

Equipment for Single Crystal Growth from Aqueous Solution

John L. Torgesen, Avery T. Horton, and Charles P. Saylor

(September 25, 1962)

The growing of large single crystals of high quality from solution requires the precise control of supersaturation and the avoidance of thermal and mechanical shock. Uniform growth conditions and cleanliness need to be maintained. Good seed crystals are necessary and the accidental introduction or generation of new nuclei should be prevented insofar as possible. In the apparatus and equipment assemblies here described, the crystal-growth bath is designed for uniform growth conditions and the exclusion of contamination. The support for the crystals provides for convenient mounting of the seeds, holds the crystals firmly, and allows their easy removal with minimum damage. A new reversing rotation mechanism promotes equal washing of the crystal surfaces and achieves uniform temperature and composition of the solution without, at the same time, producing significant mechanical stresses in the crystals. The temperature controller gives regulation of the temperature an order of magnitude more sensitive than those hitherto used and provides for stepless change of temperature. The crystals are thus free from liquid inclusions found to result from sudden acceleration of growth. The electrolytic conductance of ionic solutions may be used as a precise and sensitive measure of solution concentration and supersaturation. The crystal-growth procedures which are reported have resulted in the production of very good single crystals of a considerable variety of chemical phases.

1. Introduction

The procedure for growing large single crystals of a chemical phase from its solution in an appropriate solvent requires that a limited number of crystals be maintained in a metastable solution, that is, a solution that possesses some degree of supersaturation. Unstable conditions of supersaturation are to be avoided whereby spontaneous nucleation would result in a shower of small volunteer crystals. The procedure further requires the maintenance of supersaturation despite the removal of dissolved solute as it deposits on the faces of the growing crystal. The latter requirement may be satisfied by one of the following three general methods: (1) Removing solvent from the system as by evaporation; (2) changing the temperature of the solution in the direction toward decreasing solubility of the phase; and (3) adding solution of higher solute content while depleted solution is withdrawn to be strengthened.

[This paper describes in some detail the apparatus and equipment which has been assembled to grow large single crystals from solution under closely controlled and reproducible conditions. The changing-temperature technique was preferred to solution-addition because it requires less complex equipment and to solvent-evaporation because it seemed more amenable to control.]

Many reports have appeared in the literature on methods for growing crystals from solution [1–6].¹

We have drawn fully from the experience of others and have devised modifications and revisions to meet rather exacting requirements which we believe contribute (1) to close control of the system for the production of single crystal specimens of high quality and (2) to the reproductibility of growth conditions for studies on habit changes and the inclusion of impurities in crystals grown from purposely contaminated systems.

2. Crystal Growth Assembly

2.1. Crystal Bath

Single crystals are grown from solution contained in large glass jars 12 in. in diameter, 12 in. in height, and approximately 4½ gal in capacity. Jar covers of methyl methacrylate resin support the rotation mechanism and the temperature indicating and control devices. The jars are supported in metal frames which contain flat bottom heaters to distribute heat uniformly over the entire bottom surface and inhibit volunteer crystal growth. The bottom heater is constructed of either a bank of 25 small (15 w) lamps evenly distributed over the area of the frame or a flat spiral of coiled Nichrome wire.

The crystals are supported on glass pins situated near the ends of the arms of a "crystal tree" or "spider". The general aim is to provide support offering a minimum of interference with the external growth surfaces. When seed crystals are large it is preferable to employ twin pins to prevent rota-

¹ Figures in brackets indicate the literature references at the end of this paper.

tion of the crystal on its mount. The crystal tree (fig. 1) is constructed of glass rod and has three rows of four arms each, thus accommodating a total load of 12 crystals. Thin sleeves of polytetrafluoroethylene, covering the pins, are excellent in preventing adherence between the crystal and its support. By using a jig to fuse the pair of pins to the tree arm and a guide in drilling the seed crystals, trouble-free, even interchangeable, mounting and easy "harvesting" of the grown crystals are attained.

To promote efficient stirring of the bath and produce uniform solution temperature and concentration, the crystal tree is provided with vanes of flat glass. Two designs have been used, the first comprising plates attached between vertically adjacent tree arms at an angle of approximately 45° to the tree axis and also tilted at about the same angle. A second and more satisfactory design involves hanging the plates on the arms on glass tubing which acts as a hinge. The plates change position depending on the direction of rotation and continuously promote a transfer of solution from top to bottom in the jar.

