INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in “sectioning” the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from “photographs” if essential to the understanding of the dissertation. Silver prints of “photographs” may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106
COX, Herbert Michael, 1941-
THE MEASUREMENT OF CRYSTAL-SOLUTION-VAPOR CONTACT ANGLES AND THE GROWTH RATES OF CORRESPONDING CRYSTAL FACES.

The Ohio State University, Ph.D., 1973
Mineralogy

University Microfilms, A XEROX Company, Ann Arbor, Michigan
THE MEASUREMENT OF CRYSTAL-SOLUTION-VAPOR
CONTACT ANGLES AND THE GROWTH RATES
OF CORRESPONDING CRYSTAL FACES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Herbert Michael Cox, B.S., M.S.

****

The Ohio State University
1973

Reading Committee:
Dr. Wilfrid R. Foster
Dr. Henry E. Wenden
Dr. Dan McLachlan, Jr.

Approved By

Adviser
Department of Geology
and Mineralogy
ACKNOWLEDGMENTS

The author would like to thank the departmental secretary, Mrs. Kathleen Wuichner, for the daily secretarial and extrasecretarial assistance provided and for her consistently cheerful encouragement.

The author's advisor, Dr. Dan McLachlan, Jr., provided advice, guidance, and technical assistance throughout the entire investigation. He also helped in other innumerable ways for which he can never be adequately thanked.

It is readily acknowledged that this work would have been impossible without the patience and understanding of a devoted wife.
VITA

December 17, 1941  Born - Muskogee, Oklahoma

1960-1964  . . .  Radar Technician, United States Air Force

1964-1965  . . .  Electronic Technician, Western Electric Company, Columbus, Ohio

1965. . . . .  Electronic Technician, Rocket Research Laboratory, The Ohio State University, Columbus, Ohio

1966-1967  . . .  Associate Engineer, Western Electric Company, Columbus, Ohio

1968-1969  . . .  Elementary School Teacher, Pataskala, Ohio

1969. . . . .  B.A. (Geology), The Ohio State University, Columbus, Ohio


1970-1971  . . .  William J. McCaughey Fellow (Mineralogy), The Ohio State University, Columbus, Ohio

1971. . . . .  M.S. (Mineralogy), The Ohio State University, Columbus, Ohio

1971-1973  . . .  Teaching Associate (Mineralogy), The Ohio State University, Columbus, Ohio

FIELDS OF STUDY

Major Field: Mineralogy

Studies in Optical Mineralogy. Professor Ernest G. Ehlers
Studies in X-ray Methods. Professors Henry E. Wenden and Rodney T. Tettenhorst

Studies in Crystallography and X-ray Structure Determination. Professors Dan McLachlan, Jr., and Henry E. Wenden

Studies in Crystal Chemistry. Professor Henry E. Wenden

Studies in Phase Equilibria. Professors Wilfrid R. Foster and Ernest G. Ehlers, and John W. Kaufman

# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>ii</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. HISTORY AND THEORIES OF CRYSTAL GROWTH</td>
<td>4</td>
</tr>
<tr>
<td>II. CRYSTAL GROWTH RATE STUDIES</td>
<td>10</td>
</tr>
<tr>
<td>III. INTERFACIAL FREE ENERGIES</td>
<td>45</td>
</tr>
<tr>
<td>IV. SUMMARY</td>
<td>84</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>85</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Typical Schlieren System</td>
<td>15</td>
</tr>
<tr>
<td>2.</td>
<td>Schlieren-type Microscope</td>
<td>16</td>
</tr>
<tr>
<td>3.</td>
<td>Cross-sectional View of Hot Stage</td>
<td>21</td>
</tr>
<tr>
<td>4.</td>
<td>Tin Dendrites (Normal View)</td>
<td>26</td>
</tr>
<tr>
<td>5.</td>
<td>Tin Dendrites (Schlieren View)</td>
<td>26</td>
</tr>
<tr>
<td>6.</td>
<td>Tin Dendrites (Schlieren View) Showing Three Stages of Growth</td>
<td>28</td>
</tr>
<tr>
<td>7.</td>
<td>Tin Dendrite Limb (Schlieren View) Showing Three Stages of Growth</td>
<td>28</td>
</tr>
<tr>
<td>8.</td>
<td>Copper Sulphate Crystals (Schlieren View)</td>
<td>29</td>
</tr>
<tr>
<td>9.</td>
<td>Resorcinol Crystal (Normal View)</td>
<td>32</td>
</tr>
<tr>
<td>10.</td>
<td>Resorcinol Crystal (Schlieren View)</td>
<td>32</td>
</tr>
<tr>
<td>11.</td>
<td>Resorcinol Crystal (Schlieren View)</td>
<td>34</td>
</tr>
<tr>
<td>12.</td>
<td>Resorcinol Crystal (Schlieren View) Showing Two Stages of Growth</td>
<td>34</td>
</tr>
<tr>
<td>13.</td>
<td>Resorcinol Crystal (Schlieren View) Showing Seven Stages of Growth</td>
<td>35</td>
</tr>
<tr>
<td>14.</td>
<td>Thin Resorcinol Crystal (Schlieren View) Showing Four Stages of Growth at One Minute Intervals</td>
<td>37</td>
</tr>
<tr>
<td>15.</td>
<td>Thin Resorcinol Crystal (Schlieren View) Showing Ten Stages of Growth at Thirty Second Intervals</td>
<td>37</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES (Contd.)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>16. Resorcinol Model</td>
<td>40</td>
</tr>
<tr>
<td>17. Gibbs-Wulff</td>
<td>43</td>
</tr>
<tr>
<td>18. Solid-Liquid-Vapor Contact Angle</td>
<td>48</td>
</tr>
<tr>
<td>19. Sessile Drop</td>
<td>50</td>
</tr>
<tr>
<td>20. Sessile Drop Calculations</td>
<td>52</td>
</tr>
<tr>
<td>21. Sessile Drop Calculations</td>
<td>52</td>
</tr>
<tr>
<td>22. Sessile Drop Calculations</td>
<td>54</td>
</tr>
<tr>
<td>23. Sessile Drop Calculations</td>
<td>54</td>
</tr>
<tr>
<td>24. $\cos \theta$ vs. $\frac{3V}{\pi r^3}$ Graph</td>
<td>56</td>
</tr>
<tr>
<td>25. $\cos \theta$ vs. Drop Radius</td>
<td>57</td>
</tr>
<tr>
<td>26. Bubble Contact</td>
<td>61</td>
</tr>
<tr>
<td>27. Inverted Bubble Apparatus</td>
<td>63</td>
</tr>
<tr>
<td>28. Bubble on Uncleaned Glass Slide</td>
<td>66</td>
</tr>
<tr>
<td>29. Bubble on Clean Glass Slide</td>
<td>66</td>
</tr>
<tr>
<td>30. Bubble on (110) Face of Rochelle Salt</td>
<td>68</td>
</tr>
<tr>
<td>31. Bubble on (001) Face of Rochelle Salt</td>
<td>68</td>
</tr>
<tr>
<td>32. Bubble on Prism Face of ADP</td>
<td>70</td>
</tr>
<tr>
<td>33. Tilt Plate Method</td>
<td>72</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>34. Terpstra Goniometer</td>
<td>74</td>
</tr>
<tr>
<td>35. Terpstra Goniometer (Side View on Saddle)</td>
<td>76</td>
</tr>
</tbody>
</table>
INTRODUCTION

Perhaps no feature of crystal growth has produced as much interest, or demanded as much effort, as that of the explanation of crystal shapes, or morphology. It was the regularity of crystal shapes that stood as a mute gadfly, prompting and guiding the thoughts of philosophers and scientists to the ultimate realization of the underlying regularity of arrangement of the constituent atoms of crystalline material. The early work of Steno, Rome de Isle, Carangeot, Haüy, Weiss, and Miller, aided by the development of a precision optical goniometer through the work of Wollaston, Malus, Federov, and Goldschmidt, had given classical crystallographers the means of determining the relative dimensions and shape of the unit cell of most crystals, long before the first successful X-ray diffraction experiment\(^1\) was carried out by Friedrich and Knipping under the direction of von Laue in 1912.

