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39. Liesegang rings: how the tiger got its stripes

Time

The formation of Liesegang rings is a slow process (taking hours to days) but the experiments are simple to set up. This investigation is therefore more suitable to project work undertaken over a few weeks.

Curriculum links

Precipitation reactions.

Group size

2– 4.

Materials and equipment

Materials per group

- 20 g gelatin
- deionised water
- 2.5 g cobalt(II) chloride
- 2.5 g magnesium chloride
- 2.5 g copper(II) sulphate
- 2.5 g manganese(II) chloride
- 2.5 g copper(II) chloride
- 2.5 g potassium chromate(VI)
- 1.0 g silver nitrate
- 20 cm^3 of 880 ammonia
- 20 cm^3 of 19 mol dm^{-3} sodium hydroxide
- 20 cm^3 of 0.1 mol dm^{-3} silver nitrate solution.

Equipment per group

- test-tubes
- test-tube racks
- parafilm
- safety glasses.

Safety

Eye protection must be worn.

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Risk assessment

A risk assessment must be carried out for this activity.

Commentary

Liesegang rings were the subject of many studies at the turn of the century.[1] The production of the rings or bands can be a valuable project for chemistry students as the investigations are open-ended[2] and it is possible to design many different experiments using simple apparatus. The phenomena are fascinating and highly variable. Flicker and Ross[3] have discussed some of the theories that have been proposed to explain the rings, but there is no universally accepted theory to account for their formation. The position of the student is much closer to that of a practising scientist than when the 'right answer' is known from a secondary source.

It is now recognised that Liesegang rings are an example of an oscillating chemical reaction.[4] There has been an explosion of interest in these reactions, which began with what is known as the Belousov-Zhabotinsky (BZ) reaction. Chemical oscillations can take different forms – *eg* if a reaction mixture is stirred, periodic variations in time may be observed. For instance, one stirred BZ solution constantly changes from red to blue and back. In the absence of stirring, the concentrations may vary from place to place as well as through time. The oscillation becomes a travelling wave and can give rise to complex patterns. The BZ solution will give these effects if the solution forms a very shallow, unstirred layer.[5] Liesegang rings are rhythmic precipitation patterns occurring within a gel.

In this process of self organisation, order is appearing spontaneously from disorder. Chemists were very reluctant to accept this idea. Their resistance was rooted in popular but erroneous statements of the Second Law of Thermodynamics to the effect that, if a process occurs spontaneously, entropy or disorder tends to increase. Such statements are incomplete because classical thermodynamics also requires that the system should be near its equilibrium state. Oscillating reactions occur in systems that are far from equilibrium. Ilya Prigogine developed the theory of thermodynamics to include far from equilibrium systems and he showed that ordered structures can develop from disorder in these systems and was awarded the Nobel Prize for chemistry in 1977 for his contribution to thermodynamics.[6]

The mathematician Alan Turing showed that oscillating reactions were theoretically possible. He showed that the physical laws governing the reactions and diffusion of chemical substances could explain the way in which pattern and structure might develop in living things.[7] The physical explanation of the beautiful patterns that develop in the gels has features in common with the way a tiger gets its stripes.

Procedure

It is suggested that the students should first follow the preliminary instructions provided below. When they have set up systems which show the effects they should be asked to put forward hypotheses about the phenomena and to design experiments to test them.

Two sets of instructions are provided. The concentrations differ as the experiments come from different sources; the first set is based on a method for producing 'very perfect silver chromate rings' described in *The science masters' book*.[8]

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Esso

Preliminary instruction

Preparation of a gel containing potassium dichromate(VI) covered by silver nitrate solution

(a) Weigh out 2.5 g of gelatin and 0.025 g of potassium dichromate(VI). Add 50 cm^3 of deionised water. Heat gently, with stirring, until the solution is clear. Pour into test-tubes of various diameters so that the tubes are about two thirds full. Cover the test-tube with parafilm and leave the solution to set.

(b) Weigh out 0.85 g of silver nitrate and dissolve in 10 cm^3 deionised water. About 1 cm^3 of this solution is poured on top of the gel. The test-tube is then covered with parafilm and left undisturbed.

Over the next few days the formation of bands of colour will be observed. The experiment may be modified by pouring a small amount of the gelatin-potassium dichromate(VI) solution onto a glass slide or into a crystallising dish and, after it has set, dropping on a very small amount of silver nitrate solution. Concentric rings will be seen to develop.

Preparation of a gel containing cobalt(II) chloride covered by 880 ammonia

Weigh out 1.5 g of gelatin and 2.5 g of cobalt(II) chloride and add 50 cm^3 of deionised water. Heat gently with stirring until the solution is clear. Pour the solution into a test-tube (25 x 150 mm) until it is about two-thirds full. Cover the tube with parafilm and leave undisturbed until a gel is formed.

