Some Simple Chemical Experiments with the Microscope

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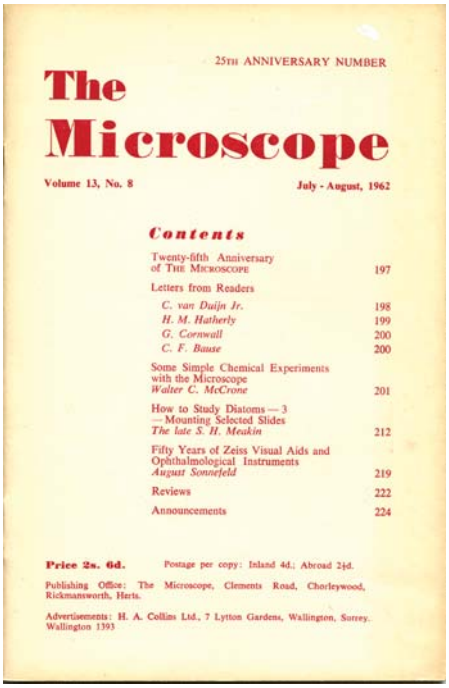
I have sometimes thought it would be possible to teach a full university chemistry curriculum at a laboratory bench equipped with a simple student's microscope, some slides and coverslips in lieu of beakers, and an alcohol lamp in lieu of a Bunsen burner. Simple microscopical experiments could be chosen to illustrate general chemistry as well as inorganic, organic, physical and analytical chemistry. I have yet to prepare such a curriculum in detail, but the following representative experiments will illustrate the possibility.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Furthermore, the experiments to be suggested have been chosen so that the equipment required as well as the chemicals are easily obtained and so that a maximum in results is obtained with a minimum of effort. It is hoped that science teachers on all levels may be tempted to expose their students to some of these experiments and that microscopists in general, but especially the hobbyists, may hereby find another string for their bows.

ELECTROMOTIVE SERIES

Let us start then with a fundamental experiment in first year chemistry — the study of the electromotive series of the elements. This series is the basis for the chemistry of storage batteries, of corrosion and of many chemical reactions. It tells us, more generally, that any element in the series will displace from solution any element below it in the series. For example, metallic zinc will displace silver from a solution of a silver salt and produce thereby metallic silver along with an equivalent amount, atom for atom, of a soluble zinc salt.

We will see how this works under the microscope. First, choose any soluble salt of silver, copper, lead or mercury (the nitrates are best, although the sulphate of copper is easier to get) (1). Now dissolve a small amount of the salt in a drop of water on a microscope slide. The amount of the salt should be no larger than a full-stop and drop of water should not fall off the tip of a drawn-out glass rod. This glass rod drawn out to a diameter at the end of about 1 mm is also convenient for crushing the crystals and stirring the drop to promote solution. When the crystals are completely dissolved add a very tiny particle of metallic zinc or magnesium and observe bubbles of hydrogen (because hydrogen is also lower in the electromotive series than zinc or magnesium) and very beautiful crystalline den-

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ELECTROMOTIVE SERIES

1. Cesium	11. Chromium	20. Hydrogen
2. Rubidium	12. Manganese	21. Antimony
3. Potassium	13. Zinc	22. Bismuth
4. Sodium	14. Cadmium	23. Arsenic
5. Lithium	15. Iron	24. Copper
6. Barium	16. Cobalt	25. Mercury
7. Strontium	17. Nickel	26. Silver
8. Calcium	18. Tin	27. Platinum
9. Magnesium	19. Lead	29. Gold
10. Aluminum		

A partial list of the elements arranged in the order of activity (electromotive series). Any element in the series in metallic form will displace from solution any element of higher number beneath it in the series.

drites of the silver, copper or lead (Figure 1); mercury will separate as tiny metallic globules since mercury is a liquid.

The electromotive series is also the basis for the recovery of expensive metals from solution. A good example is the recovery of metallic silver from photographic hydro solutions by adding copper wire. The above micro-experiment can be carried out just as well with a drop of used hypo and small piece of metallic copper.