A demountable T-joint attaches the crystal tree to the shaft of the rotation mechanism and a mercury seal at the lid of the bath prevents the loss of solvent vapor, contamination of the solution from the outside, and corrosion of bearings and other metal parts of the rotation mechanism.

Figure 1, a photograph taken during an actual growth operation with an insulation blanket momentarily removed, shows the details of the crystal tree assembly described above. The glass-cotton insulation blanket has a zipper closure for ready inspection of the crystals during growth.

2.2. Reversing Rotation Mechanism

In order that all surfaces of the growing crystal be washed approximately equally with the solution to promote uniform growth, it is necessary to provide a mechanism for rotation of the crystal tree in both directions. Two different devices have been used. The one employs a system of relays operated by a synchronous motor and cam to periodically stop a stirring motor, reverse the field connections, and start the motor in the reverse direction. A similar device has been described [2]. It has the disadvantage that rotational speeds must be slow, since the rotation starts suddenly and at full speed and the resulting jerk induces mechanical stress in the crystals and threatens the fracture of parts of the glass tree or possible jarring the crystals from their mounts. A more satisfactory rotation device employs a rack-and-pinion mechanism. The gear-rack, moved back and forth by eccentric attachment to the shaft of a slow speed motor, imparts, through the pinion gear on the tree shaft, an approximately sinusoidal rate of rotation to the crystal tree. The arrangement gives gradual deceleration and acceleration on either side of the reversal point and avoids undue mechanical stress in the growing crystals and the equipment assembly.

A drawing of the rotation mechanism is shown in figure 2.² Dimensions given here are nominal and not critical. The speed and the number of revolutions of the crystal-tree shaft in one direction are, of course, dependent on the speed of the motor, the length of the driver arm, and the diameter of the pinion gear. The arrangement shown provides a maximum speed of approximately 25 rpm and the crystal tree is rotated through about four complete revolutions between changes of direction. The height of the frame should allow removal of the motor without other disassembly. Shafts must be slightly undersize to pass through the bearings. Commercial gear-racks must be smoothed by milling a thin cut on the three plain sides. It is important that the knuckle be placed on the tree shaft in good alignment with the driver arm bearing, and it is advisable to mill a small flat on the shaft to receive the set-screw which holds the knuckle in place. The small phosphor-bronze spring, placed behind the shoe, holds the gear-rack snugly against the pinion gear, yet allows some play to prevent binding. Good quality gear-grease is essential for smooth operation.

Ball bearings are not absolutely essential for the crystal tree and driver-arm shafts, although they contribute markedly to trouble-free operation. Units equipped with porous bronze sleeve bearings throughout have given admirable service and their alignment for the crystal-tree shaft is more easily accomplished.

It is recommended that the motor³ be equipped with spiral gears in the gear-reduction train and that the position of the driver arm on the motor shaft be changed periodically to distribute wear in the gear train. Spur gears have stripped after several months of continuous operation.

3. Temperature Control

Of primary importance for the production of single crystal specimens of high quality by growth from solution is the control of temperature. Momentary temperature fluctuations, resulting in interrupted and accelerated growth rates, produce veils of mother liquor inclusions which lie parallel to the crystal faces on which deposition occurs. In addition, when the temperature-changing technique is employed, we have found that finite changes in temperature of a few hundredths of a degree will again induce the inclusion of mother liquor pockets. The close control of temperature at a given instant, together with a slow and continuous change in the temperature to maintain a uniform degree of supersaturation, can do much to minimize this effect.

3.1. Proportioning Temperature Controller

A proportioning type temperature controller, in which heat is supplied to the system in direct relation

² The design of this mechanism is based on that of a similar device observed in operation in the laboratories of the Brush Development Company, now a subsidiary of the Cleveland Corporation, Cleveland, Ohio.

³ Bodine, Type KCl-22 RM.