The regularity of shape of crystals as revealed in the regularity of interfacial angles between equivalent faces of a given crystal species has led to the elaborate system of crystal identification of "Barker's Index of Crystals"\(^2\) where thousands of crystals are catalogued
according to this property.

But along with the similarity of interfacial angles there is also a great diversity of appearances of different crystals of the same species. As long ago as 1669 Nicolaus Steno noticed that although the interfacial angles between equivalent faces of quartz crystals remained constant, the final shape of a crystal was determined by the relative rates of accretion of new material to the different faces during the growth process. Robert Boyle noted in 1691 that the shape of a crystal could be greatly modified by the rate of growth from its solution. Much later, Johnsen, in 1900, analyzed the conditions required for a face to disappear entirely if its growth rate was too great in relation to that of the adjacent faces.

The diversity of habit of crystals prompted Niggli, in 1920, to apply statistics to the subject by making measurements on hundreds of crystals of a mineral as they occur in nature and to formulate tables of probability of occurrence of the various crystal faces.

The persistence of some crystal forms and the absence of others, of both natural and synthetic crystals, has served both as a clue and as a test for theories of crystal growth. The purpose of this study was to devise an experimental method for testing the thermodynamic theories of crystal growth of Curie-Gibbs-Wulff by
correlating the growth rates and variation of growth rates of the various faces of several different crystals with the solid-liquid-vapor contact angles formed between the crystal faces and their saturated solutions.
I. HISTORY AND THEORIES OF CRYSTAL GROWTH

One of the earliest theories of growth was the thermodynamic approach of J.W. Gibbs\textsuperscript{8} who suggested, in 1878, that the equilibrium shape of a crystal should be that shape which results in the lowest surface free energy. Shortly thereafter, in 1885, P. Curie\textsuperscript{7} suggested, again on thermodynamic grounds, that the ratio of the lengths of the face normals from the center of growth of a crystal to the "capillary constants" (or surface free energies) of the respective faces should be a constant. Later, Wulff\textsuperscript{9}, in 1901, extended Gibbs's relationship by proposing that the face normals from a point inside the crystal were proportional to the surface free energies of the respective faces, in agreement with Curie.

There have been several theories of morphology proposed, based primarily upon crystal structure considerations, but having thermodynamic or kinetic justifications. One such very early theory of morphology was that proposed by Bravais\textsuperscript{10} in 1848. He suggested that the order of importance of crystal faces would be in the same order as the reticular density of their respective lattice planes. Much later, in 1937, Donnay and Harker\textsuperscript{11} took
into consideration the effect of screw axes and glide planes, of the space lattice, on the reticular density and thus extended the rule of Bravais considerably. Hartman and Perdok\textsuperscript{12,13,14}, in 1955, used what they called a "Periodic Bond Chain" or P.B.C. vector as a criterion for the stability of the various faces of crystals: the greater the number of P.B.C. vectors contained in a plane, the greater should be its stability. The faces of a crystal are divided into three classes: flat faces or F-faces, each of which is parallel to at least two P.B.C. vectors; stepped or S-faces, each of which is parallel to at least one P.B.C. vector; and kinked faces or K-faces which are not parallel to any P.B.C. vector. The most important faces would be F-faces, then S-faces, and K-faces would be very rare.

McLachlan\textsuperscript{15} introduced, in 1952, the concept of "Laminarity" to take into account those atoms not located at lattice nodes of the crystal. It may be expressed in terms of Miller indices h, k, and l, the atomic positions \( x_j, y_j, z_j \), and the interplanar spacing \( d_{hkl} \) as

\[
L_{hkl} = k d_{hkl} \left[ \sum_j G_j \cos 2\pi (hx_j + ky_j + lz_j) \right]^2 + \left[ \sum_j G_j \sin 2\pi (hx_j + ky_j + lz_j) \right]^2
\]
where $K$ is a constant and $G_j$ is a weighting factor which expresses the effect of the atom, $j$, upon the growth of the crystal.

