Electrolysis of molten zinc chloride


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Index 2.4.1
1 sheet

This demonstration shows that an ionic salt conducts electricity when molten but not when solid. Lead(II) bromide used to be used for this demonstration but this is no longer recommended because of the toxicity of both the salt and the decomposition products. Also, lead bromide decomposes into its elements to some extent upon heating, without the need for electricity.

Timing

This demonstration can be done in a 50 minute lesson. Some quite long periods of waiting are required during the experiment and it would be a good idea to have other activities planned for students during these times.

Equipment

- Bunsen burner
- Tripod
- Heatproof mat
- Pipe clay triangle
- Crucible
- 2 graphite electrodes supported in an electrode holder or bung
- Leads
- Low voltage (0–12 V) power pack
- Ammeter and/or bulb
- Clamp and stand
- Zinc chloride
- Metal spatula
- Indicator paper and/or starch iodide paper

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- Tongs
- Distilled water
- Plastic beaker
- Filter paper and funnel
- Circuit tester (optional)
- Fume cupboard if possible, or a very well-ventilated laboratory.
- Eye protection.

Procedure

Set up a heatproof mat, tripod, Bunsen burner and pipe clay triangle. Put the crucible on the pipeclay triangle, ensuring that it is stable and in no danger of falling through.

Set up the electric circuit with the power pack, ammeter and/or bulb and electrodes in series. Complete the circuit at the electrodes with a key or the metal spatula to satisfy yourself and the students that the circuit works. If it does not work and the electrodes are mounted in a bung, check that they are not broken as this is often the cause of failure of the circuit.

Clamp the electrodes just above the crucible so that they almost touch the bottom but do not touch each other. Fill the crucible to within about 5 mm of the top with powdered zinc chloride. When the solid melts it will decrease in volume as air escapes. It is important that the level of the liquid does not drop below the bottom of the electrodes. Make sure the leads are well out of the way of the Bunsen burner flame. Using long electrodes can help with this.

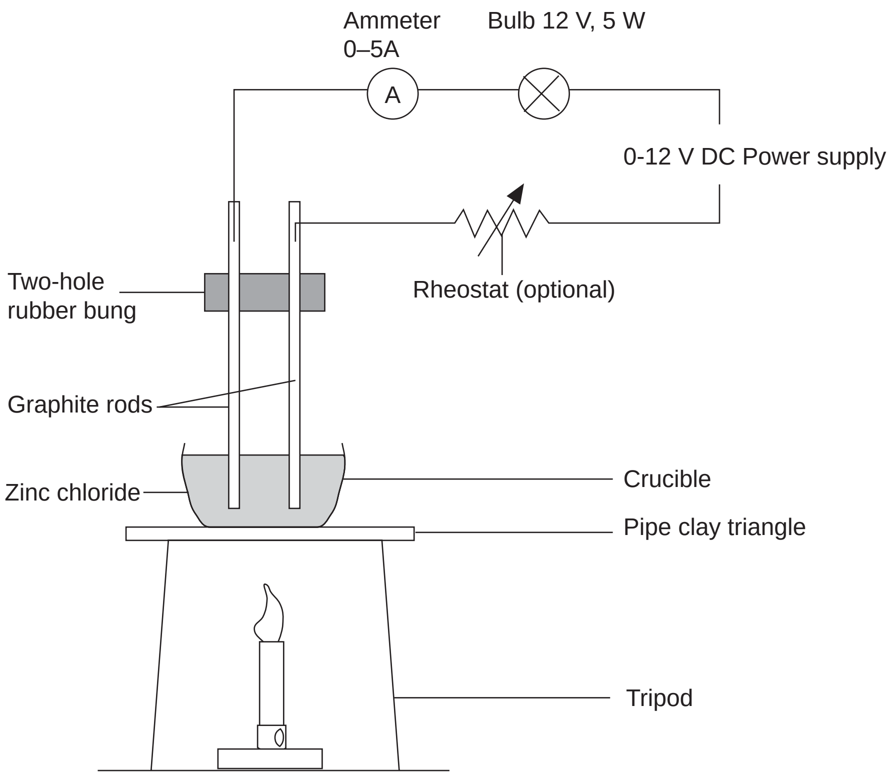

Figure 1 Apparatus for the demonstration

Show that the solid zinc chloride does not conduct electricity.

Begin to heat the crucible with a low to medium Bunsen burner flame. Watch the leads, and the bung if you are using one, to ensure you are not over-heating them. The zinc chloride should take about three or four minutes to melt. It may be tempting to use a roaring Bunsen burner flame to speed the melting up but if you do so a crust may form over the top of the zinc chloride which will prevent students from seeing what is going on. Care should also be taken that the liquid does not boil (see below).

As the salt melts, the bulb will light up and/or the ammeter will give a reading. Turn the Bunsen burner down a bit at this point. The electric current will have a heating effect and this on its own may be enough to keep the zinc chloride molten (as in the industrial electrolysis of aluminium oxide). The boiling point of zinc chloride is about 750 °C, which can easily be reached through a combination of heat from the Bunsen burner and the heating effect of the electric current. If the zinc chloride does begin to boil then it could boil over the sides of the crucible. Boiling also produces fumes of zinc chloride in the air, which rapidly solidify to form a fine powder. The bubbles of zinc chloride fumes could be confused with those of the chlorine gas being formed.