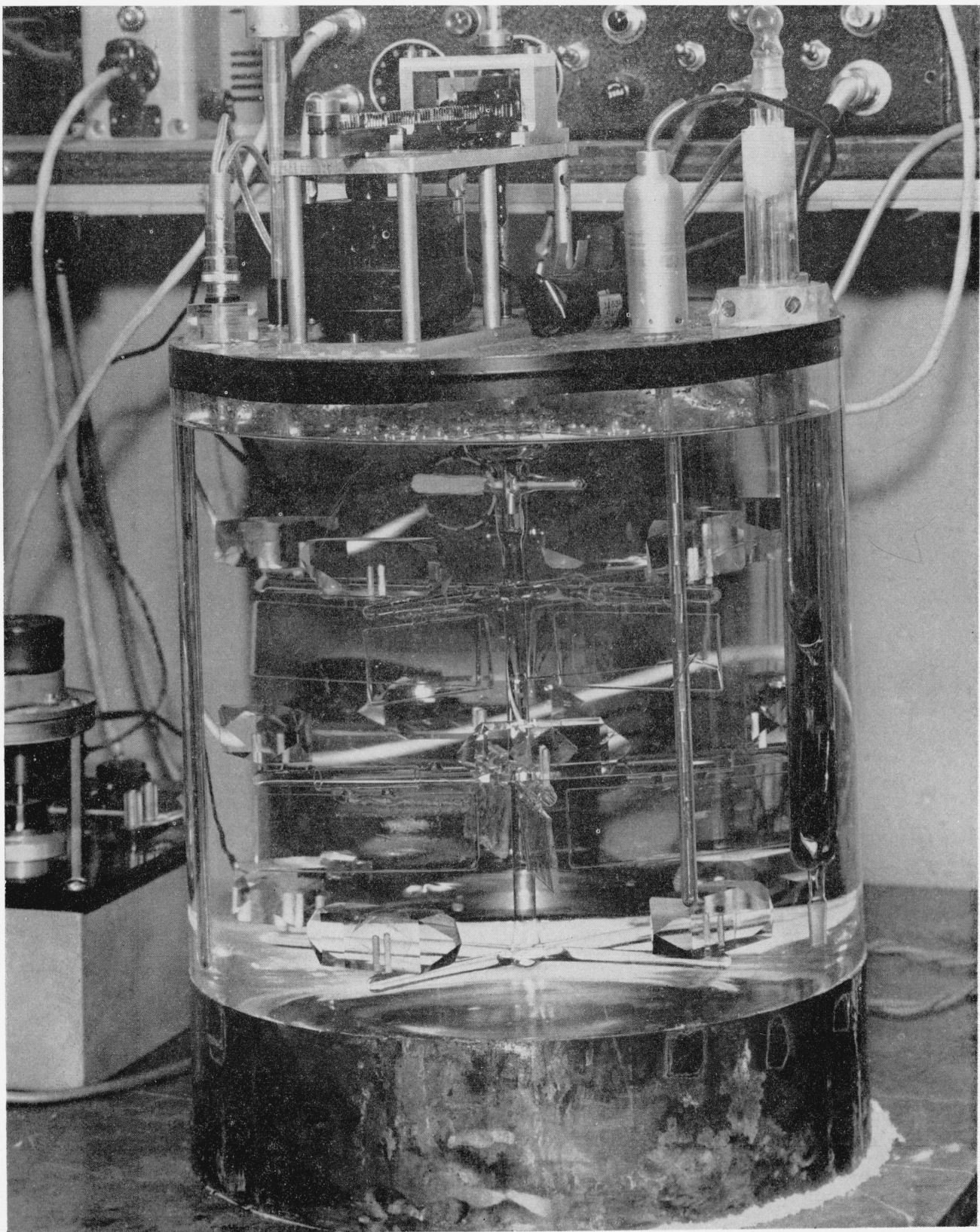


FIGURE 1. *Crystal growth assembly.*

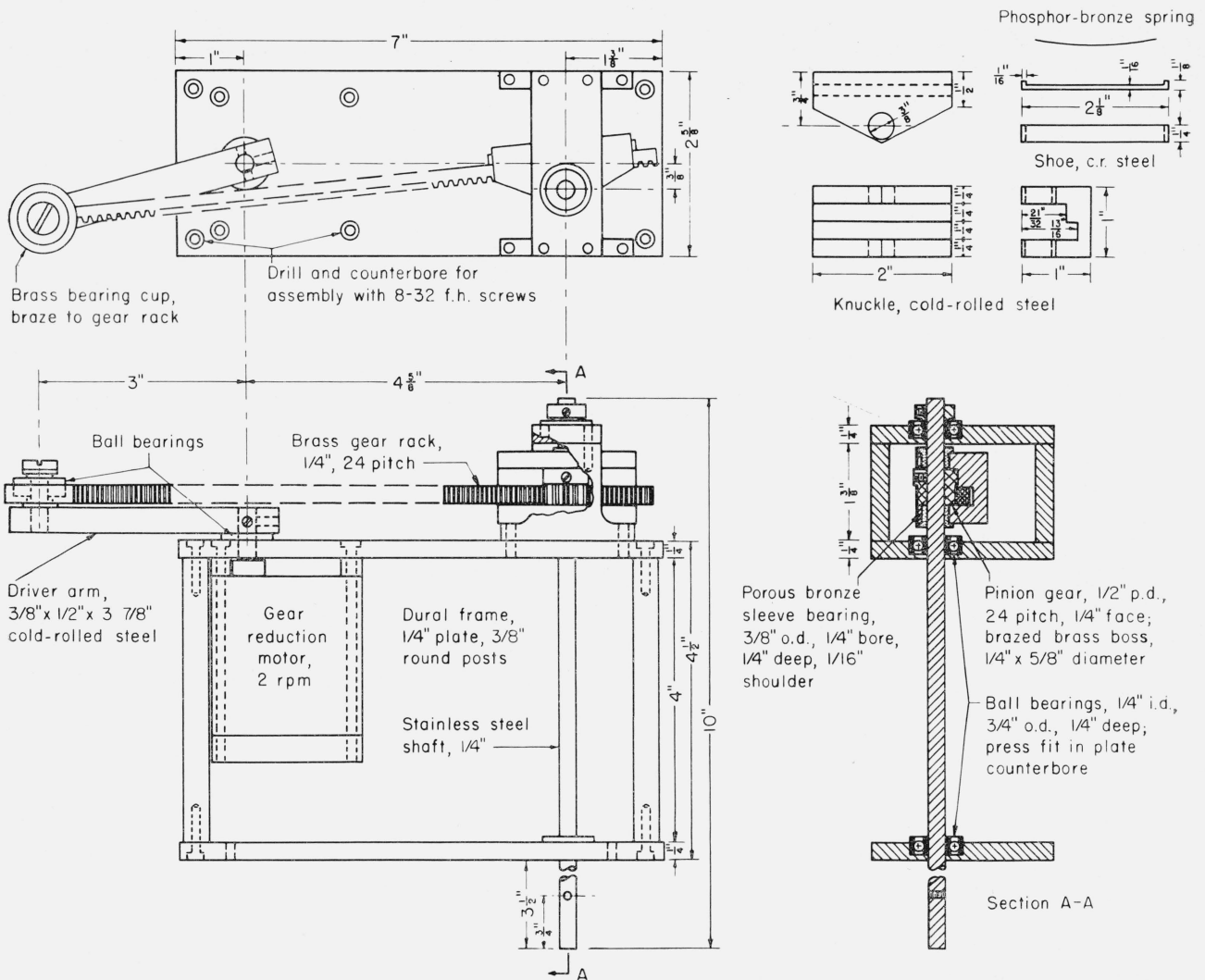


FIGURE 2. Reversing rotation mechanism.

to the departure of temperature from the desired point, is generally regarded as superior to an on-off circuit. The great majority of our crystal growth operations have been conducted with a time-proportioning "saw-tooth" controller. The instrument is similar in principle to one described by Ransom [7] and its construction closely follows that of the controller designed by Sargent [8]. The instrument time-modulates the electrical energy supplied to control heaters proportionally to any temperature departure from the control point. In conjunction with a commercial power supply,⁴ a commercial amplifier of 10^5 to 10^6 gain,⁵ and a specially-built Wheatstone bridge, a "saw-tooth" relay, whose circuit is shown in figure 3, is used.

The temperature-sensing element is a platinum coil, similar in construction to a platinum resistance thermometer to provide rapid response and coil

stability, connected as one arm of the Wheatstone bridge. The adjacent arm is a variable resistance adjustable to the desired control point. The bridge is energized with direct current from dry cells, and the bridge output is coupled to a converter and a-c amplifier. The amplified bridge signal (d-c output) is fed to the saw-tooth relay circuit to change the potential level of the saw-tooth voltage whose frequency corresponds to a selected duty cycle. As shown in figure 3, an appropriate R-C circuit is used to generate the saw-tooth voltage, the circuit being shorted periodically and momentarily by a micro-switch operated with a cam and 10 rpm synchronous motor. The duty cycle is thus of 6 sec duration. The change in potential level operates the control relay, S_2 , and switches power to the control heaters.

The potential level of the saw-tooth voltage is adjusted with coarse (R_9) and fine (R_{17}) control potentiometers, while the spring tension on the plate relay (S_2) is adjusted, so that the relay is closed 50 percent of the duty cycle when the error

⁴ DC Power Supply, Model 28M, Lambda Electronics Co., Huntington, Long Island, New York.

