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Purification and crystal growth

Almost all the physical properties of molecular crystals can be influenced by crystal purity and quality. Thus, if experimental measurements of such properties as energy and electron transfer, molecular motion or solid-state chemical reactions in molecular crystals are to be interpreted in terms of theoretical models, it is vitally important that these measurements are made as far as possible on single crystals which are as pure and perfect as possible. Unfortunately, the relatively weak short-range intermolecular forces in molecular crystals frequently render this objective difficult to achieve. For example, impurity molecules may often be incorporated into the lattice with the rather small, unfavourable enthalpy caused by localised lattice strain around the impurity site offset by a favourable entropy of mixing. Also twinning, dislocations, disorder and even strain-induced inclusions of regions of different lattice structure can occur relatively easily, with minor effects on the lattice energy but possibly major effects on physical properties.

1.1 Purification

Conventional chemical standards of purity are of little value in the field of organic solids. For example, in a three-dimensional lattice for a material of 99.9% purity, in any given direction one molecule in ten is likely to be an impurity molecule – clearly undesirable compared with any model assuming an extended regular lattice. Starting materials for molecular crystals, whether commercial or synthesised in the laboratory, must therefore be further purified in almost every case prior to crystal growth.

Purification methods fall into two classes: physical methods based on phase separation, including distillation, sublimation, recrystallisation, chromatography and zone-refining; and chemical methods, in which

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impurities that cannot be removed by physical methods are first selectively
converted to materials which can be more easily separated. Since many
organic molecules are photosensitive or readily oxidised, it is frequently
advantageous to carry out purification processes in the dark and under
inert atmospheres.

Distillation and recrystallisation
Distillation and recrystallisation are useful initial steps in purification. The
risk of thermal decomposition is reduced by vacuum distillation, and
repeated fractional distillation can lead to high purity. Recrystallisation has
the advantage of lower temperature, with less likelihood of thermal
decomposition, but requires purified solvents and may lead to incorpor-
ation of solvent in the solid product. Also, the concentrations of impurities
which are less soluble than the material being purified may actually be
increased rather than reduced by recrystallisation (e.g. anthracene as an
impurity in phenanthrene). In such cases, chromatographic methods may
be more effective or chemical methods may be required.

1.1. Continuous-chromatography apparatus.
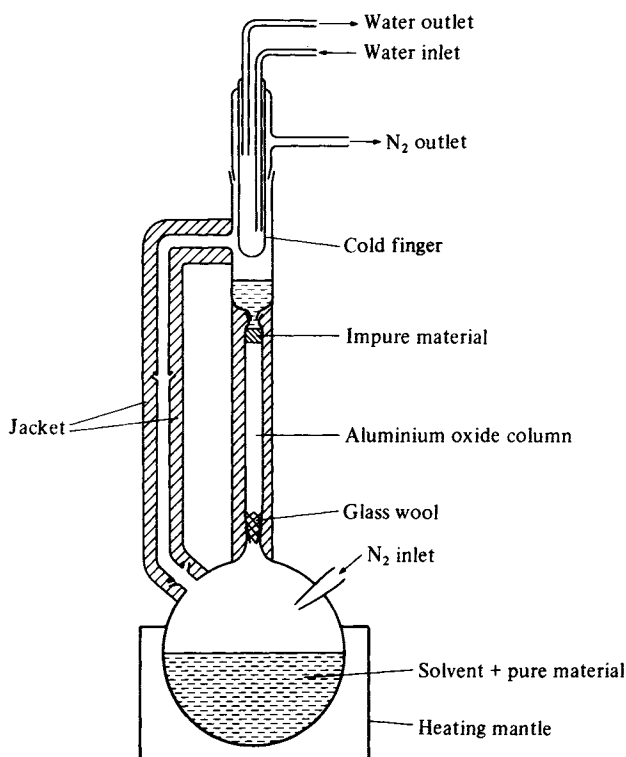
Continuous chromatography

Figure 1.1 shows a typical system for continuous chromatography[1], in which only a small volume of solvent is required for preliminary purification of a large amount of material. The adsorbent (frequently alumina or silica) and solvent are chosen according to the chemical nature of the material and the likely impurities present. The degree of purification achieved in such a system is limited owing to the large amount of material passed through a relatively small column, and the fact that impurities which are only weakly held by the adsorbent will not be effectively removed. Also, the purified material collects in the boiling solvent at a relatively high temperature, requiring careful exclusion of light and oxygen if undesirable reactions are to be avoided. Higher purity is obtained by non-continuous chromatography. The progress of the material and impurities through the column may be followed in many cases by occasional examination of fluorescence bands in the column under ultra-violet illumination. More elaborate and expensive techniques such as high-pressure liquid chromatography combine the advantages of high purity and high speed, although these are best suited to relatively small quantities of material.