PRECIPITATION OF INSOLUBLE SALTS

Many other first-year experiments can easily be adapted to the microscopic scale and, in particular, chemical reactions leading to precipitation of insoluble salts. As one example, place two droplets near each other on a slide and add barium nitrate (or chloride) to one and copper sulphate (or any soluble sulphate such as sodium, potassium, or ammonium) to the other. Leading one drop with the glass tip to the other drop in order to cause mixing will give an immediate and copious precipitate of barium sulphate. The size of the crystals will be larger and better formed. Here are a few additional experiments of this type:

1. Soluble salts of lead and iodide (potassium iodide) give beautiful orange hexagonal plates of lead iodide (Figure 2).

2. Soluble salts of silver and a chloride give tiny octahedra of silver chloride.

3. Soluble salts of potassium or ammonium mixed with a dilute drop of chloroplatinic acid give beautiful large golden octohedra.

ANALYSIS

These experiments are actually the basis for a very useful scheme of inorganic qualitative analysis. If an unknown substance is dissolved in one drop and this solution is mixed with a drop of uranyl acetate and if small black 3-sided pyramids appear then the unknown substance contained is a sodium salt. In a similar way, iodides can be detected by lead ions which form the yellow 6-sided plates, and zinc can be detected by potassium mercuric thiocyanate with which it forms drusy crosses (Figure 3). Procedures are well worked out for the identification of most cations and anions (2). The tests are rapid and precise. If you suspect a given aqueous solution may contain arsenic, a single drop tested as above with a drop of silver nitrate will give reddish skeletal plates if your suspicions are justified. The presence of gold can be easily checked by dissolving a small sample in nitric acid and adding a small crystal of potassium mercuric thiocyanate; tiny red needles covering the added crystal confirm gold.

Tests for organic compounds are also readily carried out, although we need a small source of heat such as an alcohol lamp (or a cigarette lighter) in order to melt the reactants. One test involves a reaction product formed when melted picric acid comes into contact with any fused ring aromatic compound such as anthracene, phenanthrene, pyrene, etc. In all of these cases, a yellow, orange, or red molecular addition compound is formed. Such a test can, of course, be used to detect either picric acid or a fused ring aromatic compound. The correct procedure requires that the un-

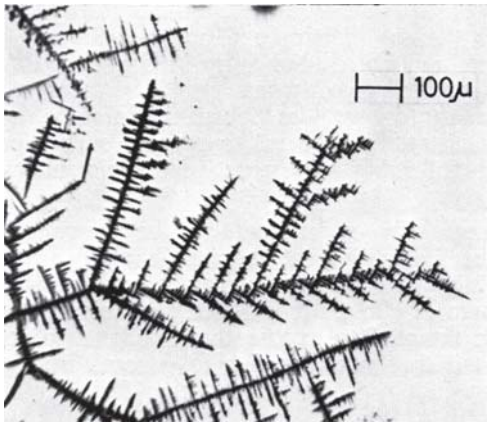

Figure 1. Dendrites of metallic lead displaced from an aqueous solution of lead nitrate by a small fragment of metallic magnesium.

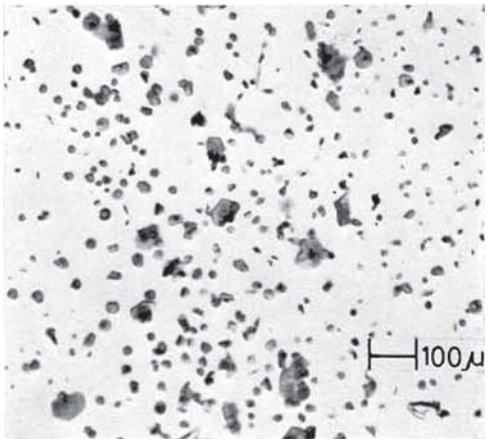

Figure 2. Crystals of orange hexagonal leaflets of lead iodide precipitated by mixing two very dilute drops of aqueous potassium iodide and lead nitrate solutions.

known be melted under a coverslip by heating slowly over a micro-flame, then cooled and allowed to crystallize. The reagent is then placed on the slide in contact with the coverslip and heated until it melts and runs under the coverslip. A yellow to red color where mixing occurs indicates a positive test.

USE OF HEAT

Many experiments can be carried out by using heat to melt the sample and then observing the preparation as it cools. A hot slide may be placed on the stage of the microscope if the top lens of the condenser is at least a ¼ inch below the slide and if low power objectives are used (at least 16 mm, but better, a 32 mm or 48 mm). Quite hot slides (200 °C or hotter) may be supported over the opening in the stage by two bits of cardboard under either end, but cooler slides (under 100 °C may be placed directly on the stage with no damage to either slide or microscope.