⁵ Brown Electronic Amplifier, Model 356358-1, Minneapolis-Honeywell Regulator Co., Brown Instruments Division, Philadelphia, Pa.

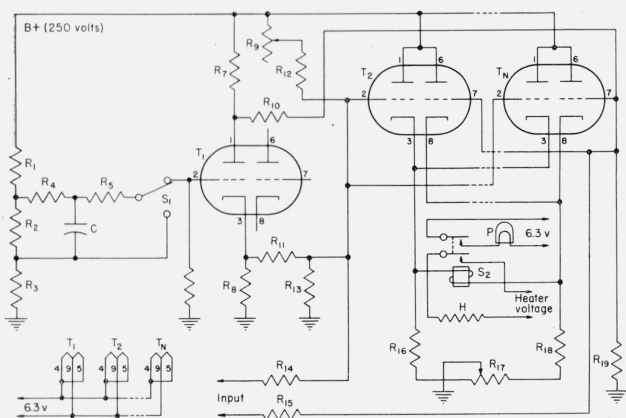


FIGURE 3. Time-proportioning sawtooth relay.

- | | |
|---|---|
| R_1 —150 kohm, $\frac{1}{2}$ w | R_{17} —2 kohm potentiometer |
| R_2, R_3 —47 kohm, $\frac{1}{2}$ w | T_1 —5751 |
| R_4 —3 meg, $\frac{1}{2}$ w | T_2, T_3 —5814A |
| R_5 —10 kohm, $\frac{1}{2}$ w | C—4 μ f, oil impregnated paper |
| R_6 —10 meg, $\frac{1}{2}$ w | S_1 —SPDT microswitch, cam operated, 10 rpm synchronous motor |
| R_7, R_8 —68 kohm, $\frac{1}{2}$ w | S_2 —DPST sensitive plate circuit relay, 2500-ohm coil |
| R_9 —2.5 meg potentiometer | P—Pilot lamp |
| R_{10}, R_{11} —1.2 meg, $\frac{1}{2}$ w | H—Heater |
| R_{12}, R_{13} —0.82 meg, $\frac{1}{2}$ w | |
| R_{14}, R_{15} —4.7 meg, $\frac{1}{2}$ w | |
| R_{14}, R_{15} —0.47 meg, $\frac{1}{2}$ w | |
| R_{16}, R_{18} —2 kohm, 10 w | |

voltage (bridge signal) is zero (bridge output shorted). Subsequent error voltages from the bridge will shift the potential level of the saw-tooth voltage up or down so that the percentage of time per duty cycle that the control heater is energized, is dependent on the magnitude and sign of the error voltage.

In normal operation the potential drop across the relay coil varies linearly with time from about 20 to 10 v during the six-second duty cycle, except for a momentary ($\frac{1}{4}$ sec) 50-v spike at the beginning of the cycle. The latter provides assurance that the relay closes and power is supplied to the heaters. Spring tension on the relay is adjusted to provide release and opening the heater circuit at about the mid-point in the normal operating range.

The sensitivity of the controller to changes in temperature is dependent on the degree of amplification of the bridge signal. It is found that an amplification factor of approximately three-quarters maximum provides a control band, from full off to full on, corresponding to a temperature interval of 0.010 to 0.015 °C. Temperature control of the crystal baths to ± 0.002 °C is obtained.

Four units as described above have been in service for a number of years. Their performance has been very satisfactory for the extended periods required in crystal growth experiments. They are composed of mechanical relays, switches, motors, and common electronic components which are subject to failure, and failure of temperature control is disastrous to crystal growth experiments. Electronic tubes of the best quality are used and these are tested for performance and life expectancy whenever possible, that is, at the completion of each crystal growth experiment. Figure 3 shows some choice as to the number of 5814A tubes in parallel to supply current

to the relay coil. While one tube would probably do the job, we actually use four in parallel as a precaution against failures. It has been our experience that the units may be depended upon to operate continuously without breakdown for periods up to 6 months. We have not conducted growth operations to exceed more than one-half this period. Our laboratory is provided with an independent and regulated a-c power supply, separate and distinct from the building supply, to avoid interruptions in electrical service.

