from magnetite. Iron pyrites, the shiny "fool's gold", is not used: getting rid of its sulphur costs too much, and the sulphur dioxide pollutes the air. It is used to make sulphuric acid instead.

> DID YOU KNOW?
> **Iron ore in Nepal**
>
> Nepal has iron ore too. Iron was smelted on a small scale in the hills for centuries, in charcoal furnaces, and blacksmiths turned it into khukuris, plowshares and sickles. A large deposit of iron ore, mostly hematite, was found at Dhaubadi in Nawalparasi in 2016, and a government company has been set up to mine it, though no mine works there yet. Nepal still has no blast furnace: its steel mills melt scrap or roll steel brought from abroad.

Steps of extraction of iron

Iron is extracted from hematite in four steps.

1. Crushing and pulverization

The big lumps of hematite are broken into small pieces in jaw crushers and then ground into a powder in ball mills.

2. Concentration

The powdered ore is washed in a stream of water. Hematite is heavy (about 5 g/cm^3), so it settles, while the lighter sand and clay are carried away: **gravity separation**. If the ore is magnetite, it is separated with a magnet instead: **magnetic separation**.

3. Calcination

The concentrated ore is heated strongly in a furnace with only a little air. This:

- drives off water: $2Fe_2O_3 \cdot 3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$
- decomposes any carbonate: $FeCO_3 \rightarrow FeO + CO_2$
- turns iron(II) oxide into iron(III) oxide, so that it doesn't join the sand to make slag and waste iron: $4FeO + O_2 \rightarrow 2Fe_2O_3$
- burns off impurities as gases: $S + O_2 \rightarrow SO_2$, $4As + 3O_2 \rightarrow 2As_2O_3$, and phosphorus as its oxide.

The ore also becomes porous, so the gases in the blast furnace get into it more easily.

4. Smelting (reduction) in the blast furnace

The calcined ore is reduced to iron in a **blast furnace**: a tall steel tower, 30 meters or more high, lined inside with fire bricks to stand the heat. It is narrow at the top, widens downward, and narrows again near the bottom, ending in the **hearth**, where the molten iron collects.

The charge. A mixture of calcined ore, **coke** (nearly pure carbon, made by heating coal without air) and **limestone** ($CaCO_3$) goes in at the top, in a ratio of about 8 : 4 : 1 by mass. Coke is the fuel, and it makes the reducing agent; limestone is the flux.

The hot blast. Air preheated to about 1,000 °C (in tall stoves called Cowper stoves, heated by burning the furnace's own waste gas) is blown in through pipes called **tuyeres** (say "tweer") at the top of the hearth.

As the charge sinks slowly down the furnace and the hot gases rise up through it, the reactions take place in four zones, from the bottom up:

i. Zone of combustion (1,300–1,500 °C), at the bottom, near the tuyeres. The coke burns in the hot air and gives out a great deal of heat:

$$C + O_2 \longrightarrow CO_2 + \text{heat}$$

Right in front of the tuyeres the gas is hotter still, near 2,000 °C. This zone heats the whole furnace.

ii. Zone of fusion (1,200–1,300 °C), just above it. The carbon dioxide rising from below meets more hot coke and is reduced to **carbon monoxide**. This reaction takes in heat, so the temperature falls a little:

$$CO_2 + C \longrightarrow 2CO - \text{heat}$$

Here the spongy iron coming down from above **melts** ("fusion" means melting), and so does the slag. Molten iron dissolves some carbon (partly as iron carbide, $3Fe + C \rightarrow$