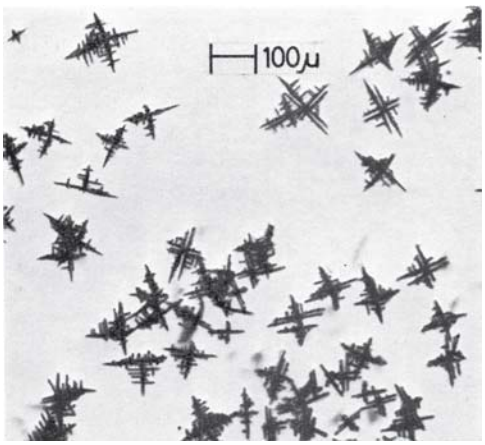

Figure 3. Crystals of zinc mercuric thiocyanate obtained by adding a small crystal of potassium mercuric thiocyanate to a dilute aqueous drop containing a zinc salt.

If we place a small piece of thymol under a coverslip and heat it gently, it will quickly melt and spread out under the slip. If now the preparation is cooled to room temperature, the thymol melt can be made to crystallize by touching a small crystal of thymol to the melt at the edge of the coverslip. If you observe the crystals as they grow, you will see slow but steady growth of angular crystals and these crystals will be permeated with air bubbles (air is soluble in the thymol melt but is rejected by the growing crystals). This phenomenon is similar to the formation of blow-holes in metals, and indeed, thymol is used to simulate the crystallization of a metal.

POLARIZED LIGHT

There is, however, one thing we cannot see in this experiment with thymol without a minor but necessary modification to our microscope. We must be able to use polarized light, and to do this we need a polarizer. Fortunately, Polaroid films are readily available and can be easily cut to fit any microscope. An old pair of Polaroid glasses may even be sacrificed for the purpose. We need two Polaroid filters, one below the preparation and one above, and both can be placed wherever they are most convenient. One is usually placed

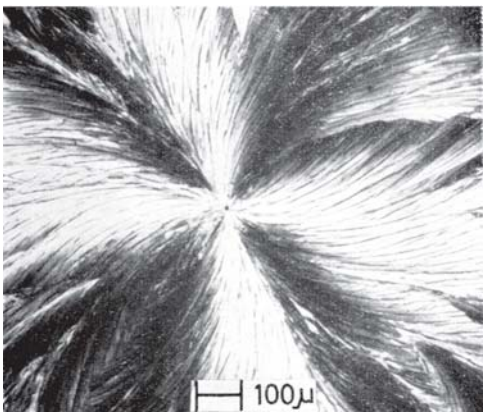

Figure 4. Crystals of TNT grown from the melt (crossed polars).

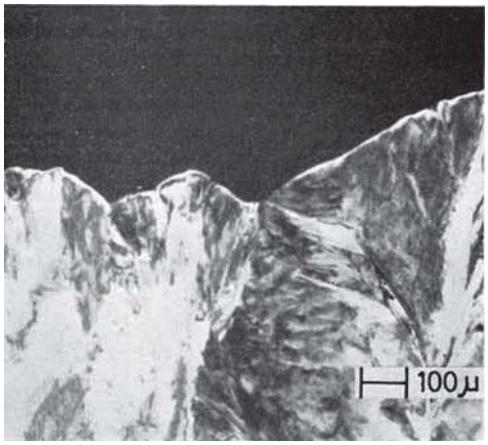

Figure 5. Crystals of aspirin (acetyl salicylic acid) grown from the melt (crossed polars).

just below the substage condenser, and many microscope substages have a filter holder in the proper position. The other Polaroid filter is placed either in the body tube above the objective or on top of the eyepiece. It should not be placed inside the eyepiece because any scratches or dust on it will be too nearly in focus when looking through the microscope.

Finally, the two filters must be rotated with respect to each other so that the illuminated field of the microscope is as dark as possible (crossed Polaroids). Now, with the field as dark as possible, place a crystallized preparation of thymol on the stage and observe the display of polarization colors shown by this compound. Repeat the melting and crystallization of the thymol, but this time press down on one edge of the coverslip as crystallization occurs in order to obtain a wedge-shaped crystal preparation. The polarization of colors is an obvious function of thickness. The actual series of colors as they increase with thickness is identical with Newton's series of interference colors. Some compounds show anomalous polarization when crystallized as a wedge preparation. Picric acid is a good example of this.