This is similar, in form at least, to the structure factor equation:

$$F_{hkl} = \left[ \sum_j F_j \cos 2\pi (hx_j + ky_j + lz_j) \right]^2$$

$$+ \left[ \sum_j F_j \sin 2\pi (hx_j + ky_j + lz_j) \right]^2$$

The comparison would seem to support the idea that the prominence of a face (hkl) is proportional to the intensity of the X-ray diffraction from the (hkl) planes, but since there is no direct relationship between the $G_j$ terms of the laminarity equation and the $f_j$ terms of the structure factor equation, this would not appear to be true.

However, Schneer in 1959, using the morphological data of Niggli and Braun, substituted the probability, $P_{hkl}$, of Niggli for the $F_{hkl}$ values in a Fourier summation. He obtained the equivalent of an electron density plot for barite and anglesite which located the positions of the heavy atoms with surprising accuracy.

Kossel, in 1927, and Stranski, in 1928, made detailed studies of the mechanism of crystal growth by
considering the energy of attachment of molecules at all possible positions on the surface of an isotropic crystal. Those positions with the greatest energy of attachment are considered to be the most favored positions for attachment during the growth process. The growth process was visualized as the addition of molecules one by one along the strip at the edge of a partially completed layer. When the strip was filled, there would be a delay due to the greater amount of energy required to start a new strip. After strips had been added until the new layer was completely filled, there would be a very long wait until a two dimensional nucleus could be generated on the new surface. Such a growth process would be of a discontinuous and sporadic nature with long intervals between successive layers.

Observed rates of growth were greater than what could be expected from the impingement rate of molecules on the position of the repeatable step. However, it was shown in 1921 by Volmer and Estermann\textsuperscript{23} that a highly mobile population of adsorbed molecules takes part in the growth process, providing the means of feeding the preferred point of attachment on the advancing edge of new layers.

Burton, Cabrera, and Frank\textsuperscript{24} demonstrated, in 1951, that new layers could not be formed at reasonable degrees
of supersaturation because of the large energy of formation of two dimensional nuclei and suggested an alternate means of new layer initiation. It was proposed by Frank at the Bristol Symposium on Crystal Growth, in 1949, that the presence of self-perpetuating screw dislocations would obviate the necessity of two dimensional nucleation. Subsequent searches by J.B. Griffin, Verma, and Indenbom, among many others, soon produced hundreds of verifying observations of the existence of spiral dislocations on growing crystal faces.

Crystal growth was viewed from a different perspective with the diffusion and adsorption theories. In 1897, Noyes and Whitney, with a study of dissolution phenomena, led Nernst, in 1904, to a generalized theory of heterogeneous reactions in which he assumed the surface reaction was instantaneous and the overall reaction was linear with the concentration gradient. This would appear to be applicable, however, only in those cases where the incorporation of solute into the crystal is extremely rapid and the overall process is diffusion limited. However, this approach did serve to attract attention to the influence of the nutrient environment itself. Volmer's work, in 1921, with the nature of the adsorbed state of molecules from the vapor state, also provided a base for the consideration of adsorption effects on crystals grown
from solution. Work by Marc, Freundlich, Buckley, and Wells shed a great deal of light on the effect of impurities and dyes upon the rates of growth of various faces of crystals.
II. CRYSTAL GROWTH RATE STUDIES

Methods of Measuring Crystal Growth Rates

Several methods for measuring crystal growth rates have been developed. They have included: (a) measuring the distance grown in each direction from the marked origin of growth; (b) observing the crystal growth with a microscope equipped with a traveling crosshair eyepiece, and measuring the face positions at intervals of time; (c) use of an analytical balance when only the face of interest is exposed for growth; (d) use of a torsion balance to measure the torque produced by growth of a single face; (e) use of interferometry techniques; and (f) photographing, with a movie camera, the crystal as it grows and measuring the displacement per unit time from the film or from the projected image.