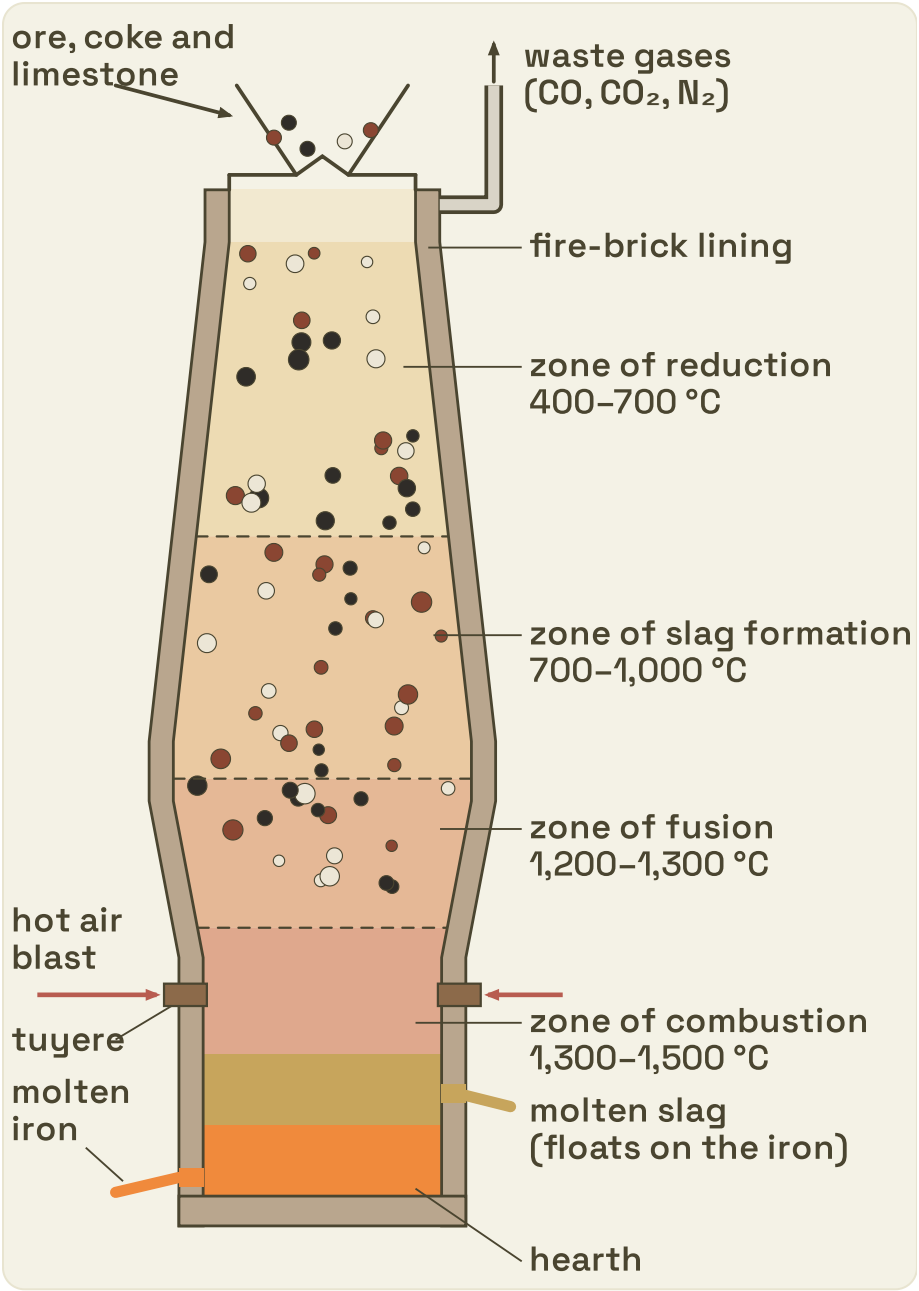


Figure 10.2 *A blast furnace, cut in half. The charge goes in at the top through the cup and cone, which keep the gases in; hot air is blown in through the tuyeres near the bottom. The charge sinks through zones that get*

hotter and hotter, while the hot gases rise against it. Temperatures as they are given for the course; real furnaces differ a little from one to another.

Fe_3C), and silicon, phosphorus and sulphur from the impurities. Any iron oxide that reaches this far is reduced by the coke itself:

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

iii. Zone of slag formation (700–1,000 °C), in the middle. The limestone breaks down into lime (calcium oxide) and carbon dioxide:

$$CaCO_3 \longrightarrow CaO + CO_2$$

The lime, a basic oxide, joins with the sand of the gangue, an acidic oxide, to make **slag**, calcium silicate:

$$\underset{\text{flux}}{CaO} + \underset{\text{gangue}}{SiO_2} \longrightarrow \underset{\text{slag}}{CaSiO_3}$$

iv. Zone of reduction (400–700 °C), near the top. The rising carbon monoxide reduces the iron oxide to iron:

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

It is too cool here for iron to melt, so the iron formed is a solid full of holes, **spongy iron**, which sinks into the hotter zones and melts. (The reduction really happens in steps, $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$, from the top of the furnace down into the zone of slag formation; the overall equation is the one above.)

What comes out. At the bottom, the molten iron collects in the hearth, with the lighter molten slag floating on it, which also keeps the iron from being oxidized again by the blast. The slag is run off through the **slag hole**, higher up, and the iron through the **tap hole** at the bottom, every few hours. The **waste gases** (nitrogen, carbon dioxide and some carbon monoxide) leave at the top and are burnt to heat the Cowper stoves. The iron from the blast furnace, about 93–95% iron with 3.5–4.5% carbon and some silicon, manganese, phosphorus and sulphur, is called **pig iron**.