The appearance of crystals as they crystallize from the melt and the polarization colors shown are characteristic of the compound and dependable identification of fusible compounds has been based on this test (3). A few common compounds that work well in this respect are DDT, TNT (Figure 4), paraffin wax or any other wax, naphthalene, benzoic acid, camphor and aspirin (Figure 5). An aspirin tablet works very well, although it will also contain many small starch grains showing black polarization crosses between crossed polars.

POLYMORPHISM

Sooner or later, if you melt and study additional substances, you will encounter polymorphism. This is a normal occurrence shown by most compounds and means that a given compound can crystallize in different crystal forms, or polymorphs. Each polymorphic form has a different shape, polarization colors, melting point, etc. Rhombic and monoclinic sulphur are good examples of polymorphs. Other compounds which can melt and observe different forms, and indeed, even observe the transformation of one form to the other include mercuric iodide, ammonium nitrate and cholesteryl acetate. These changes occur spontaneously as the preparation cools on the microscope stage. Compounds vary in the case with which they show the unstable form but the ones given above are absolutely certain each and every time. Others which may or may not show two different forms include DDT, Vanillin (Figure 6), mononitro-naphthalene and acetanilide. A hit here is to melt the crystals completely and allow the melt to stand undisturbed and unseeded until crystals finally appear in the supercooled melt. These will often be the unstable form.

LIQUID CRYSTALS

One of the compounds suggested above to illustrate polymorphism (cholesteryl acetate) also illustrates another very interesting phenomenon — a liquid crystal or, more scientifically, a medomorphic phase. A liquid crystal is not really as highly ordered on a molecular scale as a normal crystal and it flows as if it were a liquid, yet it does have sufficient molecu-

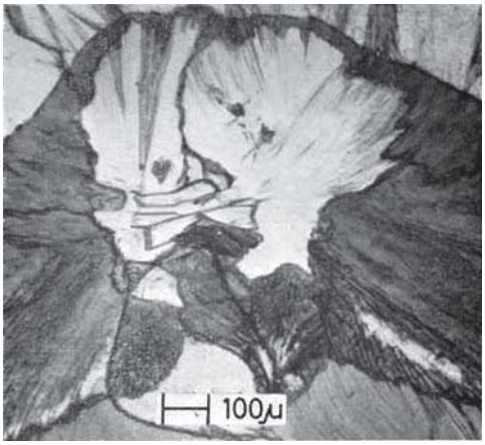

Figure 6. Crystals of vanillin grown from the melt showing two crystal forms: unstable light in color and stable, dark.

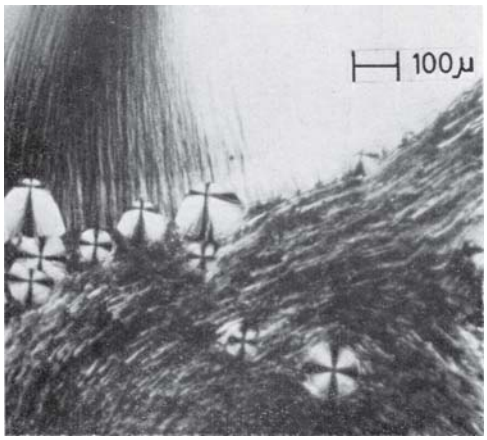

Figure 7. Crystals (spherulites) of the stable polymorph of cholesteryl acetate growing in the liquid crystalline phase on cooling after complete melting (crossed polars).

lar order to show polarization colors. When cholesteryl acetate or other cholesteryl esters are melted and cooled, the first phase to appear between crossed Polaroids is the liquid crystal crystalline phase. This phase can be observed to flow like a liquid as the very beautiful spherulites of the stable solid phase nucleate and grow through the preparation (Figure 7).

OTHER METHODS

There are other ways to crystallize compounds besides the two already described (precipitation and from the melt), and these (sublimation and from solution by evaporation of the solvent) also present possible experiments of interest. Many compounds, particularly organic compounds, can be sublimed to give well-formed and characteristic crystals. The procedure is to heat a few crystals very slowly under a coverslip and to stop heating before melting occurs and at the point when a visible clouding of the underside of the coverslip appears. The precipitation is then observed directly without removing the coverslip. Mercuric iodide, hexamethylenetetramine (Figure 8) and caffeine sublime to give well-formed crystals. Many other compounds sublime under the same conditions though the crystals may not be so perfect (e.g., naphthalene).

