

### 3.17 Metal apparatus

#### Platinum

Platinum is used mainly for crucibles, dishes and electrodes; it has a very high melting point (1773 °C), but the pure metal is too soft for general use, and is therefore always hardened with small quantities of rhodium, iridium or gold. These alloys are slightly volatile at temperatures above 1100 °C, but retain most of the advantageous properties of pure platinum, such as resistance to most chemical reagents, including molten alkali carbonates and hydrofluoric acid (the exceptions are dealt with below), excellent conductivity of heat, and extremely small adsorption of water vapour. An alloy consisting of 95% platinum and 5% gold is known as a 'non-wetting' alloy and fusion samples are readily removed from crucibles composed of this alloy; removal is assisted by keeping the crucible tilted while the melt is solidifying. Crucibles made of this alloy are used in preparing samples for X-ray fluorescence investigation.

A recent development is the introduction of ZGS (zirconia grain stabilised) platinum. This is produced by adding a small amount of zirconia (zirconium(IV) oxide) to molten platinum, which leads to modification of the microstructure of the solid material with increased hot strength and greater resistance to chemical attack. Whereas the recommended operating temperature for pure platinum is 1400 °C, the ZGS material can be used up to 1650 °C. Apparatus can also be constructed from TRIM, which consists of palladium coated with ZGS platinum; this permits stouter apparatus with the corrosion resistance of ZGS platinum at an appreciably cheaper price.

Use a platinum triangle to support platinum crucibles during heating, or a silica triangle if platinum is not available; avoid Nichrome and other metal triangles. Pipeclay triangles usually contain enough iron to damage the platinum. Hot platinum crucibles must always be handled with platinum-tipped crucible tongs as unprotected brass or iron tongs produce stains on the crucible. Platinum vessels must not be exposed to a luminous flame, nor should they be allowed to come into contact with the inner cone of a gas flame; this disintegrates the surface of the metal, causing it to become brittle, probably through formation of platinum carbide.

At high temperatures platinum permits the flame gases to diffuse through it, and this may cause the reduction of some substances not otherwise affected. Hence if a covered crucible is heated by a gas flame, there is a reducing atmosphere in the crucible; but with an open crucible, diffusion into the air is so rapid this effect is not appreciable. If iron(II) oxide is heated in a covered crucible, it is partly reduced to metallic iron, which alloys with the platinum; sodium sulphate is similarly partly reduced to the sulphide. So, in the ignition of iron compounds or sulphates, it is advisable to place the crucible in a slanted position with free access of air.

There are several procedures where platinum apparatus may be used without significant loss:

1. Fusions with (a) sodium carbonate or fusion mixture, (b) borax and lithium metaborate, (c) alkali bifluorides, and (d) alkali hydrogensulphates (slight attack in the last case above 700 °C, which is diminished by the addition of ammonium sulphate).
2. Evaporations with (a) hydrofluoric acid, (b) hydrochloric acid in the absence of oxidising agents which yield chlorine, and (c) concentrated sulphuric acid (a slight attack may occur).
3. Ignition of (a) barium sulphate and sulphates of metals which are not readily reduced, (b) the carbonates, oxalates, etc., of calcium, barium and strontium, and (c) oxides which

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are not readily reducible, e.g. CaO, SrO, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, ThO<sub>2</sub>, MoO<sub>3</sub>, and WO<sub>3</sub>. (BaO, or compounds which yield BaO on heating, attack platinum.)

Platinum is **attacked** under the following conditions, and these procedures must not be conducted in platinum vessels:

1. Heating with the following liquids: (a) aqua regia, (b) hydrochloric acid and oxidising agents, (c) liquid mixtures which evolve bromine or iodine, and (d) concentrated phosphoric acid (slight, but appreciable, action after prolonged heating).
2. Heating with the following solids, their fusions, or vapours: (a) oxides, peroxides, hydroxides, nitrates, nitrites, sulphides, cyanides, hexacyanoferrate(III), and hexacyanoferrate(II) of the alkali and alkaline earth metals (except oxides and hydroxides of calcium and strontium); (b) molten lead, silver, copper, zinc, bismuth, tin, or gold, or mixtures which form these metals upon reduction; (c) phosphorus, arsenic, antimony, or silicon, or mixtures which form these elements upon reduction, particularly phosphates, arsenates, and silicates in the presence of reducing agents; (d) sulphur (slight action), selenium, and tellurium; (e) volatile halides (including iron(III) chloride), especially those which decompose readily; (f) all sulphides or mixtures containing sulphur and a carbonate or hydroxide; and (g) substances of unknown composition. Also heating in an atmosphere containing chlorine, sulphur dioxide or ammonia, whereby the surface is rendered porous.

Solid carbon, however produced, presents a hazard. It may be burnt off at low temperatures, with free access to air, without harm to the crucible, but it should never be ignited strongly. Precipitates in filter paper should be treated in a similar manner; strong ignition is only permissible after **all** the carbon has been removed. Ashing in the presence of carbonaceous matter should not be conducted in a platinum crucible, since metallic elements which may be present will attack the platinum under reducing conditions.

### ✓ Cleaning and preservation of platinum ware

All platinum apparatus (crucibles, dishes, etc.) should be kept clean, polished and in proper shape. If a platinum crucible becomes stained, a little sodium carbonate should be fused in the crucible, the molten solid poured out on to a dry stone or iron slab, the residual solid dissolved out with water, and the vessel then digested with concentrated hydrochloric acid; this treatment may be repeated, if necessary. If fusion with sodium carbonate is without effect, potassium hydrogensulphate may be substituted; a slight attack of the platinum will occur. Disodium tetraborate may also be used. Sometimes the use of hydrofluoric acid (**care**) or potassium hydrogenfluoride may be necessary. Iron stains may be removed by heating the covered crucible with a gram or two of pure ammonium chloride and applying the full heat of a burner for 2–3 min.

All platinum vessels must be handled with care to prevent deformation and denting. Platinum crucibles must on no account be squeezed with the object of loosening the solidified cake after a fusion. Boxwood formers can be purchased for crucibles and dishes; these are invaluable for reshaping dented or deformed platinum ware.

### Other metals

**Platinum-clad stainless steel laboratory ware** This is available for evaporating solutions of corrosive chemicals. These vessels have all the corrosion resistance of platinum

up to about 550 °C. The main features are (1) much lower cost than similar apparatus of platinum; (2) an overall thickness about four times that of similar all-platinum apparatus leading to greater mechanical strength; and (3) lower susceptibility to damage by handling with tongs, etc.

**Silver apparatus** The chief uses of silver crucibles and dishes in the laboratory are for the evaporation of alkaline solutions and for fusions with caustic alkalis; during fusion the silver is slightly attacked. Gold vessels (m.p. 1050 °C) are more resistant than silver to fused alkalis. Silver melts at 960 °C, so take care when heating it over a bare flame.

**Nickel ware** Nickel crucibles and dishes are used for fusions with alkalis and with sodium peroxide (**care**). In the peroxide fusion a little nickel is absorbed into the mass, but this is usually not objectionable. No metal entirely withstands the action of fused sodium peroxide. Nickel oxidises in air, hence nickel apparatus cannot be used for operations involving weighing.

**Iron ware** Iron crucibles may be substituted for those of nickel in sodium peroxide fusions. They are not so durable, but are much cheaper.

**Stainless steel ware** Beakers, crucibles, dishes, funnels, etc., made of stainless steel are available commercially and have obvious uses in the laboratory. They will not rust, are tough, strong, and highly resistant to denting and scratching.

**Metal crucibles and beaker tongs** Crucibles, evaporating basins and beakers which have been heated need to be handled with suitable tongs. Crucible tongs should be made of solid nickel, nickel steel or another rustless ferroalloy. For handling hot platinum crucibles or dishes, platinum-tipped tongs must be used. Beaker tongs are available for handling beakers of 100–2000 mL capacity. An adjustable screw with locknut limits the jaw span of the tongs, allowing them to be adjusted for the container size.