DID YOU KNOW?

Why "pig" iron?

The molten iron used to be run out along a sand channel into rows of small side molds. The row looked like a sow feeding her piglets, so the bars were called pigs. Today most molten pig iron goes straight, still liquid, to the steel plant next door.

CAREFUL

Carbon monoxide does the reducing

It is easy to think the coke reduces the ore. Most of the reducing in a blast furnace is done by the gas **carbon monoxide**, made from the coke; the coke's other job is to burn and give the heat. Exam questions often ask for this: "Coke acts as a fuel and as a source of the reducing agent, carbon monoxide."

CAREFUL

Different books, different temperatures

The four zones are not separate rooms: the temperature rises smoothly from about 200 °C at the top of a real furnace to about 2,000 °C in front of the tuyeres, and books give slightly different ranges for each zone (the zone of reduction as 250–700 °C or 400–700 °C, for example). Any range close to the ones above is accepted, as long as the order is right: reduction at the top (coolest), then slag formation, fusion, and combustion at the bottom (hottest).

Check 2

In which zone of the blast furnace does limestone react with sand?

a zone of combustion
b zone of fusion
c zone of slag formation
d zone of reduction

Check 3

Molten slag is useful inside the blast furnace because it:

a reduces the iron oxide
b burns to give heat
c floats on the molten iron and protects it from the hot air
d dissolves the coke

Forms of iron

Pig iron is hard but **brittle**: a bar of it breaks rather than bends when hammered. How useful iron is depends almost entirely on how much carbon it contains.

	Cast iron	Steel	Wrought iron
Carbon	2–4.5%	about 0.1–1.5% (up to 2%)	less than 0.1%
How it is made	pig iron melted again, with scrap, and poured into molds	most carbon burnt out of pig iron with oxygen, then the right amount kept or added	almost all carbon removed (by heating it in a furnace lined with iron oxide)
Properties	hard, brittle; can't be hammered into shape and is hard to weld; melts at a lower temperature, so it is easy to cast	hard and strong yet tough; can be rolled, hammered and welded; its hardness can be set by its carbon and by heat treatment	the purest (about 99.5% iron), soft, tough, easily hammered and welded; rusts less
Uses	manhole covers, pipes, stoves, engine blocks, karahis	rods for buildings, bridges, vehicles, tools, utensils (stainless steel), blades	chains, ornamental gates and railings (rarely made today; mild steel has replaced it)

DID YOU KNOW?

How steel is made from pig iron

In a steel plant, molten pig iron is poured into a huge pear-shaped vessel and pure oxygen is blown onto it at faster than the speed of sound (the basic oxygen process). The oxygen burns away most of the carbon as carbon monoxide, and silicon and phosphorus as oxides, which join with lime to make slag. In well under an hour, a few hundred tonnes of pig iron become steel. Adding chromium and nickel makes **stainless steel**, which doesn't rust: that is the steel of a Nepali kitchen's plates and glasses. Alloys are explained in Grade 9 Optional Science: Alloys.

Flow sheet of the extraction of iron

All the steps can be shown in one chart, called a **flow sheet**, with what goes in and what comes out at each step.