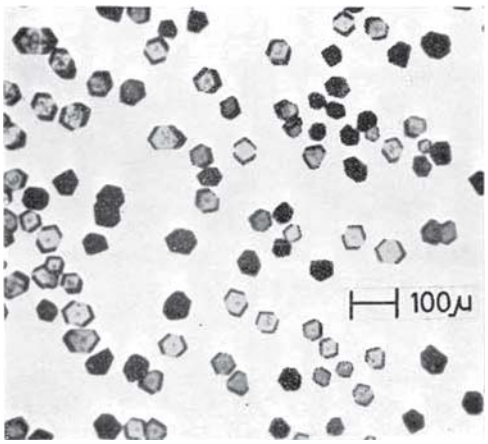

Figure 8. Crystals of hexamethylene tetramine (Urotropine) formed by sublimation from a microscope slide to a coverslip.

Crystallization of water-soluble compounds from a drop of water on a slide is a useful technique and a good way to study crystals. No heat is used and the best crystals appear on slow evaporation at room temperature of a deep drop of saturated solution. This last sentence is very important and we should emphasize slow evaporation, room temperature, deep drop and saturated solution. The procedure, in a bit more detail, is as follows:

1. Using the drawn-out glass tip, place a small drop on a clean microscope slide, being careful not to spread the drop.
2. Add a small mount (size of hole in the letter "a") of the water-soluble salt to be recrystallized.
3. Crush the crystals and stir the drop with the glass tip. Be sure to hold the rod vertically so that the drop does not spread.
4. Add additional crystals, if necessary.
5. Continue crushing crystals and stirring drop.
6. As crust forms at edge of drop, push into drop with vertical glass tip, being careful to avoid spreading the drop.

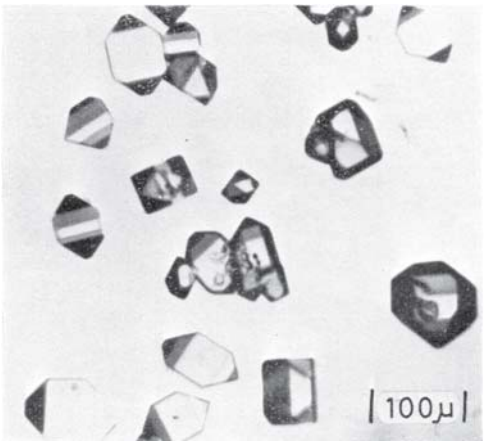

Figure 9. Crystals of ammonium dihydrogen phosphate growing in an aqueous drop as the water evaporates.

7. Continue as above until the well-formed crystals completely beneath the top of the drop begin to grow.

Properly done, very perfect crystals can be grown of such compounds as sodium chloride, lead nitrate, any of the alums, ammonium dihydrogen phosphate (Figure 9), sodium nitrate, ammonium perchlorate, borax, copper sulphate, and potassium dichromate. This list of compounds includes at least one compound in each of the six different crystal systems. Other water-soluble compounds can also be recrystallized in a similar manner, although the best results are usually obtained with the more soluble compounds and more insoluble ones such as calcium sulphate, barium carbonate, etc., should be recrystallized by the precipitation methods as described above.

Finally, one dramatic experiment may be suggested to illustrate the mechanism of crystal growth. Crystals are assumed now to grow as a result of imperfections and the spiral growths associated with growth nucleation at imperfections can be observed very nicely with cadmium iodide. An aqueous solution of this salt saturated 50–60 °C is observed during cooling using either axial illumination for better contrast or reflected light. Spectacular spiral steps will be visible, slowly revolving on the flat faces of each growing plate.

I doubt I have proved my contention that a full university curriculum in chemistry under the microscope is possible; however, we have outlined a number of experiments which illustrate a variety of chemical and physical principles. Given more space, many more such experiments could be suggested. Perhaps the reader may be induced to develop new experiments on his own.

REFERENCES

1. To make easier the accumulation of the chemicals and materials used in these experiments, McCrone Associates is offering a kit containing small vials of most of the compounds (more than 30 in all), the drawn-out glas tip and two small squares of Polaroid suitable for adaptation of a medical microscope for the use of polarized light. This kit may be purchased post paid from McCrone Associates, 449 E. 31st Street, Chicago, Ill., U.S.A., for $6.00; or from McCrone Associates, The Old Slaughterhouse, Ann's Place, Albion Street, Southwick, Sussex, England, for £2 2s. 0d.

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3. McCrone, W.C.: Fusion Methods in Chemical Microscopy (1957, Interscience Publishers, London and New York).