3.2. Continuous Temperature Change

Growth of single crystals from solution by the temperature-changing technique, and this usually means lowering the temperature as growth proceeds, requires that the setting of the Wheatstone bridge in the control circuit must be changed. Initially this was done manually, decreasing the resistance in the setting arm of the bridge by an amount proportional to the desired change in temperature. The twice-daily change of 0.02 to 0.04 °C in earlier growth operations led to inclusions of mother liquor in certain areas of the crystals. This was particularly true in the case of ammonium dihydrogen phosphate, where inclusions of varying size and up to almost 1 mm in length, appearing in the position of the advancing prism corner, marked each temperature shock to which the system was subjected. The effect demanded an arrangement whereby the temperature could be changed continuously.

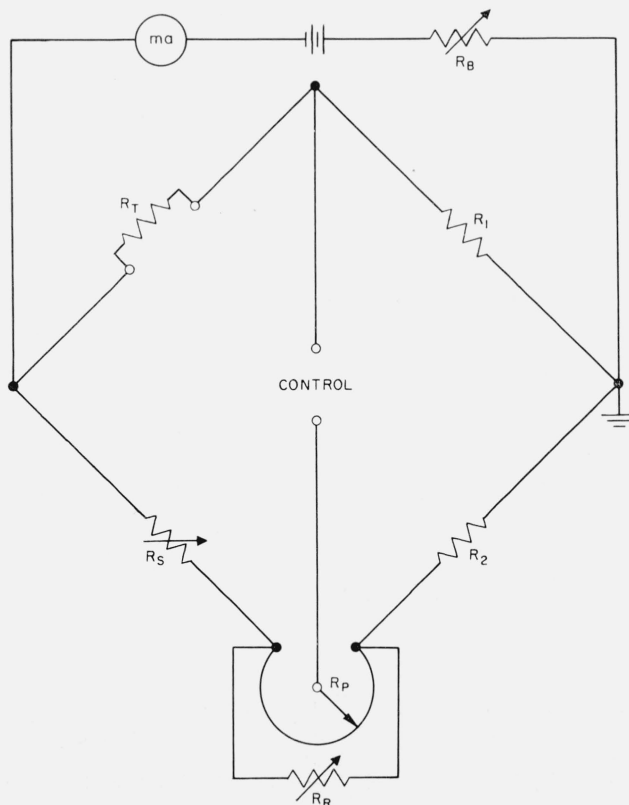


FIGURE 4. Modified Wheatstone bridge.

Transfer of resistance from one arm of the bridge to another, as with a slide-wire potentiometer driven by a synchronous motor, will unbalance the bridge continuously and cause the temperature control point to shift. The rate of temperature change may be governed by the size of a shunt across the potentiometer. We have constructed several bridges of this type in accordance with the diagram given in figure 4. Precision components are employed since satisfactory performance depends on resistor stability, slide-wire uniformity, low contact resistance in the switches, etc.

The ratio arms of the bridge, R_1 and R_2 , consist of two 50-ohm precision resistors (General Radio Type 500). A decade resistor of 1.0 ohm-per-step in series with one of 0.1 ohm-per-step (both General Radio Type 510) plus a fixed precision resistor of 25 ohms constitute the setting arm of the bridge, R_s . A platinum coil of 25.5 ohms resistance at 0 °C and a temperature coefficient of 0.1 ohm per degree C is the fourth arm, R_T , and the temperature-sensing element of the control system. As stated above, this coil is constructed in the same manner as a precision resistance thermometer in order that it have low lag and adequate sensitivity. A 100-ohm 10-turn potentiometer (Beckman Instrument Co.), R_P , is connected as shown. The slider must be in the output circuit to avoid variable contact resistance in the bridge circuit. A similar bridge [9], but constructed with the slider contact in the bridge circuit in one arm to add or remove resistance, gave some contact resistance trouble. The shunt, R_R , is a 0.1 ohm-per-step decade resistance unit (General Radio Type 510). A 0.1 turn-per-day synchronous motor and gear train drives the slider, transferring resistance in normal temperature-dropping operation from the setting arm to one ratio arm. A dial mounted on the drive shaft indicates position and is necessary in making small temperature adjustments.

The circuit does not give a change in temperature precisely linear with time due principally to bridge balance relationships with the resistors small and near the same size. A slight nonlinearity is introduced also by the fact that the sensing-arm resistance is not strictly linear with temperature. However, at the maximum setting of the shunt, with R_s set to control the temperature in the neighborhood of 50 °C, the deviation from linearity is less than 3 percent as the slider is moved from one extreme position to the other. Actually, the bridge may be made practically linear by increasing the resistance in the ratio arms sufficiently. Such revision would, however, require a large d-c supply to maintain sufficient current (20 ma, controlled by R_B) for adequate sensitivity in the control system.