Carefully pour 880 ammonia on top of the gel until the tube is almost full. Cover the tube with parafilm. The tube should be left to stand for a few days when bands will be observed to form.

This is the basic procedure suggested by Schibeci and Carlsen.[2] They tried out a variety of systems to produce Liesegang bands and obtained successful results with the following:

Gel containing	Solution on top
cobalt(II) chloride	880 ammonia
magnesium chloride	sodium hydroxide (19 mol dm^{-3})
magnesium chloride	880 ammonia
copper(II) sulphate	silver nitrate (0.1 mol dm^{-3})
manganese(II) chloride	880 ammonia
uranyl nitrate	880 ammonia
uranyl nitrate	sodium hydroxide (19 mol dm^{-3})
uranyl nitrate	silver nitrate (0.1 mol dm^{-3})
copper(II) chloride	sodium hydroxide (19 mol dm^{-3})
potassium chromate(VI)	silver nitrate (0.1 mol dm^{-3})

The article by these authors[2] is particularly helpful because they also give combinations which, they found, did not give the banded effects.

Extension

Further lines of investigation could include the following.

1. Obtaining a three dimensional effect. Liesegang[1] describes patterns like the skins of an onion forming when a block of dichromate gelatin is placed in silver nitrate solution.
2. Varying the concentrations of the reagents.
3. Adding a mixture of substances to the gel – *eg* cobalt(II) chloride, magnesium chloride and manganese(II) chloride.
4. Using test-tubes of differing diameter and glassware of different shapes.
5. Replacing the gelatin with another material to give a gel: Flicker and Ross describe an experiment using agar.[3] Sharbaugh and Sharbaugh describe, in a beautifully illustrated article,[9] their researches using gels prepared by mixing equal volumes of water glass or sodium silicate (density 1.06 g cm^{-3}) and 0.5 mol dm^{-3} ethanoic acid.
6. Looking at geometrical relationships in the patterns formed: is the spacing between the bands uniform? Are the bands rings or spirals?
7. Discovering what happens to the bands when they reach the bottom of the tube.

References

1. R. E. Liesegang, *Chemische reactionen in gallerten*. Dresden und Leipzig: Theodor Steinkopff, 1924.
2. R. A. Schibeci and C. Carlsen, *J. Chem. Ed.*, 1988, **65**, 365.
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5. P. W. Atkins, *Atoms, electrons, and change*. New York: Scientific American Library, 1991.
6. P. Coveney and R. Highfield, *The arrow of time*. London: W. H. Allen, 1990.
7. A. M. Turing, *Philos. Trans. R. Soc. B*, 1952, **237**, 37.
8. *The science masters' book*, part II, series 1.
9. A. H. Sharbaugh and A. H. Sharbaugh, *J. Chem. Educ.*, 1989, **66**, 589.

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▼ A set of instructions is provided which will enable you to produce the phenomena known as Liesegang rings. When you have seen for yourself some of the beautiful effects that can be produced, design an experiment to investigate the ring formation. There is no universally accepted theory to explain this phenomenon so it is up to you to frame hypotheses and to design experiments to test your ideas.

Two chemicals which, in solution, form a sparingly soluble precipitate are required. A gel containing one of the chemicals is prepared first. An aqueous solution of the other chemical is then placed in contact with the gel and after a while periodic precipitation patterns appear in the gel.

The patterns of rings or bands were named after Dr Raphael Liesegang who was the first scientist to make a systematic study of the phenomenon. Until 25 years ago they might have been classed as a scientific curiosity although they were studied in depth by physical chemists interested in certain specialised areas. Liesegang described the rings as rhythmic precipitation patterns occurring within a gel. It is now recognised that they are an example of a chemical reaction that oscillates in time and space. The spontaneous appearance of patterns is remarkable because the system is self-organising – the motions of billions of molecules have synchronised to create patterns in time and space. Liesegang thought that the banded effects seen in rocks, on the wings of butterflies and the skins of animals might have a similar origin to that of the effects he observed.

In 1957 some workers made and photographed in colour about a 100 experiments in silica gels. Thirty years later they compared the appearance of the gels with that in the original photographs. Recently a school in Kent planned to investigate the effect of microgravity on Liesegang rings by designing an experiment to be sent into space on board a US space shuttle. It probably won't be possible for you to make such ambitious plans but there are many other interesting lines of investigation.

Sets of instructions are provided which should enable you to produce very clear Liesegang ring systems in a preliminary experiment.

