Chemical Engineering

Industrial-scale processes

Extraction of metals from ore

LD Chemistry Leaflets

C5.1.2.2

The thermite process

Aims of the experiment

- To introduce the chemistry of aluminium
- To produce iron by the thermite process
- To understand the thermite process as an exothermic redox reaction
- To identify iron on the basis of its ferromagnetism

Principles

The reducing effect of aluminium was recognised by Tissier as long ago as 1856. Other researchers started to use this. One problem was that the crucible often shattered due to the intensity of the reaction. Hans Goldschmidt solved the problem in 1897 by discovering a more restrained reaction process. On initial ignition of an aluminothermic mixture, a controlled exothermic reaction occurs at one single point, which then continues throughout the whole mixture. Goldschmidt was therefore the founder of the thermite process, which from that point on found technological applications.

With that it became possible to produce carbon-free metals, which were required for alloys for the steel industry. In this way it became possible to produce metals whose ores were difficult to reduce, as well as such metals that form carbides when reduced with coal (e.g. Cr, Si, B, Co, V, Mn).

Goldschmidt also recognised that the heat being released during the reaction could be used for welding. The first thermite welding on tram lines took place in 1899 in Essen, Germany. Today it is used world-wide as a process for mobile welding.

The reaction on which the thermite process is based is a redox reaction between aluminium and the oxide of the metal which is to be produced. The formal reaction equation is:

Aluminium + Metal oxide → Aluminium oxide + Metal

Here, the aluminium is oxidised and the metal oxide is reduced.

Aluminium is a highly non-noble metal (E°= -1.68 V). It would be oxidised at room temperature by oxygen in the air if it were not protected from this by a layer of aluminium oxide on the surface (passivation). Furthermore, the proportion of oxygen in the air is only around 21 %. In pure oxygen, aluminium foil burns after electrical ignition in around a fiftieth of a second