Motion Picture Studies

In the present investigation, relative rates of growth of the various faces of crystals were of great interest. A sixteen millimeter Bolex movie camera was available; so it was decided that method (f), above,
would be tried. A frame suitable for mounting the camera in position above a standard Leitz microscope, equipped with a temperature controlled hot stage, was constructed. One roll of film was used to determine the correct exposure and a second roll was used to record the growth of ammonium chloride dendrites. Some disadvantages immediately became apparent.

Even at the slowest camera speed of 12 frames per second and the comparatively rapid action of dendritic growth, an entire 100 foot roll (six minutes) of film might be used to record a single experiment and most of the frames were wasted for measurement purposes. There was so little change from one frame to the next that only about one frame per hundred was really needed. If, instead of filming continuously, single frame exposures were taken at regular intervals to save footage, dozens of experiments could be filmed before a 100 foot (4,000 frames) roll would be exhausted. Setup time for almost any experiment is considerable so that weeks might pass before results could be seen. Development cost for a fraction of a roll is the same as for a complete roll, so that the cost of having segments of a roll developed would also be prohibitively expensive.
Schlieren Type Microscope for Measuring Crystal Growth Rates

It seemed as if there should be a way to get all of the information of a series of individual movie frames on one photograph that could be developed in the laboratory. It was decided that if only the outline of an object were to be visible, all else being dark, several exposures could be made on the same photograph. That photograph could, in fact, be an instantly developing "Polaroid" type which would yield a finished picture within less than a minute.

Schlieren photography has long been used to reveal refraction effects of otherwise transparent substances. It is an optical system that shows a strong difference in intensity of light that proceeds through a test area in a straight line and light that deviates from a straight line, due to refraction effects, as it passes through the test area. Light will also deviate from a straight line, however, as a result of diffraction effects such as occur where light passes by an edge of an object. It was thought that if a schlieren microscope system could be modified so as to allow only diffracted light to get through the system, then most objects, whether transparent or opaque, would appear dark with a bright outline on a dark background. That is just what was desired to allow multiple
exposures on a single photograph.

Schlieren photography is in general a rather old art whose history up to 1942 is carefully surveyed with 144 references in a review of 136 pages by Schardin\textsuperscript{42}. Among the early writers are R.W. Wood\textsuperscript{43}, in 1890, and T.H. Tufts\textsuperscript{44}, in 1902. The history through the period covered by Schardin up to the present shows increasing uses of schlieren photography for such purposes as recording the turbulence of air around hot bodies, the flow of liquids, the shock fronts in air associated with supersonic projectiles in ballistics and aeronautics, and in the study of explosives.

The application of the schlieren principle to microscopy, however, is a relatively new subject, initiated by members of McCrone Associates of Chicago, Illinois, since 1966, and published by Dodd\textsuperscript{45,46} and McCrone\textsuperscript{47}. The present instrument differs from that described by Dodd-McCrone as (a) a single large aperture is used, rather than a myriad of small ones, in order to minimize refraction effects; (b) the position of the aperture and stop is reversed (which really has no effect on the performance); and (c) the slightly different optical system used obviates the necessity of the transfer lens of the Dodd-McCrone instrument. In addition, whereas the Dodd-McCrone instrument is finely adjusted to maximize sensitivity to
refraction effects, the present apparatus is adjusted to a very low sensitivity in order to enhance the diffraction effects and minimize the refraction effects (thus concentration gradients in the solution would not lighten the background).

Typical Schlieren System

Figure 1 is a schematic diagram of a typical schlieren system. Light from the source is concentrated by the condensing lens at the focal point of the first lens. A knife edge placed at that point intercepts half of the light, the remainder of the light being collimated by the first lens and brought to a focus by the second lens at its focal point. The second knife edge is positioned so as to intercept half of the remaining light. The result is a gray background with inhomogenieties in the test area showing up as darker or lighter areas depending upon whether the refracted light is bent toward or away from the second knife edge.