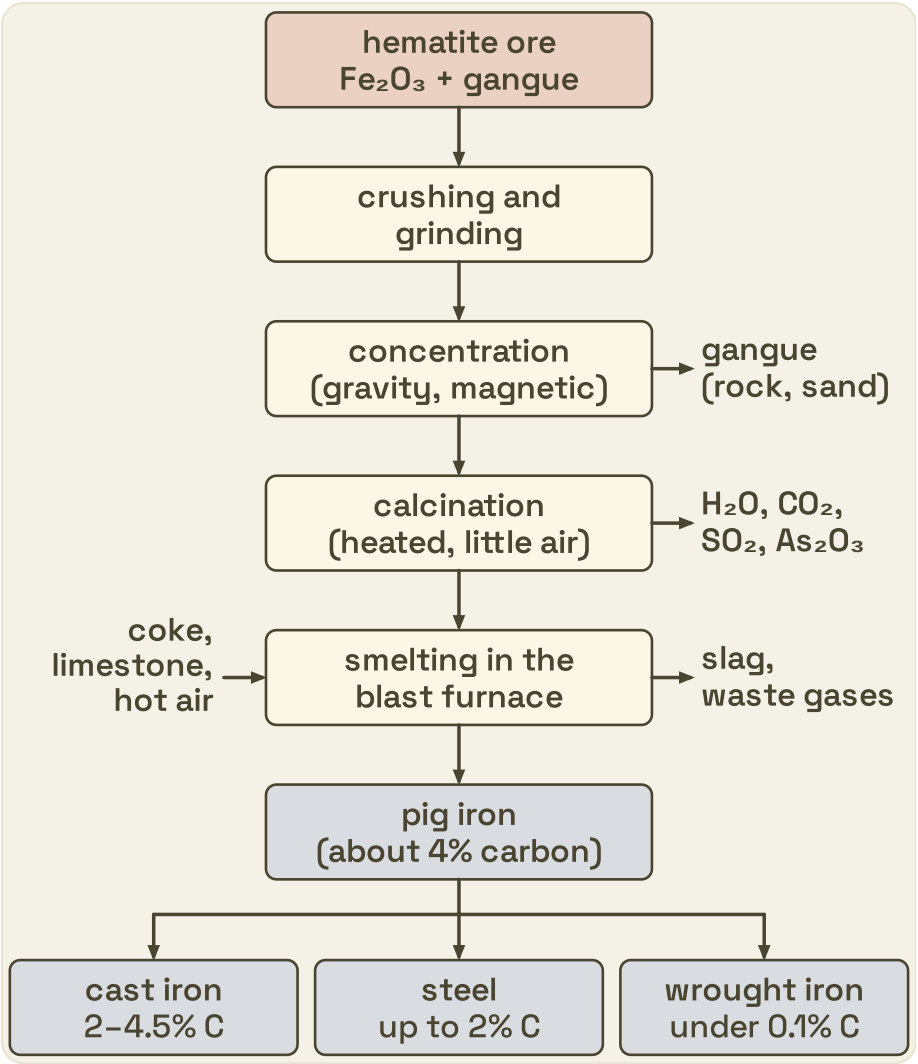


Figure 10.3 *The flow sheet of the extraction of iron from hematite. Down the middle, the steps; on the left, what is added; on the right, what is removed.*

WORKED EXAMPLE

Iron from a tonne of ore

A tonne (1,000 kg) of concentrated ore contains 80% hematite, Fe_2O_3. (i) What mass of iron can be got from it? (ii) What volume of carbon monoxide, measured at STP, is needed for every kilogram of iron made? (Fe = 56, O = 16, C = 12; 1 mole of a gas at STP = 22.4 L)

Answer

(i) Mass of Fe_2O_3 = 80% of 1,000 kg = 800 kg. Iron is 112/160 of Fe_2O_3:

$$m_{\text{Fe}} = 800 \times \frac{112}{160} = 560 \text{ kg}$$

(ii) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$: 3 moles of CO ($3 \times 22.4 = 67.2$ L at STP) give 2 moles of iron (112 g).
For 1 kg = 1,000 g of iron:

$$V_{\text{CO}} = 1000 \times \frac{67.2}{112} = 600 \text{ L}$$

i. **560 kg of iron.**

ii. **600 L of CO at STP for every kilogram of iron.**

YOUR TURN

Limestone for the sand

The ore going into a furnace carries 30 kg of sand, SiO_2. What mass of limestone, $CaCO_3$, is needed to turn it all into slag, and what mass of slag, $CaSiO_3$, is made? (Ca = 40, Si = 28, C = 12, O = 16)

Answer

$CaCO_3 \rightarrow CaO + CO_2$, then $CaO + SiO_2 \rightarrow CaSiO_3$: one mole of $CaCO_3$ (100 g) for each mole of SiO_2 (60 g), making one mole of $CaSiO_3$ (116 g).
Limestone: $30 \times 100 \div 60 =$ **50 kg**. Slag: $30 \times 116 \div 60 =$ **58 kg**.

10.3 Physical properties and uses of iron, copper, aluminium, silver and gold

All five are typical metals: they are shiny (have **luster**), conduct heat and electricity, are **malleable** (can be beaten into sheets) and **ductile** (can be drawn into wires), and are solids at room temperature. But they differ a great deal, and each is used for what it does best.

Property	Iron (Fe)	Copper (Cu)	Aluminium (Al)	Silver (Ag)	Gold (Au)
Color	silvery gray	reddish brown	silvery white	shiny white	yellow
Density (g/cm^3)	7.87	8.93	2.70	10.5	19.3
Melting point (°C)	1,538	1,085	660	962	1,064
Boiling point (°C)	2,861	2,562	2,519	2,162	2,856
Electrical conductivity (best is 1st)	5th	2nd	4th	1st	3rd
Malleability and ductility	malleable and ductile, less than copper	very malleable and ductile	very malleable and ductile	very malleable and ductile	the most malleable and ductile of all metals
Magnetic?	yes (ferromagnetic, up to 770 °C)	no	no (weakly paramagnetic)	no	no

Iron

Pure iron is a silvery gray, fairly soft metal, attracted strongly by a magnet. It is the cheapest of all metals and, as steel, the most used: far more steel is made each year than all other metals together.