The control range of the bridge described is from 0 to 100 °C approximately. The rate of temperature change, over a maximum of 100 days without resetting R_s , is from 0 to 0.15 °C per day in steps of 0.015 °C per day approximately.

Of the total heat supplied to the baths for maintenance of temperature near 50 °C, about 50 percent is supplied continuously through the bottom heaters and variable transformers. The controlled heat is supplied through two finger heaters introduced

through and supported by the lid of the bath. The finger heaters are of Nichrome wire wound on a mica strip and enclosed in a glass tube which has been silvered on the inside. The silver coating effects better radiation of heat and, when grounded, serves as a shield to prevent 60-cycle radiation from interfering with conductivity measurements used to determine the solution concentration and supersaturation [10].

The temperature of the crystal-growth baths is measured with platinum resistance thermometers and a Type G-1 Mueller thermometer bridge (Leeds and Northrup No. 8067). A four-pole, silver-contact selector switch, accommodating several thermometers, makes convenient the transfer from one thermometer to another. Future plans include the installation of a multipoint recorder system of adequate sensitivity to provide a more complete history of crystal-growth operations and a warning system.

3.3. Measurement of Solution Concentration

The electrolytic conductance of ionic solutions has been found to be a precise and sensitive measure of the concentration of these solutions at a given temperature in the saturation region. The measurements are made with an immersion conductance cell of new design (shown at the extreme right in fig. 1) and they provide a means to monitor with precision the growth conditions of supersaturation which obtain during the crystal-growth operation. Details on the design of conductance cells, the measurement procedures, and conductivity data for ammonium dihydrogen phosphate solutions are given in a concurrent publication appearing elsewhere [10].

4. Crystal Growth Procedure

Sufficient solution is prepared from distilled water and solute of the best available quality to fill the crystal-growth jar to within an inch or two of the top. The concentration of the solution corresponds to saturation at the desired growth temperature. The solution is filtered hot through fritted glass filters to remove insoluble material, which may run as high as several hundredths of 1 percent even in analytical reagent grade materials. On transfer to the growth jar, the temperature is raised well above that corresponding to saturation (usually 4 to 5 °C) to insure complete solution and the absence of nuclei which would induce volunteer growth. In this step a separate jar lid is used which holds a motor stirrer and long glass propeller. The temperature control and measurement devices are inserted and, using conductivity measurements or a pilot crystal as a guide, the temperature is decreased to the saturation point. Meanwhile seed crystals which have been cut or cleaved from parent single crystal material or which have been grown in crystallizing dishes to sufficient size (usually by solvent-evaporation methods) are drilled and mounted on the crystal tree which has been attached to its own lid and rotation mechanism. Drilling can usually be done with

ordinary steel twist drills and a small variable-speed drill press, with the seed crystal immersed in a saturated solution of the same material. For crystals which cleave readily, dental burrs with an inverted-cone shape have been used successfully. With seed crystals not large enough for mounting on twin pins, single pins have been used. In these cases it is advisable to place a short length of small plastic tubing on the pin and above the seed to assist in holding the seed in place during the planting operation and in the early stages of growth.

When saturation conditions have been established in the bath, the temperature is raised slightly and the seeds are planted by simple exchange of equipment. The bath temperature is held above saturation for a few hours until the seeds have dissolved slightly, as evidenced by the first noticeable rounding at the corners and edges. This is done to remove the small individual crystals which may be on the surface of the seed as a result of cutting or drilling operations and would tend to induce polycrystalline growth. The temperature is then lowered to the saturation point and the temperature-dropping procedure begun.

The temperature-dropping program selected depends on the temperature coefficient of solubility of the solute, the number, habit, and size of the crystal seeds, the growth habit and mechanism including the type and number of self-perpetuating growth centers, and the degree of supersaturation that will induce spontaneous nucleation. In the absence of previous knowledge, caution is recommended with a new material until some information on the behavior of the system has been gained. If high quality material is the goal, one does not normally expect to push growth rates from solution to exceed a deposition of 1 mm per day normal to the fastest growing crystal face. This condition will lead to quite different temperature programs for different materials. For ammonium dihydrogen phosphate the area of actively growing crystal does not increase with growth time from uncontaminated solutions. As the saturation concentration versus temperature curve is roughly linear over the range used, the temperature program consists of a constant dropping rate after the habit is fully established. The initial seed will have additional imperfections, pits, and vicinal faces that grow very much faster than an established pyramid face, so initially much lower supersaturations are needed.