Sublimation

Processes such as chromatography or recrystallisation, which may lead to incorporation of solvent in the molecular crystal, are best followed by further purification by sublimation. This eliminates all traces of volatile solvents and also involatile impurities such as any thermally polymerised material. In the simplest sublimation apparatus, the material is heated in an evacuated chamber containing a cold finger on which the vaporised material is condensed. Impurities with vapour pressures similar to the material being purified will not be removed using this apparatus, and in such cases gradient sublimation is preferred, in which the material is sublimed down a gradual temperature gradient along a horizontal tube. The temperature gradient is produced by a furnace containing two or more zones of different temperature, and the tube may be continuously evacuated or sealed following initial evacuation. Entrainer sublimation is carried out in a slow flow of inert gas (e.g. nitrogen) usually at atmospheric pressure (figure 1.2). Volatile impurities are usually best separated by entrainer sublimation or in continuously evacuated systems, although in these conditions relatively involatile constituents may be swept down the tube by other vapour species, leading to contamination or poor separation. This effect may be minimised by subliming the material through a layer of adsorbent such as charcoal or glass wool to condense the less volatile

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materials. After gradient sublimation has been carried out, the tube is cut
into zones containing material of different purity, and the material from the
purest zones may be used as starting material for further sublimation
stages. The process may need to be carried out several times to achieve
reproducible material of a high degree of purity. The ultimate degree of
purity will depend on the temperature gradient and rate of sublimation
(ideally both low) as well as on the thermal stability of the material and the
extent to which trace impurities of similar volatility were present in the
original sample.

Zone-refining
A more convenient method for carrying out many successive cycles of
purification for materials which can be melted without decomposition is
zone-refining. This process, developed in 1952 by W. G. Pfann[2] for
purification of inorganic semiconductor materials, involves repeated
passage of a narrow molten zone along a rod of the material to be purified.
Impurities which are more soluble in the melt than in the host solid are
carried along the rod in the direction of movement of the molten zone.
Impurities which are less soluble in the melt than in the host solid will tend
to solidify first as the zone progresses, and thus move in a direction opposite
to that of the molten-zone movement, in steps whose maximum length is
equal to that of the molten zone. More passes are therefore needed to move
the latter impurities a given distance along the rod than for the former. If the
relative solubility of an impurity in the solid and molten phases is known, it
is possible to develop theoretical models for calculation of the progress of

**1.2.** Entrainer-sublimation furnace.
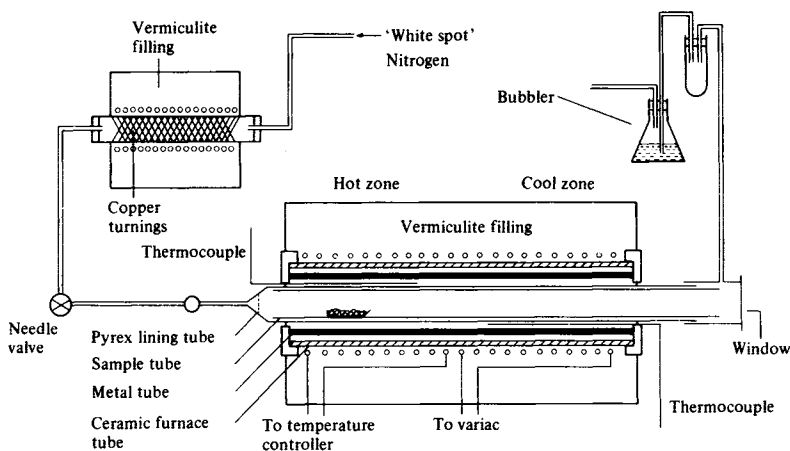
the purification and the resulting distribution of impurity along the length of the rod at various stages of zone-refining.