Uses: as steel, for the rods and frames of buildings and bridges, railway lines, vehicles, ships, machines, tools, pipes and wire; as stainless steel, for kitchen utensils, sinks and surgical instruments; as cast iron, for stoves, manhole covers and heavy pans; in electromagnets and the cores of transformers and motors (soft iron); and the iron in our blood's hemoglobin carries oxygen, so iron tablets are given for anemia.

Copper

Copper and gold are the only common metals with a color of their own; all the others are silvery or gray. It conducts electricity better than any metal except silver, and

costs far less, and it is very ductile.

Uses: electric wires and cables, the coils of motors, fans and transformers; water pipes and the bottoms of cooking pots (it carries heat well and doesn't react with water); copper water vessels (the gagri and karuwa); alloys such as **brass** (copper and zinc) and **bronze** (copper and tin), used for statues, bells, utensils and coins.

DID YOU KNOW?

The metal statues of Patan

For centuries the Newar metalworkers of Patan have cast statues of copper and its alloys by the lost-wax method: the figure is made in wax, covered with clay, the wax melted out, and molten metal poured in its place. Many are then fire-gilded: a paste of gold dissolved in mercury is spread on the copper and heated until the mercury boils off, leaving a thin, lasting layer of gold. The mercury vapor is poisonous, so the work must be done with great care and good air.

Aluminium

Aluminium is light, only a third as dense as iron or copper, and it doesn't rust: a thin, tough layer of aluminium oxide forms on it at once in air and protects the metal underneath. It conducts heat and electricity well, and is very malleable.

Uses: cooking pots, pressure cookers and kitchen foil; window frames and doors; the frames and bodies of aircraft, buses and bicycles (as light alloys such as duralumin); overhead power lines (light, and good conductors, with a steel core for strength); drink cans and food packaging; and paint for metal roofs and tanks.

DID YOU KNOW?

Once dearer than gold

Aluminium is the most common metal in the Earth's crust, yet in the 1850s it cost more than gold, because nobody could get it out of its ore cheaply: Napoleon III of France is said to have kept aluminium plates for his most honored guests. In 1886 Charles Martin Hall in America and Paul Héroult in France found, independently, how to extract it by electrolysis, and its price fell to a small fraction. It still takes a great deal of electricity, which is why recycling a can saves about 95% of the energy of making a new one.

Silver

Silver is a shining white metal, the best conductor of heat and electricity of all metals, and the best reflector of light. It is soft, so for jewelry and coins it is hardened with a little copper. In air with traces of hydrogen sulphide it tarnishes black (silver sulphide).

Uses: jewelry, ornaments and utensils for worship; coins and medals; mirrors (a thin silver coat behind glass); electrical contacts and the conducting lines printed on solar panels; in medicine and water filters (silver kills germs); and silver bromide was the light-sensitive part of photographic film.

Gold

Gold is a soft, heavy, yellow metal that never tarnishes. It is the most malleable and ductile of all metals: it can be beaten into gold leaf so thin, about a ten-thousandth of a millimeter, that light shows green through it.

Uses: jewelry and ornaments; held by banks and governments as wealth (gold reserves); electrical contacts in phones and computers (it never corrodes); in dentistry; and as gold leaf on temples and statues. Pure gold is too soft for jewelry, so it is mixed with copper or silver. Its purity is given in **carats**: pure gold is 24 carat, and 22-carat gold is 22 parts gold in 24.

WORKED EXAMPLE

A tola of gold

In Nepal, gold is sold by the tola (11.66 g). (i) What is the volume of one tola of pure gold, of density 19.3 g/cm³? (ii) How much pure gold is there in one tola of 22-carat gold?

Answer

(i)

$$V = \frac{m}{\rho} = \frac{11.66}{19.3} = 0.604 \text{ cm}^3$$

That is a cube only about 8.5 mm on each side.
(ii) 22 carat means 22/24 of the mass is gold:

$$11.66 \times \frac{22}{24} = 10.69 \text{ g}$$

i. **About 0.60 cm³.**

ii. **About 10.7 g of pure gold.**

Check 4

Overhead power lines are made of aluminium, with a steel core, rather than copper because aluminium:

a conducts electricity better than copper

b is much lighter, conducts well and costs less

c has a higher melting point

d is magnetic

10.4 Chemical properties with dilute acids, and gold with aqua regia

How a metal reacts with acids depends on where it is in the **reactivity series**:

K, Na, Ca, Mg, **Al**, Zn, **Fe**, Pb, (H), **Cu**, Hg, **Ag**, Pt, **Au**

Metals above hydrogen can push hydrogen out of an acid: they give their electrons to the acid's hydrogen ions, which become hydrogen gas. Metals below hydrogen can't.