### 3.18 Heating apparatus

#### Burners

The ordinary Bunsen burner is still widely employed for providing moderately high temperatures, and more specialised burners such as Meker Burners can reach slightly higher temperatures for ignition purposes. The maximum temperature is reached when the regulator is adjusted to admit slightly more air than required to produce a non-luminous flame; but too much air will give a noisy flame, unsuitable for combustion or ignition in quantitative analysis. Owing to the different combustion characteristics and calorific values of the common gaseous fuels – natural gas, liquefied petroleum (bottled) gas – burners vary slightly in their dimensions, including jet size and aeration controls. Unless it is of the 'all gases' type, which can be adjusted, choose the appropriate burner to obtain maximum efficiency from the available gas supply.

### Hotplates

Electrically heated hotplates are available in a very wide range of shapes and sizes with controls varying from simple 'low, medium, high' to very advanced thermostats and temperature monitoring. They should satisfy all standard safety requirements, with totally enclosed wiring protected from possible chemical spillages. The best hotplates incorporate a magnetic stirrer; they are valuable for getting substances into solution rapidly before dilution to standard volumes. Low-temperature heating can always be carried out on steam baths, which are usually available with thermostatically controlled heater units.

### Electric ovens

The most convenient oven is an electrically heated, thermostatically controlled drying oven having a temperature range from room temperature to about 250–300 °C; the temperature can be controlled to within  $\pm 1-2$  °C. Electric ovens are mainly used for drying precipitates or solids at comparatively low temperatures.

### Microwave ovens

Microwave ovens are now being used very extensively for drying and heating. They are particularly valuable when determining moisture contents of materials, as water is removed very rapidly on exposure to microwave radiation. They also give greatly reduced drying times for precipitates.

### Muffle furnaces

An electrically heated furnace of muffle form should be available in every well-equipped laboratory. The maximum temperature should be about 1200 °C.

### Air baths

An electric oven should not be used for drying solids and precipitates at temperatures up to 250 °C in which acid or other corrosive vapours are evolved. An air bath may be constructed from a cylindrical metal (copper, iron or nickel) vessel, its bottom pierced with numerous holes. A silica triangle, legs appropriately bent, is inserted inside the bath for supporting an evaporating dish, crucible, etc. The whole set-up is heated by a Bunsen flame, shielded from draughts. The insulating layer of air prevents bumping by reducing the rate at which heat reaches the contents of the inner dish or crucible. An air bath of similar construction but with special heat-resistant glass sides may also be used; this gives visibility inside the air bath.

### Infrared lamps and heaters

Powerful infrared lamps with concentrating reflectors are available commercially and are useful for evaporating solutions and drying even relatively large quantities of solid materials. If the lamps are mounted above the liquid to be heated, evaporation will occur rapidly, usually without spattering. Specially designed infrared units can be used with a number of dishes simultaneously, and the heat can be directed to both the top and bottom of the

containers simultaneously. Take care when handling the lamps; they can become extremely hot and are fragile immediately after use and before they have cooled down.

### Immersion heaters

An immersion heater, consisting of a radiant heater encased in a silica sheath, is useful for the direct heating of most acids and other liquids (except hydrofluoric acid and concentrated caustic alkalis). Infrared radiation passes through the silica sheath with little absorption, so a large proportion of heat is transferred to the liquid by radiation. The heater is almost unaffected by violent thermal shock due to the low coefficient of thermal expansion of the silica.

### Heating mantles

Heating mantles consist of a flexible 'knitted' fibreglass sheath that fits snugly around a flask and contains an electrical heating element which operates at black heat. The mantle may be supported in an aluminium case which stands on the bench, but for use with suspended vessels the mantle is supplied without a case. Electric power is supplied to the heating element through a control unit which may be either a continuously variable transformer or a thyristor controller, so the operating temperature of the mantle can be smoothly adjusted. Heating mantles are particularly designed for the heating of flasks and find wide application in distillation operations. For details of the distillation procedure and description of the apparatus employed, consult a textbook of practical organic chemistry.<sup>[5]</sup>