Preliminary instructions

Preparation of a gel containing potassium dichromate(VI) covered by silver nitrate solution.

(a) Weigh out 2.5 g of gelatin and 0.025 g of potassium dichromate(VI). Add 50 cm^3 of deionised water. Heat gently, with stirring, until the solution is clear. Pour into test-tubes of various diameters so that the tubes are about two-thirds full. Cover the test-tube with parafilm and leave the solution to set.

(b) Weigh out 0.85 g of silver nitrate and dissolve in 10 cm^3 deionised water. About 1 cm^3 of this solution is poured on top of the gel. The test-tube is then covered with parafilm and left undisturbed.

Over the next few days the formation of bands of colour will be observed. The experiment may be modified by pouring a small amount of the gelatin-potassium

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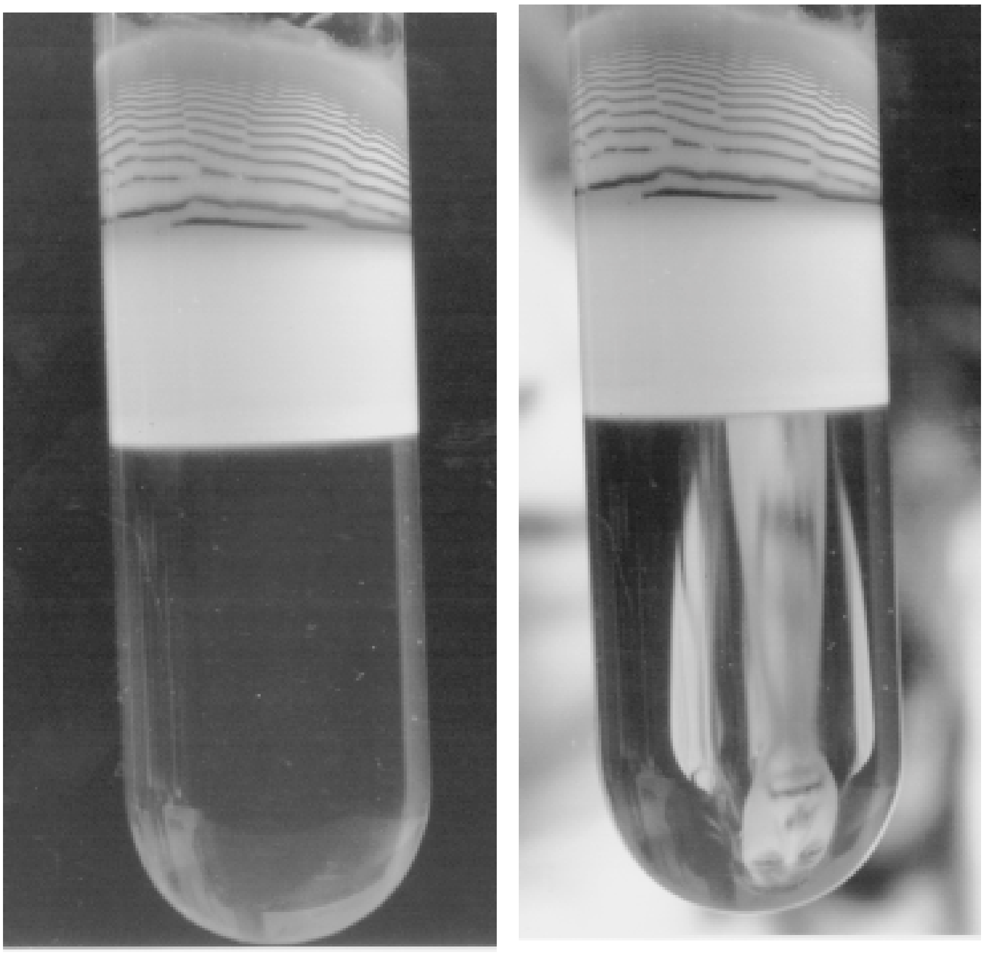
dichromate(VI) solution onto a glass slide or into a crystallising dish and, after it has set, dropping on a very small amount of silver nitrate solution. Concentric rings will be seen to develop.

Preparation of a gel containing cobalt(II) chloride covered by 880 ammonia solution.

Weigh out 1.5 g gelatin and 2.5 g cobalt(II) chloride and add 50 cm^3 deionised water. Heat gently with stirring until the solution is clear. Pour the solution into a test-tube (25 x 150 mm) until it is about two-thirds full. Cover the tube with parafilm and leave undisturbed until a gel is formed. Carefully pour 880 ammonia solution on top of the gel until the tube is almost full. Cover the tube with parafilm. The tube should be left to stand for a few days when bands will be observed to form.



Photographs of Liesegang rings