With dilute hydrochloric acid and dilute sulphuric acid

Iron reacts readily. Bubbles of hydrogen rise, and the solution turns pale green with iron(II) ions:

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2 \uparrow$$

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2 \uparrow$$

(The iron goes only to Fe^{2+}: hydrogen ions are not strong enough to take its third electron.)

Aluminium is high in the reactivity series, yet at first nothing seems to happen: its thin coat of oxide keeps the acid off. Once the acid has eaten through the coat, the reaction is fast, and the solution stays colorless:

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2 \uparrow$$

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2 \uparrow$$

Copper and **silver** are below hydrogen, so they don't react with dilute hydrochloric acid or dilute sulphuric acid:

$$Cu + HCl \longrightarrow \text{no reaction} \qquad Ag + H_2SO_4 \longrightarrow \text{no reaction}$$

(Copper does dissolve very slowly in these acids if air is bubbled through for a long time, because oxygen takes its electrons: $2Cu + 4HCl + O_2 \rightarrow 2CuCl_2 + 2H_2O$. This is why sour pickles should not be kept in copper pots.)

The gas is tested by bringing a burning splinter to the mouth of the tube: hydrogen burns with a squeaky **pop**.

With dilute nitric acid

Nitric acid is different. Besides being an acid, it is a strong **oxidizing agent**: its nitrate part (nitrogen in the +5 state) takes electrons from a metal more strongly than its hydrogen ions do. So when a metal reacts with nitric acid, the hydrogen ions don't become hydrogen gas; instead the nitrogen is **reduced** to a lower state, giving one of the **oxides of nitrogen** (or, with very dilute acid, ammonium nitrate). In general, nitric acid gives no hydrogen with metals. (Only magnesium and manganese give some hydrogen, with very dilute, cold nitric acid.) And because its nitrate takes electrons so strongly, nitric acid dissolves copper and silver, which are below hydrogen.

Which product forms depends on how dilute the acid is: the more dilute, the further the nitrogen is reduced.

Nitrogen's product	Its oxidation state	Formed with
nitrogen dioxide, NO_2 (brown)	+4	concentrated acid
nitric oxide (nitrogen monoxide), NO (colorless)	+2	dilute acid (about 1 : 1 with water)
nitrous oxide, N_2O	+1	more dilute acid, with reactive metals
ammonium ion, NH_4^+ (stays in the solution as NH_4NO_3)	−3	very dilute, cold acid, with reactive metals like iron and zinc

Nitric oxide is colorless, but the moment it reaches the air at the mouth of the tube, it joins with oxygen to make brown **nitrogen dioxide**:

$$2NO + O_2 \longrightarrow 2NO_2$$

So brown fumes over the tube tell you nitric oxide is being made.

Copper dissolves in dilute nitric acid, the solution turns blue with copper(II) nitrate, and nitric oxide comes off:

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

Silver dissolves in dilute nitric acid as silver nitrate, a colorless solution:

$$3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO\uparrow + 2H_2O$$

Iron with cold, dilute nitric acid gives iron(II) nitrate and ammonium nitrate, both of which stay dissolved:

$$4Fe + 10HNO_3 \longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

With slightly stronger (still dilute) acid, iron gives nitric oxide and is oxidized all the way to iron(III):

$$\mathrm{Fe} + 4\mathrm{HNO_3} \longrightarrow \mathrm{Fe(NO_3)_3} + \mathrm{NO}\uparrow + 2\mathrm{H_2O}$$

(Concentrated nitric acid doesn't dissolve iron at all: it forms a thin film of oxide on the iron's surface that stops the reaction. The iron is then said to be **passive**.)

Aluminium reacts only slowly with dilute nitric acid, because of its oxide coat, giving aluminium nitrate and nitric oxide:

$$\mathrm{Al} + 4\mathrm{HNO_3} \longrightarrow \mathrm{Al(NO_3)_3} + \mathrm{NO}\uparrow + 2\mathrm{H_2O}$$

Concentrated nitric acid makes aluminium passive, like iron, which is why concentrated nitric acid can be carried in aluminium tanks.

CAREFUL

Which equation will the exam want?