## 3.19 Desiccators and dry boxes

### Desiccators

A desiccator is a covered glass container designed for the storage of objects in a dry atmosphere; inside the base is a drying agent, such as anhydrous calcium chloride (largely used in elementary work), silica gel, activated alumina or anhydrous calcium sulphate (Drierite). Silica gel, alumina and calcium sulphate can be obtained which have been impregnated with a cobalt salt so that they are self-indicating; the colour changes from blue to pink when the desiccant is exhausted. The spent material can be regenerated by heating in an electric oven at 150–180 °C (silica gel); 200–300 °C (activated alumina); 230–250 °C (Drierite); it is therefore convenient to place these drying agents in a shallow dish situated at the bottom of the desiccator, allowing easy removal for baking as required.

The action of desiccants can be considered from two viewpoints. The amount of moisture that remains in the closed space of the desiccator is related to the vapour pressure of the in exhausted desiccant, i.e. the vapour pressure measures the extent to which the desiccant can remove moisture, and therefore measures its efficiency. A second factor is the weight of water that can be removed per unit weight of desiccant, i.e. the drying capacity. In general, substances that form hydrates have higher vapour pressures but they also have greater drying capacities. Remember that a substance cannot be dried by a desiccant which has a vapour pressure greater than the vapour pressure of the substance itself.

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**Table 3.4** *Comparative efficiency of drying agents*

Drying agent	Residual water per litre of air (mg)	Drying agent	Residual water per litre of air (mg)
CaCl <sub>2</sub>	1.5	Al <sub>2</sub> O <sub>3</sub>	0.005
NaOH (sticks)	0.8	CaSO <sub>4</sub>	0.005
H <sub>2</sub> SO <sub>4</sub> (95%)	0.3	Molecular sieve	0.004
Silica gel	0.03	H <sub>2</sub> SO <sub>4</sub>	0.003
KOH (sticks)	0.014	Mg(ClO <sub>4</sub> ) <sub>2</sub>	0.002
		P <sub>2</sub> O <sub>5</sub>	0.000 02

The relative efficiencies of various drying agents will be evident from the data presented in Table 3.4. These values were determined by aspirating properly conditioned air through U-tubes charged with the desiccants; they are applicable, strictly, to the use of these desiccants in absorption tubes, but the figures may reasonably be applied as a guide when selecting desiccants for desiccators. It would appear that a hygroscopic material such as ignited alumina should not be allowed to cool in a covered vessel over 'anhydrous' calcium chloride; anhydrous magnesium perchlorate or phosphorus pentoxide would be satisfactory.

The normal (or Scheibler) desiccator is provided with a porcelain plate having apertures to support crucibles, etc. The plate is supported on a constriction situated roughly halfway up the wall of the desiccator. For small desiccators, it is possible to use a silica triangle with the wire ends suitably bent. The ground edge of the desiccator should be lightly coated with white vaseline or a special grease in order to make it airtight.

It is advisable that any substance which is to be weighed should be kept in a vessel with a lid as tightly fitting as possible while it is in the desiccator.

Cooling of hot vessels within a desiccator is also an important problem. A crucible which has been strongly ignited and immediately transferred to a desiccator may not have attained room temperature even after 1 h. The situation can be improved by allowing the crucible to cool for a few minutes before transferring to the desiccator, and then a further cooling time of 20–25 min is usually adequate. The inclusion in the desiccator of a metal block (e.g. aluminium), upon which the crucible may be stood, also helps to ensure that temperature equilibrium is reached.

When a hot object, such as a crucible, is placed in a desiccator, about 5–10 s should elapse for the air to become heated and expand before putting the cover in place. When reopening, the cover should be slid away very gradually in order to prevent any sudden inrush of air, which might blow material out of the crucible. Air rushes in to fill the partial vacuum created when the expanded gas content of the desiccator cools down.

A desiccator is frequently employed for the thorough drying of solids. Its efficient operation depends upon the condition of the desiccant, which should be renewed at frequent intervals, particularly if its drying capacity is low. A vacuum desiccator is advisable when dealing with large quantities of solid.