In practice it is not possible to use such calculations to predict the number of zone passes needed to achieve a certain degree of purity in a molecular solid, since there are usually several impurities present whose identity, concentration and solubility are unknown. Instead, automatic zone-refining apparatus is used to pass a large number of molten zones through the sample over several days. For a sample containing several impurities, some more and some less soluble in the melt than in the host solid, a typical impurity distribution along the length of the zone-defined rod is shown in figure 1.3. Segregation of impurities at the ends of the rod may be observed as a discoloration of the material in many cases, while examination under an ultra-violet light source, which excites fluorescence is a more sensitive guide to purity (see chapter 4). If material from the central portion of the rod is not of adequate purity, the central regions of several rods may be combined and subjected to further zone-refining until the limiting purity level is attained for the new sample. The ultimate limiting purity is determined by the point at which the impurity concentration in the end zones is high enough for the solid crystallising at the zone edge to be of the same composition in consecutive zone passes. This point is determined by the solubility ratio of the impurity in the solid and melt, and by the ratio of the total length of the sample to the length of the molten zone. Indirectly, the rate of zone movement is also important. If the zone moves too rapidly, impurity molecules are trapped at the advancing solidifying surface, and in extreme cases molten regions may be entrapped also. With slow zone movement through materials of high purity, back-diffusion of impurity molecules may become the chief factor limiting purity. Photochemical reactions of the material being zone-refined may be avoided by carrying out the operation in the dark, but any thermal reactions will inevitably limit ultimate purity.

Figure 1.4 shows a typical automatic zone-refining apparatus capable of passing several molten zones simultaneously through the sample. Since

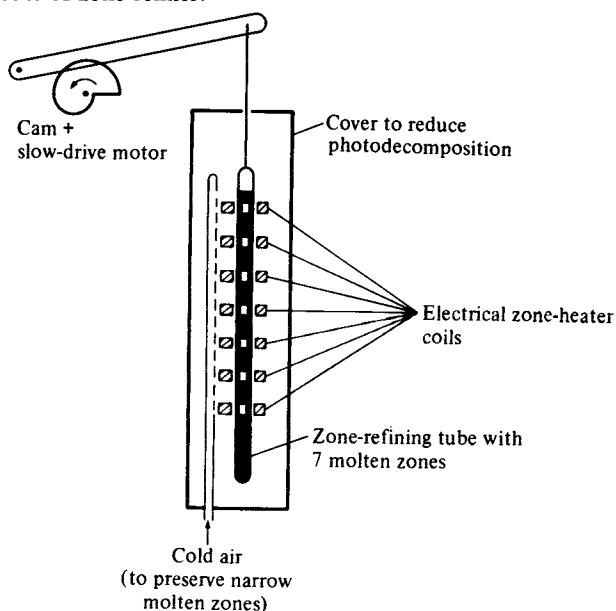**1.3.** Impurity distribution along a zone-refiner tube.
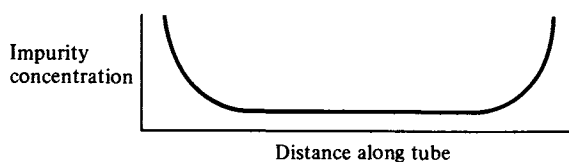
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most molecular solids are poor thermal conductors, the sample tube is usually 1 cm or less internal diameter. Wider tubes require more powerful heaters to maintain the whole cross-sectional area of the tube in a molten state, resulting in wider zones at the outer tube surface. Very narrow tubes are also inadvisable since any bubbles forming in the molten zone may lead to discontinuities in narrow samples. The starting material is prepared by loading a long tube, sealed at one end, with powdered material and then evacuating the tube. An inert gas (e.g. argon) is admitted to a pressure of about 10 cmHg before the sample is melted, from the bottom upwards, and sealed. Melting and sealing should be carried out rapidly to avoid excessive sublimation of the material, and it is advisable to use a loose plug of glass wool in the upper end of the tube to prevent accidental contamination of the vacuum line during this operation. To commence zone-refining, the sample should be re-melted, from the top downwards, and loaded into the pre-heated zone-refining apparatus while still completely molten to avoid risk of the tube cracking.