For iron and dilute nitric acid, exams usually expect the ammonium nitrate equation, $4\mathrm{Fe} + 10\mathrm{HNO_3} \rightarrow 4\mathrm{Fe(NO_3)_2} + \mathrm{NH_4NO_3} + 3\mathrm{H_2O}$, for cold, very dilute acid. Both equations above are real: which one happens depends on how dilute and how cold the acid is. Write the conditions beside the equation ("cold, very dilute $\mathrm{HNO_3}$"), and you are right either way.

WORKED EXAMPLE

Checking an equation by electrons

Show that $3\mathrm{Cu} + 8\mathrm{HNO_3} \rightarrow 3\mathrm{Cu(NO_3)_2} + 2\mathrm{NO} + 4\mathrm{H_2O}$ is balanced both by atoms and by electrons.

Answer

Atoms. Left: 3 Cu, 8 H, 8 N, 24 O. Right: 3 Cu; H: $4 \times 2 = 8$; N: $3 \times 2 + 2 = 8$; O: $3 \times 6 + 2 + 4 = 24$. Balanced.

Electrons. Each copper atom gives 2 electrons ($\mathrm{Cu} \rightarrow \mathrm{Cu^{2+}}$): $3 \times 2 = 6$ given. Nitrogen goes from +5 in $\mathrm{HNO_3}$ to +2 in NO, taking 3 electrons: $2 \times 3 = 6$ taken. Six given, six taken: balanced. The other 6 nitrate ions don't change; they stay as the nitrate in copper nitrate.

Gold and aqua regia

Gold doesn't react with dilute or concentrated hydrochloric acid, sulphuric acid, or even nitric acid. But a mixture of **3 parts concentrated hydrochloric acid and 1**

part concentrated nitric acid dissolves it. Alchemists called the mixture **aqua regia**, "royal water", because it dissolves gold, the king of metals.

The two acids react together, giving nitrosyl chloride and chlorine (shown in many books as "nascent chlorine", written [Cl]):

$$HNO_3 + 3HCl \longrightarrow NOCl + 2H_2O + 2[Cl]$$

The chlorine attacks the gold, making gold(III) chloride, which dissolves in the extra hydrochloric acid as **chloroauric acid**, a yellow solution:

$$Au + 3[Cl] \longrightarrow AuCl_3$$

$$AuCl_3 + HCl \longrightarrow HAuCl_4$$

Overall, with nitric oxide coming off:

$$Au + HNO_3 + 4HCl \longrightarrow HAuCl_4 + NO\uparrow + 2H_2O$$

What is really happening: nitric acid on its own **can** take a few electrons from gold, but the gold ions it makes take them straight back, so almost nothing dissolves. In aqua regia, every gold ion that forms is grabbed at once by four chloride ions, as the very stable ion $AuCl_4^-$. The gold ions are locked away, so more gold keeps dissolving. Nitric acid does the oxidizing; hydrochloric acid's chloride holds on to the gold.

Silver doesn't dissolve in aqua regia, although it dissolves in nitric acid alone: the silver chloride it forms is insoluble, and coats the silver with a white skin that stops the reaction.

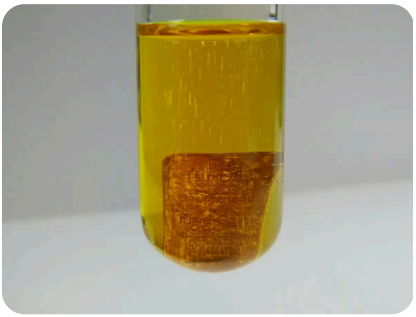


Figure 10.4 *A small gold bar dissolving in aqua regia. The yellow is chloroauric acid, $HAuCl_4$; the fine bubbles are nitric oxide.*
Photo: Daniel Grohmann, CC BY-SA 3.0

A STORY FROM SCIENCE

Two Nobel medals in a bottle

In April 1940, when Germany invaded Denmark, two German physicists had left their gold Nobel Prize medals with Niels Bohr in Copenhagen for safety. Taking gold out of Germany was a crime, and the medals were engraved with their names. The Hungarian chemist George de Hevesy dissolved both medals in aqua regia and left the bottle of orange liquid on a shelf in the laboratory. The soldiers who searched the building never looked at it. After the war, the gold was got back out of the solution, and the Nobel Foundation cast the medals again from it.