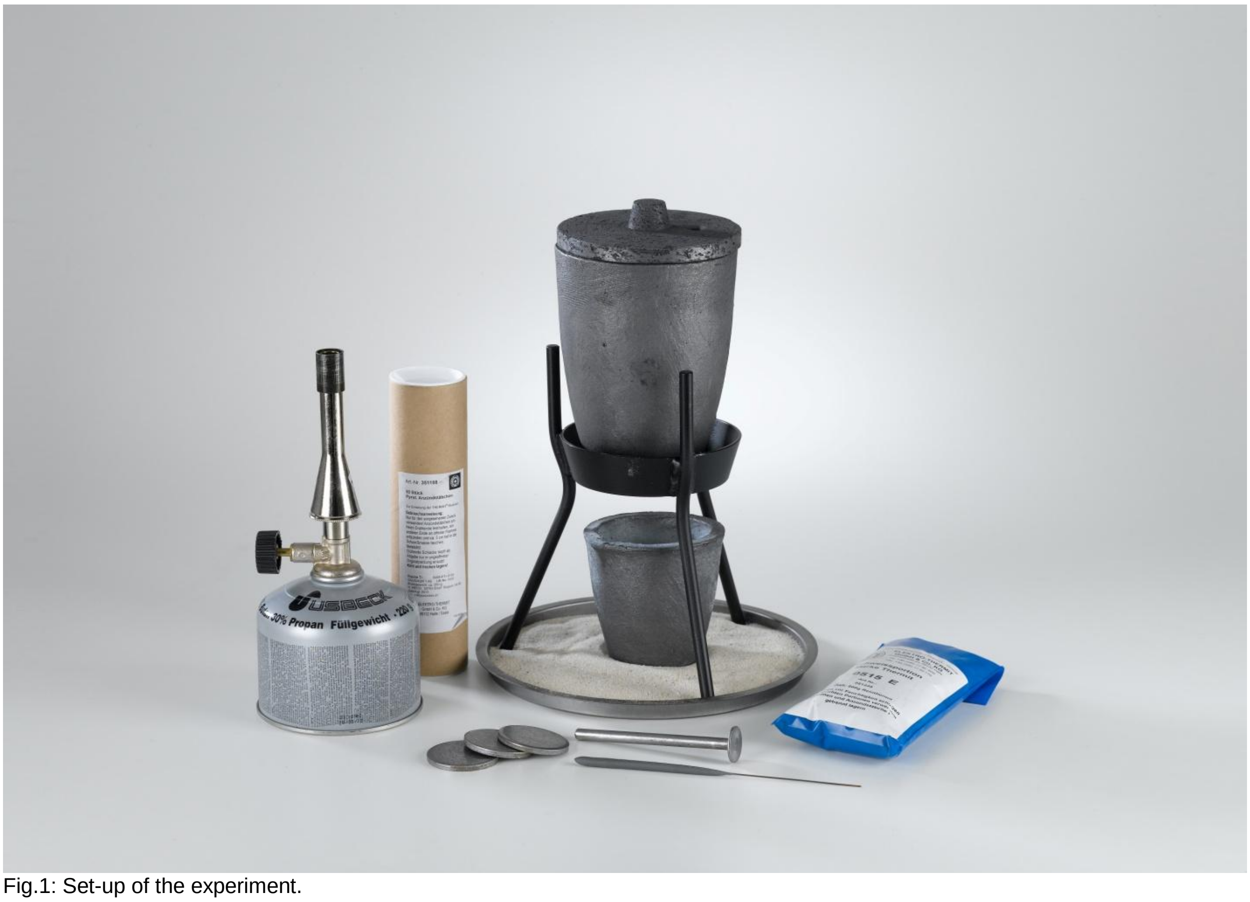

Fig.1: Set-up of the experiment.

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with intense production of light and heat. This is made use of in, for example, photographic flashguns.

According to Hess's law, for the reaction of aluminium with iron oxide, the enthalpy of reaction can be calculated from the standard bond enthalpies of the oxide.

$2\ Al + 3/2\ O_2 \rightarrow Al_2O_3$ $\Delta H = -1675$ kJ/mol

$2\ Fe + 3/2\ O_2 \rightarrow Fe_2O_3$ $\Delta H = -826$ kJ/mol

$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2\ Fe$

$\Delta H = -1675$ kJ/mol + 826 kJ/mol = -849 kJ/mol

This is therefore a strongly exothermic reaction which makes it possible to achieve temperatures of up to 2400 °C and thus produce iron in liquid form.

To start the reaction, the passivation by the aluminium oxide layer on the surface of the aluminium must be overcome. This is achieved by supplying a high activation energy. The thermite mixture ignites at a temperature above 1500 °C. As Goldschmidt has shown, it is not necessary to heat the whole mixture at once, with the disadvantage of an excessively violent reaction. To start the reaction, it is sufficient to supply activation energy locally at one point. The heat energy created through the local reaction provides sufficient activation energy for the bordering areas, so that the reaction spreads out in a controlled manner across the thermite mixture.

The thermite reaction was described by Ostwald as "A blast furnace that fits in a vest pocket", as it enables the mobile production of iron in small quantities, independently of external energy sources.

For example, for welding railway tracks, the gap in the track is encased by a mould consisting of silica sand hardened by CO_2 and sealed with a fireproof plastic moulding agent. The track ends are then pre-heated with a gas flame to dry them (see risk assessment). Then the mixture of iron and aluminium oxide at 2400 °C produced in a crucible is poured into the mould where it melts the track ends and bonds them together. After a cooling period of three to four minutes, the mould and the aluminium oxide residues are removed. The rail is then ground smooth after it has completely cooled.

In the experiment presented here, the method described above for the mobile production of thermite steel will be carried out. Evidence that iron results from the process, and it is not aluminium that is melted, will be provided by a magnet.

Risk assessment

Before starting the experiment, make sure that the crucibles used are absolutely dry, also damp thermite portions must not be used. Therefore store the thermite portions in a dry place.

The reaction cannot be extinguished as it requires no external oxygen. Attempts to extinguish with water or moisture in general lead to the formation of hydrogen. This in turn reacts with oxygen in the air to form water, which in turn reacts again with aluminium or iron to form hydrogen. The result is an explosive chain reaction.

$2\ Al + 3H_2O \rightarrow 3H_2 + Al_2O_3$

$2\ Fe + 3H_2O \rightarrow 3H_2 + Fe_2O_3$

$H_2 + 1/2\ O_2 \rightarrow H_2O$

For safety reasons, the experiment should therefore be carried out in a fume cupboard. The experimenter should wear a lab coat and protective goggles. The safety screen of the fume cupboard should be closed after igniting the mixture. Due to the heat generated, the crucibles must only be handled with crucible tongs until they have cooled down.

In case the mixture does not ignite, do not look directly into the crucible, as it can still take a few minutes after the ignition attempt for a reaction to occur. Use the igniter included for ignition.

Be careful when cooling down the regulus under running water, as hot steam will rise.

So that they stay dry, do not rinse the used crucibles with water.

Equipment and chemicals

1 Thermite experiment 661 540
1 Cartridge burner, DIN type 666 714
1 Gas igniter, mechanical................................ 666 731
1 Crucible tongs, 200 mm 667 035
1 Measuring scoop, PP, 50 mL 604 222
1 Magnet with hole 510 15
Optional:
1 Heat-resistant cover plate, ceramic fibre 667 104
1 Heat-resistant gloves.................................... 667 614
Also required:
Hammer
Aluminium foil

Set-up and preparation of the experiment

Before starting to set up the experiment, the reaction crucible, the receiver crucible and the lid must be dried over the Cartridge burner.

The experiment must be set up on a fireproof base in the fume cupboard. If required, place a heat-resistant plate underneath.

Pour dry sand into the spill tray and distribute it evenly. Place the crucible stand on the spill tray and insert the dried reaction crucible.