Bubbles of gas form at the positive electrode and this product smells of bleach and swimming pools. To confirm that the gas is chlorine, hold a piece of moist indicator paper close to the bubbles – the paper turns red and the edges may start to bleach. A more convincing test is to use moist starch iodide paper, which turns black in the presence of chlorine.

It is also possible to see crystals of zinc forming on the negative electrode. These can form a bridge across the electrodes, effectively shorting the circuit.

Electrolyse the molten salt for about 15 minutes with the current adjusted to about 0.5 A. Check the current every few minutes to ensure it remains more or less constant as there is a tendency for it to increase slowly. During this period there is little for students to do so they could carry out another activity, such as writing up the experiment. If you have access to a webcam or video camera and a data projector these could be set up to allow students to see what is going on inside the crucible as the experiment progresses. If not, allow the students to view the experiment in groups of two or three. They should observe which electrode the bubbles are forming at, smell the bleachy gas being produced with great care and look for crystals of zinc around the negative electrode.

You could set the apparatus up on a wooden board to show students and then move it into the fume cupboard for the electrolysis. If you do this, check beforehand that the stands etc fit in the fume cupboard and move the apparatus before you start the electrolysis.

It is not recommended that you try to remove the Bunsen burner and cool the salt while still electrolysing it to show that the salt only conducts when molten. The heating effect of the electric current will keep the salt molten for several minutes and when it does cool, a crust will form that is very difficult to melt again. Instead, ensure that you pointed out at the start of the experiment that the solid does not conduct.

After 15 minutes, turn off the power pack and Bunsen burner and remove the electrodes from the crucible. If this is not done while the salt is still molten, the electrodes will stick. Leave the crucible to cool for about 10 minutes. You may be able to see zinc crystals on the electrode and on the surface of the mixture in the crucible. You could stop at this point, but to convince students that a metal really has been made you could separate the zinc from the remaining zinc chloride as described below.

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When the crucible is cool to the touch, put it into a beaker of distilled water. If the water is at all basic (like most hard tap water), the zinc ions will flocculate, forming large particles that are very hard to remove from the zinc metal so do use distilled water if you possibly can. The zinc chloride will dissolve in the water (this may take some time) and can be decanted off. Swirl the beaker so that the zinc metal concentrates in the centre then decant off most of the liquid. Filter the remainder and show students the shiny pieces of metal left on the paper.

Dry the metal carefully between further sheets of filter paper and test it with a circuit tester to prove that you have a metallic product. Given that the starting material was zinc chloride and you have made chlorine during the electrolysis, most students will have little difficulty in accepting that the metal is zinc.

Health and safety

The electrolysis can be carried out in a well-ventilated open laboratory as the amount of chlorine generated in 15 minutes is small enough (less than 60 cm^3) to be acceptable in an averaged sized laboratory. However, chlorine can cause asthma attacks and you may prefer to do the experiment in a fume cupboard to reduce the smell.

Your employer's risk assessment should be consulted before carrying out this activity. This activity is covered by model (general) risk assessments widely adopted for use in UK schools, such as those provided by CLEAPSS, SSERC, ASE and DfES. Bear in mind, however, that these assessments may need some modification to suit local conditions.

It is recommended that you always rehearse demonstrations before carrying them out in front of a class.

Answers

1. Zn^{2+} and Cl^-.

2. The salt does not conduct when it is solid because the charged particles (ions) from which it is made are held in place in the ionic lattice and cannot move. Therefore, these particles cannot carry the charge.

3. Once the salt is molten, the ions are no longer held in place and are free to move. As they are charged, they can carry the current.

4. Moist indicator paper can be used to test for chlorine gas. The paper turns red and is then bleached if chlorine is present. Alternatively, moist starch iodide paper turns black in the presence of chlorine.

5. Chlorine is made at the positive electrode. Chloride ions are negative and so are attracted to the positive electrode, where they give up an electron to become neutral.

6. $2\,Cl^- \rightarrow Cl_2 + 2\,e^-$

7. Zinc metal is made at the negative electrode. Zinc ions are positive and so are attracted to the negative electrode, where they receive electrons to become neutral.

8. $Zn^{2+} + 2\,e^- \rightarrow Zn$

References

A description of the electrolysis of lead(II) bromide can be found in:

T. Lister, *Classic Chemistry Demonstrations*, London: Royal Society of Chemistry, 1995.

A microscale version of the experiment is described in:

Safer Chemicals, Safer Reactions, Uxbridge: CLEAPSS School Science Service, 2003. This document is provided on the CLEAPSS Science Publications CDROM, updated annually.

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1. Which ions are present in zinc chloride, $ZnCl_2$?

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2. Why does the salt not conduct when it is solid?

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3. Why does it conduct when it is molten?

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4. How can you test for the presence of chlorine gas?

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5. At which electrode is the chlorine gas made? Why?

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6. Write an equation for the formation of Cl_2 gas from chloride ions.

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7. At which electrode is the zinc metal produced? Why?

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8. Write an equation for the formation of zinc metal from zinc ions.

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