Check 5

Which of these metals gives no hydrogen with dilute sulphuric acid, but dissolves in dilute nitric acid?

a iron
b aluminium
c copper
d gold

Check 6

Aqua regia is a mixture of:

a 1 part concentrated HCl and 3 parts concentrated HNO_3
b 3 parts concentrated HCl and 1 part concentrated HNO_3
c equal parts of concentrated HCl and H_2SO_4
d 3 parts concentrated H_2SO_4 and 1 part concentrated HNO_3

IN SHORT

- **Metallurgy:** extracting a metal from its ore and purifying it. An **ore** gives its metal easily and profitably; **gangue** is the rock mixed with it; a **flux** joins the gangue to make **slag**.
- Steps: crushing and grinding, concentration, roasting or calcination, reduction (smelting or electrolysis), refining.
- **Iron** is extracted from **hematite**, Fe_2O_3 (70% iron): crushing, gravity separation, calcination (water, CO_2, S and As driven off; $FeO \rightarrow Fe_2O_3$), smelting in the **blast furnace** with coke and limestone.
- Blast furnace zones, bottom up: **combustion** (1,300–1,500 °C) $C + O_2 \rightarrow CO_2$; **fusion** (1,200–1,300 °C) $CO_2 + C \rightarrow 2CO$, iron melts; **slag formation** (700–1,000 °C) $CaCO_3 \rightarrow CaO + CO_2$, $CaO + SiO_2 \rightarrow CaSiO_3$; **reduction** (400–700 °C) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$. Carbon monoxide is the main reducing agent.
- **Pig iron** (about 4% carbon) becomes **cast iron** (2–4.5% C), **steel** (up to 2%) or **wrought iron** (under 0.1%).
- **Physical properties:** silver conducts best, then copper, gold, aluminium, iron; aluminium is the lightest (2.7 g/cm³) and gold the densest (19.3 g/cm³) and most malleable; only iron is magnetic.
- Iron and aluminium give **hydrogen** with dilute HCl and H_2SO_4 (aluminium slowly at first, its oxide coat); copper and silver don't, being below hydrogen.
- **Nitric acid** is an oxidizing agent: with metals it gives **oxides of nitrogen**, not hydrogen. $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$; $3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$; cold, very dilute with iron: $4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$. NO turns brown ($NO_2$) in air.
- **Aqua regia** (3 HCl : 1 HNO_3, concentrated) dissolves gold: $Au + HNO_3 + 4HCl \rightarrow HAuCl_4 + NO + 2H_2O$.

Exercise

1. Choose the correct option

a. The main ore from which iron is extracted is:

a bauxite
b hematite
c iron pyrites
d copper pyrites

b. The flux used in the extraction of iron is:

a coke
b silica
c limestone
d hot air

c. The hottest part of the blast furnace is the:

a zone of combustion
b zone of fusion
c zone of slag formation
d zone of reduction

d. Which form of iron has the least carbon?

a pig iron
b cast iron
c steel
d wrought iron

e. Which metal reacts with dilute hydrochloric acid to give hydrogen?

a copper
b silver
c iron
d gold

f. When copper reacts with dilute nitric acid, the gas given off is:

a hydrogen
b nitric oxide
c nitrogen
d oxygen

g. Which metal does not dissolve in aqua regia?

a gold
b copper
c iron
d silver

2. Give reasons

a. All ores are minerals, but all minerals are not ores.

b. The ore of iron is calcined before it is put in the blast furnace.

c. Limestone is added to the charge of a blast furnace.

d. Coke is used in the blast furnace.

e. Aluminium seems not to react with dilute hydrochloric acid at first, though it is above hydrogen in the reactivity series.

f. Nitric acid does not give hydrogen with most metals.

g. Gold dissolves in aqua regia but not in nitric acid alone.

3. Differentiate between

i. Roasting and calcination

ii. Cast iron and steel

iii. Action of dilute sulphuric acid and dilute nitric acid on copper

4. Answer the following questions

a. What is metallurgy? Describe its main steps briefly.

b. Draw a labeled diagram of a blast furnace showing its zones.

c. Describe the reactions that take place in the different zones of a blast furnace, with equations.

d. Write the physical properties and two uses each of iron, copper, aluminium, silver and gold.

e. How do copper, silver and iron react with dilute nitric acid? Write the equations. Why are brown fumes seen at the mouth of the test tube?

f. What is aqua regia? How does it react with gold?

5. Numerical problems

a. 5.6 g of iron filings are added to excess dilute hydrochloric acid. (i) What mass of hydrogen is given off? (ii) What volume does it occupy at STP? (Fe = 56, H = 1)

b. Which gives more hydrogen at STP with excess dilute sulphuric acid: 2.7 g of aluminium or 5.6 g of iron? Show your working. (Al = 27, Fe = 56)

c. 19.05 g of copper dissolves completely in dilute nitric acid. What volume of nitric oxide is formed at STP? (Cu = 63.5)

d. A gold bangle has a mass of 23.3 g and a volume of 1.30 cm^3. Is it pure gold? (density of pure gold 19.3 g/cm^3)

Found a mistake? Please tell us.