Cover the exit hole with a dry closing plate and insert a dry thermite portion.

Caution! Under no circumstances use thermite portions which have become damp. Danger of explosion!

Close the reaction crucible with the lid and place the receiver crucible centrally below the exit hole.

Performing the experiment

Ignite an ignition stick on the Bunsen burner and insert it into the thermite portion through the hole in the lid of the reaction crucible.

Immediately close the safety screen of the fume cupboard and observe the exothermic reaction.

Caution! Only handle the crucible with the tongs. Temperatures of up to 2500 °C prevail.

When the receiver crucible has cooled down (the crucible and contents must not glow red), turn the crucible over using crucible tongs. If the regulus does not fall out on its own, gently hit the bottom of the crucible with a hammer.

The regulus can be cooled down under running water.

Caution! Rising steam! Wear goggles!

The iron in the melt has a higher density than aluminium oxide and sinks to the bottom. Aluminium oxide slag and iron lumps can be separated from each other by gentle taps with the hammer. To show that iron has actually been produced and not a block of aluminium, the regulus can be investigated with a magnet. A piece of aluminium foil can also be investigated with the magnet for comparison.

Allow all items to cool completely before tidying up! Do not cool with water, so that the parts remain dry.

Observation

After starting the reaction, bright sparks fly out of the opening in the lid of the reaction crucible. A brightly shining, liquid metal pours into the receiver crucible.

The receiver crucible glows red on the outside. The contents glow brightly white while pouring into the receiver crucible, then during cooling yellow, orange and finally just red, before it ceases to glow.

When the regulus is cooled under water, steam rises. The solid obtained consists of two separate layers. The black slag crumbles when hit off with the hammer, while the metallic part remains solid.

When the resulting metal block is investigated with the magnet, a distinct attraction by the magnet is established. In contrast, aluminium foil is not attracted to the magnet. When the slag is investigated with the magnet, a slight attraction by the magnet can possibly also be established.

Result

The strength of the exothermic reaction can be recognised by the sparks that jump out of the opening in the lid. The melting points of iron and aluminium oxide are 1539 °C and 2050 °C, respectively. The reaction temperature must therefore be higher than this.

The temperature during cooling can be estimated from the colour of the embers. A body at a given temperature emits a spectrum of electromagnetic radiation characteristic for its temperature. The maximum of the spectrum corresponds with the perceived colour of the light. With increasing temperature, the maximum of the emitted light spectrum shifts from the long to shorter wavelength range.

Tab.1: Relationship between the glow colour and the temperature of a body.

T [°C]	Glow colour
400	Grey embers
525	Start of red embers
700	Dark red embers
850	Cherry red embers
950	Bright red embers
1100	Yellow embers
1300	Start of white embers
1500	Fully white embers

The steam that rises on cooling under water shows that the regulus is considerably hotter than 100 °C at this point in time.

As already mentioned, the reaction is a redox reaction in which aluminium is oxidised to aluminium oxide and iron oxide is reduced to metallic iron.

Oxidation:

$2\ Al + 3\ O^{2-} \rightarrow Al_2O_3 + 6\ e^-$

Reduction:

$Fe_2O_3 + 6\ e^- \rightarrow 2\ Fe + 3\ O^{2-}$

Overall reaction:

$2\overset{0}{Al} + \overset{+III}{Fe_2O_3} \rightarrow \overset{+III}{Al_2O_3} + 2\ \overset{0}{Fe}$

For thermite welding, grey iron (II/III) oxide (magnetite) is often used instead of red iron (III) oxide (haematite). The redox reaction is then:

Oxidation:

$8\ Al + 12\ O^{2-} \rightarrow 4\ Al_2O_3 + 24\ e^-$

Reduction:

$3\ Fe_3O_4 + 24\ e^- \rightarrow 9\ Fe + 12\ O^{2-}$

Overall reaction:

$8\overset{0}{Al} + 3\ \overset{+II/+III}{Fe_3O_4} \rightarrow 4\ \overset{+III}{Al_2O_3} + 9\ \overset{0}{Fe}$

The identification test with the magnet shows that iron has actually been formed. The weak paramagnetism of aluminium cannot be established using the magnet. Iron, on the other hand, is ferromagnetic, and is therefore attracted by the magnet. The slag can also be weakly attracted by the magnet. This is because, alongside aluminium oxide, it still contains some iron.

Cleaning and disposal

Return the sand to the packet provided for it using the measuring scoop. The slag can be removed from the reaction crucible by gently tapping on the excess protruding from the hole in the crucible using the supplied slag pin.

The parts of the apparatus should not be rinsed, as they must remain dry. Instead, the slag dust should be removed from the crucible as thoroughly as possible using a dry paper towel. Return the dry and cooled parts to the polystyrene box for storage.

Aluminium oxide slag and the steel regulus can be disposed of in the collecting container for inorganic solid substances.