Present Instrument Design

The system described above would obviously be unsuitable for our purposes. However, the general principle was used in the design of an instrument represented by Figure 2.
Figure 1. Typical schlieren system.
Figure 2. Schlieren-type microscope.
Optical System

The instrument was designed around a standard Leitz microscope. A substage assembly was added to the microscope which includes the first stop, which corresponds to the first knife edge of the typical schlieren system described, and the first lens of the system. The circular stop differs from the linear knife edge so that the system is equally sensitive to deviations of the light path in any direction. The stop consists of a one-tenth inch diameter black disc centered in a two-tenths inch hole. Translucent tape serves to hold the disc in place and also to scatter the light that is partially brought to a focus by the concave condensing mirror. The stop allows a narrow ring of light into the system at the focal point of the first lens. A mechanism consisting of two translation screws at right angles provides centering of the stop assembly with the optical axis of the system. Since the light enters the system and is scattered at the focal point of the first lens, it leaves the first lens as an evenly illuminated collimated circle of light whose diameter is equal to that of the second lens of the microscope. The collimated beam of light is brought to a focus as a small ring of light at the focal plane of the second lens. The second stop of the system is located on that focal
plane and consists of a black disc with a small hole slightly smaller than the inside diameter of the focused ring of light. Therefore, none of the light passes through the second stop.

If a transparent object is placed on the specimen stage, located between the first and second lens, it may refract the light due to refractive index variations or it may diffract the light at the object's boundary or at internal or surface irregularities of the object. An opaque object will only diffract the light at its boundaries. The light that is either refracted or diffracted has a chance of getting through the small hole in the second stop; however, the hole was made enough smaller than the focused light ring so that only very strongly refracted light or diffracted light will pass.

In use, the microscope may be focused as usual by raising or lowering the tube; however, only the light that is diffracted will pass the second stop. An image is then formed on a ground-glass plate after being magnified by the filar eyepiece and reflected from a partially silvered mirror. The unreflected light goes through the beam-splitter to form an image on the film when the shutter release is activated. When the object is brought into focus as seen through the ground-glass viewer, it is also in focus at the film.
The entire camera assembly may be moved out of the way by lowering the camera lock, raising the camera and camera support arm, and swinging the camera ninety degrees. The camera lock may then be tightened and observations made directly through the microscope eyepiece.

Light Source

The light source proved initially to be a problem. An "American Optical" model 651 lamp provided adequate illumination for the eye but required ten seconds exposure on the fastest Polaroid film available (3200 ASA). A 1200 watt air-cooled, high-pressure mercury vapor lamp was installed and provided excellent pictures at 1/125 second; however, the ultraviolet radiation hazard, heavy transformer, and necessity of compressed air made the system less than ideal. The final and best solution found was to use the American Optical lamp for direct observation and to mount in front of the lamp a small electronic flash unit for photography purposes. The flash unit used was a "Kako Elite-5" model xenon flash intended for mounting on a hand-held 35 millimeter camera. It operates from standard 110 volts AC and has a pivot mount that enables the flash unit to be swung into position in front of the lamp to take a picture and rapidly pivoted back out of the way so that the continuous light from the American Optical
lamp may be used for direct observation. The flash is activated by a synchronized switch in the camera assembly when the shutter is opened. The shutter speed used was 1/125 second, but the flash duration is only about 1/1000 second. High speed (3200 ASA) Polaroid black and white film was used for all exposures.