1.2   Crystal growth

Although some of these purification techniques (e.g. sublimation) are capable of producing good-quality single crystals, crystal growth is

1.4. A zone-refiner.

Cam +
slow-drive motor

Cover to reduce
photodecomposition

Electrical zone-heater
coils

Zone-refining tube with
7 molten zones

Cold air
(to preserve narrow
molten zones)

usually regarded as a separate stage following sample purification. Because intermolecular forces are weak, molecules arriving at a growing crystal surface are subject to only weak orientating forces. It is therefore necessary to limit the rate of growth of molecular crystals very carefully to allow time for the arriving molecules to settle to their equilibrium positions and to avoid formation of voids or defects. Optimum growth rates for molecular crystals are at least a factor of ten smaller than those for ionic crystals, where the aligning forces are strong. Crystals may be grown from vapour, solution or molten phases, each of which has its own advantages and problems.

Vapour growth
Crystals grown from the vapour-phase are solvent-free and have well-defined faces which aid orientation. They can also have low dislocation contents if grown carefully. Very thin flake crystals may be formed if vapour growth is too rapid. Slower growth, clean surfaces with a minimum of growth-nucleation sites and suitable choice of inert-gas pressure in the apparatus can help to produce large crystals by this method. For example, anthracene sublimed *in vacuo* forms bulky crystals, whereas thin flakes are formed by sublimation under 15 cmHg pressure of nitrogen[3]. Very low growth rates may be achieved by use of very small temperature gradients in the sublimation apparatus. Although this can be achieved in a cylindrical furnace with windings of increasing pitch, a more effective arrangement uses a sublimation chamber with large flat glass upper and lower faces separated by a short gap. The faces are held at temperatures high enough to sublime the sample in question, with the upper face marginally cooler than the lower face. This may be done using two electrically-heated metal blocks contacting the cell faces, with careful temperature control, or by immersing the cell in a suitable heating bath with the upper face in contact with a metal plate connected to rods protruding from the heating bath and acting as heat leaks to provide an automatic small temperature drop for the upper surface of the cell. In either case a controlled, localised additional heat leak at one point on the upper surface may temporarily be introduced to initiate formation of a seed crystallite.

Because different components generally have different vapour pressures, it is often difficult to grow uniform crystals of two-component systems (e.g. mixed crystals or charge-transfer complexes) by sublimation, but the above cell, with its short sublimation path length, has been used successfully for some two-component systems. Figure 1.5 shows an alternative arrangement[4] using a vertical furnace with a temperature gradient symmetrical

about the hottest point half way up the furnace. As the sublimation tube is slowly raised through the furnace, material evaporating from the lower end condenses at the same temperature at the upper end of the tube, first in a capillary to form an oriented seed crystal, and then in the main part of the upper end of the tube. The capillary acts as a seed-selector, since crystals whose growth direction is not exactly along the capillary axis will rapidly terminate at the walls, leaving only one crystallite whose growth direction coincides with the capillary axis emerging from the capillary tip into the main part of the tube.

Melt growth
Capillary seed-selectors are also important in the Bridgmann–Stockbarger method of crystal growth from the melt[5]. A sealed ampoule of the molten sample, with a short capillary tip at its lower end, is slowly lowered through a furnace with a sharp temperature gradient between the upper zone, which is just above the melting point, and the lower zone, which is just below the melting point. The single crystallite selected by the capillary grows into a