On one occasion in an effort to accelerate the growth of ammonium dihydrogen phosphate crystals of 2 cm diam, we increased the temperature drop-rate to 0.2 °C per day. Growth on (101) faces became polycrystalline, with small individual crystals originating particularly from corners and edges. The supersaturation in this experiment increased to better than 10 percent. We normally grow ammonium dihydrogen phosphate crystals in the temperature range from 40 to 50 °C at a temperature-dropping rate of approximately 0.10 °C per day under which conditions deposition on the (101) faces is approximately 0.5 mm per day. With much smaller seed crystals of uranyl nitrate hexahydrate,

sodium chlorate, etc., the temperature-dropping rate in initial stages of growth does not exceed 0.02 °C per day.

Finished crystals are taken individually from the crystal tree, dried quickly with soft paper tissue, and, if the growth temperature has been as much as 5 to 10 °C above ambient laboratory temperature, they are transferred to a warm air-bath for subsequent slow cooling to avoid thermal shock and cracking. In this operation the evaporation of adhering solution and subsequent growth leaves the crystal faces far from perfect. For an improvement on this technique we have often immersed the crystals immediately in 50–50 propylene glycol-water mixture at essentially the same temperature as the crystal bath, followed by washing in ethyl alcohol. In some cases etching of the crystal surface has been observed.

A high degree of preservation of the surfaces would involve the transfer of the crystal from the growth medium to an inert medium at exactly the same temperature, avoiding as much as possible both deposition and dissolving the crystalline material while the adhering solution is removed from contact with the crystal faces. The inert medium must neither etch the crystal surfaces nor "salt-out" dissolved solute. It may be miscible or immiscible with the saturated solution. In the latter case, it would appear that a considerable density difference would enhance the removal of solution. Our experiments in this connection have not resulted in a procedure to be recommended.

5. Conclusion

With crystal-growth units assembled as described above, we have successfully grown single crystal specimens of ammonium dihydrogen phosphate, potassium dihydrogen phosphate, uranyl nitrate hexahydrate, strontium dichromate, sodium chlorate, sodium nitrate, and oxalic acid dihydrate. In representative cases these single crystals have been judged to be excellent so far as control of dislocations, twinning, and inclusion of foreign substances are concerned. This judgment has been largely based upon single crystal X-ray diffraction, optical examinations between crossed polarizers, microscopical searches for discontinuities or inclusions, and the observation of reflections from cleavage surfaces. Corroborative information has come from chemical or spectrochemical analysis for impurities present in the mother liquor but not definitely detectable in the crystals. Imperfections associated with the junction between seed and growth are not considered in this context.

The procedures have been followed in a great many experiments on the growth of ammonium dihydrogen phosphate in the presence of selected impurities. The equipment has performed satisfactorily for us and its design and assembly are presented for those with an interest in the growth of large single crystals from aqueous solution.

We express appreciation to Herbert Lowey for expert machine work in the construction of various parts of the equipment, in particular the reversing rotation mechanism. We are very much indebted to Jack Sargent⁶ for his assistance in the design of the temperature-control relay.

⁶ Now with Panellit, Inc., Chicago, Ill.

6. References

- [1] A. C. Walker and G. T. Kohman, *Trans. Am. Inst. Elec. Engrs.* **67**, 12 (1948).
- [2] A. N. Holden, *Discussions Faraday Soc.* **1949**, No. 5, 312.
- [3] A. E. Robinson, *Discussions Faraday Soc.* **1949**, No. 5, 315.
- [4] A. C. Walker, *J. Franklin Inst.* **250**, 481 (1950).
- [5] H. E. Buckley, *Crystal Growth*, Ch. 2, (John Wiley & Sons, Inc., New York, N.Y., 1951).
- [6] A. V. Shubnikov and N. N. Sheftal, *Growth of Crystals*, Vol. **1** (1958) Consultants Bureau, Inc. New York, N.Y. (First Conference on Crystal Growth of the Institute of Crystallography, Academy of Sciences USSR, 1956).
- [7] F. A. Ransom, *Control Eng.* **1**, 1 (1952) (McGraw-Hill Book Co., Inc., New York, N.Y.).
- [8] J. Sargent (informal communication, 1955).
- [9] T. W. Thomas and L. G. Finch, *J. Sci. Instr.* **34**, 118 (1957).
- [10] J. L. Torgesen and A. T. Horton, *J. Phys. Chem.* **67**, (1963).

(Paper 67C1-116)