Temperature Controlled Hot Stage

A temperature-controlled hot stage was also incorporated into the system in order to control the growth of crystals from solution while under observation. The hot stage was constructed by R. Versic similarly to the one described by K.A. Jackson and J.D. Hunt and reported at the 1966 International Conference on Crystal Growth. A cross-sectional view of the hot stage is shown in Figure 3. Two heat sinks are separated by an adjustable air gap. A gap of 1/4 inch was used in this work. The heat sinks are composed of brass bars, one 4" x 2" x 1" and the other 4" x 1" x 1". Both heat sinks have two 3/16 inch holes drilled through their lengths, one for a nichrome heating element and the other for liquid or air coolant as needed. In addition, each sink has a hole drilled for a thermometer and a hole for a thermistor temperature sensing element. The smaller sink also has a four-inch square by two-inch deep container soldered to it for the use of
Figure 3. Cross-sectional view of hot stage.
Although the hot stage was built with the capability of maintaining a set temperature gradient across the air gap, for the purpose of this study the two heat sinks were maintained at the same temperature and crystal growth was initiated and maintained by lowering the temperature of both sinks equally and simultaneously. The currents flowing through the nichrome heating elements of the two heat sinks were individually controlled by separate variacs so that they both were at the same temperature. The two variacs were controlled together by a YSI Thermistemp(R) model 71 Temperature Controller manufactured by Yellow Springs Instrument Co., Inc. The thermistor temperature sensing device was placed in the heat sink that includes the liquid container. In this study the container was kept partially filled with water so that small glass vials containing saturated solutions could be stored at the operating temperature of the hot stage.

Optical Cells

Optical cells for the specimens studied were constructed by first placing as a spacer a small rectangle of No. 1 thickness cover glass slide about one centimeter by two centimeters on a standard 27 millimeter by 47 millimeter
petrographic microscope slide. A standard No. 1 thickness 22 millimeter square cover glass was then placed over the glass rectangle leaving a space on three sides of the rectangle. A small wooden C-clamp was then tightened over the sandwich affair. Epoxy cement was run along the edge of the two open parallel sides and along the edge of the third open edge, except for a small sixteenth-inch gap in the center. The cement was allowed to run in about one-sixteenth of an inch between the cover glass and the slide on the three edges and then all excess cement was wiped off, preventing it from moving in any further from the edges.

The following day, after the cement had hardened, the glass rectangle spacer could be removed, as well as the C-clamp. This resulted in a cell of thickness equal to that of the cover glass (about .152 millimeter), two parallel sides completely sealed off, one side completely open, and the opposite side sealed except for a small one-sixteenth inch space by which the cell could be completely filled by capillary action.

Results from Schlieren Type Microscope Studies

Opaque Dendrites

Tin dendrites were produced in the optical cell for study by allowing a solution containing stannous
chloride to make contact with metallic zinc. The zinc replaces the tin ions in solution forcing the precipitation of metallic tin as dendrites.

A thin sliver of zinc about one millimeter by ten millimeters was cut from a thin zinc sheet which had been produced by allowing molten zinc to fall several feet onto a glass surface. The zinc so produced was bright and clean and free of surface oils. The thin slice of zinc was then pushed into the optical cell through the open end and positioned along one side of the cell.

A solution was prepared by diluting a saturated solution of concentrated hydrochloric acid and stannous chloride with distilled water. The dilute solution was then transferred with a medicine dropper to the small gap left in the closed end of the cell. The cell filled with the solution evenly by capillary action and the medicine dropper was removed when the cell was full.

An aqueous solution of stannous chloride would also have formed tin dendrites upon contact with zinc metal, but such solutions hydrolize readily to form a fine milky precipitate of the basic salt Sn(OH)Cl. Each of the precipitated particles, too small to be individually resolved through the microscope, is a point of diffraction and the resultant diffracted light from the millions of particles present floods the schlieren system with
unwanted background light. The precipitation is prevented, however, by a hydrogen ion excess so the hydrochloric acid solution remains perfectly clear.

One undesirable consequence of using hydrochloric acid solution is the formation of hydrogen bubbles on the surface of the zinc. After a few minutes growth, however, the dendrites grow beyond the limit of the bubbles and they present no further problem.

Figure 4 is a picture of tin dendrites produced as described above. The picture was taken through the schlieren microscope but in what may be referred to as a "normal mode." The "normal mode" produces a picture that is similar to that which would be obtained through a normal microscope and is obtained by removing the second stop from the schlieren system. The second stop is the opaque disc with a small hole through its center which is located at the focal plane of the microscope's objective lens.

The second stop is physically located in a small tube which screws into the bottom of the sliding inner tube of the microscope barrel. Its removal, then, is a simple matter of removing the sliding tube, unscrewing the small tube, and replacing the sliding tube back in the microscope barrel. The microscope is then returned to the "schlieren mode" by the reverse process, namely, replacing
Figure 4. Tin dendrites (normal view).