1.5. Apparatus for crystal growth from the vapour phase.
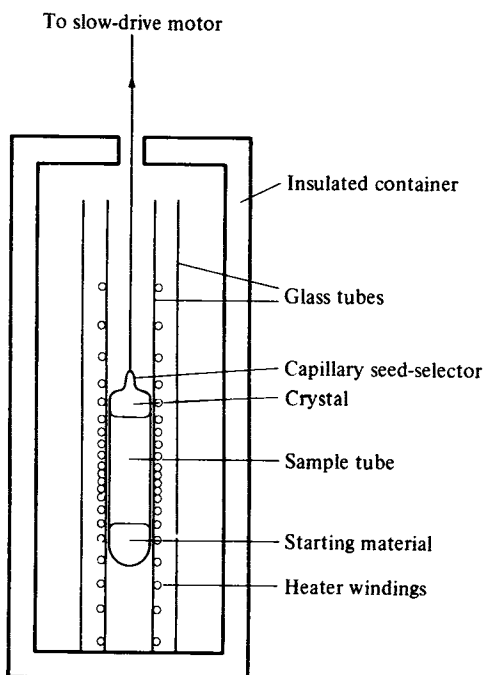
large single crystal as the ampoule is lowered. Disadvantages of this technique are that the crystal adopts the shape of the ampoule, leading to absence of external faces aiding orientation, and that the crystal grows at a very high temperature. Cooling to room temperature must be done carefully and slowly to minimise crystal strain, which may nevertheless still be a serious problem, particularly if the crystal sticks to the glass ampoule in places. Passing through any phase transitions which occur between the melting point and room temperature may also lead to strain. Although careful annealing can minimise these problems, the dislocation density in melt-grown crystals is still higher than in crystals grown by other techniques. Advantages of the technique are the larger size of crystals which can be grown and the fact that many impurities tend to prefer the molten phase, so that crystal growth from the melt incorporates an added stage of purification. An alternative method for growing crystals from the melt is the Kyropoulos–Czochralski method, in which a seed crystal is dipped into the surface of the molten material and withdrawn slowly so as to pull out a growing single crystal[6]. This method provides crystals with well-formed faces, less prone to strain from contact with surroundings. In practice it is difficult to use for most molecular crystals owing to the problem of sublimation of the sample material from the upper surface of the melt and onto the seed and growing crystal. Both methods are clearly unsuitable for materials which decompose on melting and for growth of mixed crystals of uniform composition; solution growth offers a better alternative for such materials.

Solution growth
Crystal growth from solution occurs well below the melting point of the solid, thus minimising risk of thermal decomposition and giving low strain and dislocation content. Also, the crystals grow freely in their natural habit, so aiding optical identification of the crystallographic axes. Incorporation of solvent into the crystals is a disadvantage which may sometimes be minimised by careful choice of solvent.

There are four main approaches to crystal growth from solution. In the simplest, the solvent is allowed to evaporate slowly from a solution at room temperature. Oxidation by the air and influx of dust particles providing an excess of nucleation sites may be avoided by allowing the solvent to evaporate in a flow of nitrogen. Careful initial filtration of the solution and use of new, unscratched flasks helps to minimise the number of nucleation sites and produce large crystals, and the flask should be left undisturbed in a fairly constant temperature environment for the

duration of the crystallisation process, which may be up to several weeks.

In a second approach, a hot concentrated solution is slowly cooled in a temperature-programmed thermostat bath. As saturation is approached, a seed crystal is introduced. Stirring the solution and rotating the seed crystal slowly are both helpful in obtaining uniform crystal growth. Although this approach yields larger crystals, it is also more expensive to set up and requires a much larger amount of the material, so generally the first approach is explored initially.

The third approach uses diffusion of solvents or solutes as a means of slowly approaching the solubility limit of the material to be crystallised. For example, solutions of an electron donor and an electron acceptor may be allowed to diffuse together across porous barriers with eventual growth of crystals of charge-transfer complexes or salts, and slow diffusion of a miscible but poor solvent for a material into a solution of the material in a good solvent will gradually lower the solubility and approach saturation. This approach can work for materials which are soluble only in solvents of low volatility and which have a low temperature-coefficient of solubility, where the first two approaches would not work well.

In the fourth approach, the species forming the crystal are generated in close proximity to the growing crystal by electrochemical oxidation or reduction in a technique known as electro-crystallisation[7]. This technique is very useful for relatively rapid preparation of good-quality crystals of charge-transfer salts which form highly conducting materials[8]. Controlled current and controlled potential conditions have both been used success-fully, and the technique can be used with relatively small amounts of the materials concerned. The crystals grow from inert-metal electrodes in solution, and in some cases crystals have continued to grow even after one end of the crystal emerged above the surface of the solution, suggesting that growth actually takes place at the electrode–crystal interface.

Detailed description of the numerous variations on the methods outlined in this chapter is beyond the scope of this text. However, it is clear that the range of available methods is wide, so that with care and patience good-quality crystals of high purity should be obtainable for a great many molecular crystal materials. In view of the increasing complexity of experiments investigating properties of molecular crystals, the importance of devoting sufficient time and attention to the initial purification and crystal growth processes cannot be over-emphasised. Effort invested in these stages is nearly always amply repaid in improved experimental data and simpler data interpretation.