Figure 5. Tin dendrites (schlieren view).
the second stop in the microscope system.

Figure 4 should be compared with Figure 5 which is a picture of the same tin dendrite taken in the "schlieren mode." The comparison of the two figures demonstrates the general characteristics of the schlieren type microscope as applied to opaque objects. All areas that were either dark or bright in the "normal mode" picture are dark in the "schlieren mode," the outline, only, of the object being revealed as a bright line.

Figure 6 is a "schlieren mode" picture of a tin dendrite showing three different stages of growth. It is obvious at a glance what portions are growing, their relative rates, and what morphological changes accompany the growth. Figure 7 shows a single dendrite limb in three stages of growth under greater magnification to reveal details.

Transparent Crystals

The instrument is equally useful for the study of transparent crystals. Figure 8 is a picture, taken in the "schlieren mode," of copper sulphate crystals which were allowed to nucleate spontaneously as the temperature of the hot stage was lowered below saturation. Because the crystals are transparent, the margins of both the upper and lower surfaces are visible as diffraction lines.
Figure 6. Tin dendrites (schlieren view) showing three stages of growth.

Figure 7. Tin dendrite limb (schlieren view) showing three stages of growth.
Figure 8. Copper sulphate crystals (schlieren view).
Some faces are also visible as bright areas due to the extreme refractive effect of the inclined surface. Otherwise, the crystals are dark, as was desired.

In general, however, more control was necessary over the site of nucleation and the orientation of the crystals than was afforded by spontaneous nucleation. The construction of the optical cell made seeding of the solution easy, especially in the case of resorcinol, an organic substance, \( \text{C}_6\text{H}_6\text{O}_2 \), whose growth characteristics were of particular interest.

A very small amount of resorcinol, as it comes from the laboratory bottle, was sprinkled onto a glass slide and observed with a binocular microscope. A number of small acicular crystals, about one millimeter long, were picked out for seed purposes. One of the small seed crystals was slipped into the open end of the optical cell and pushed into a central position with a small rectangle of glass cut from a No. 1 thickness cover slip.

The optical cell with the enclosed seed was placed on the controlled temperature hot stage and allowed to come to operating temperature. A small amount of saturated resorcinol solution was transferred by medicine dropper from a glass vial, maintained at the temperature of the hot stage by storage in the water-filled reservoir described earlier, to the small gap in the closed end of
the optical cell. The cell then filled with saturated solution by capillary action.

The crystal could be observed through the microscope and the temperature of the controller adjusted as necessary for equilibrium. Normally the temperature would then be raised a few hundredths of a degree to dissolve the crystal back to a very small seed. When the temperature was again dropped to the equilibrium temperature, the crystal would regrow to near its original size but with possible sites for surface nucleation dissolved away.

The orientation of the crystal is also partially known because of the acicular, or needle-like nature of the original seed crystal. It is known that when resorcinol is grown under conditions such that acicular crystals are formed, i.e., high specific supersaturation, the crystals are elongate parallel to the c-axis. The c-axis is then fixed for the crystal observed under the microscope as horizontal and parallel to the prominent zone.

A resorcinol crystal grown from such an implanted seed is shown in "normal mode" in Figure 9 and in "schlieren mode" in Figure 10. Surface irregularities and internal impurities are readily apparent in the schlieren photograph, whereas they are almost totally obscured in the "normal mode" photograph.

Figure 11 is a "schlieren mode" picture of a
Figure 9. Resorcinol crystal (normal view).

Figure 10. Resorcinol crystal (schlieren view).
different resorcinol crystal showing a single stage of growth and may be compared with Figure 12, which is a picture of the same crystal showing two stages of growth. Since both top and bottom edges of the crystal are displayed equally well, a double outline is seen for each exposure. This fact does make interpretation slightly more confusing; and when a large number of exposures are made, showing an equal number of growth stages, interpretation is difficult. An example may be seen in Figure 13 of seven stages of growth of a resorcinol crystal, resulting in fourteen separate outlines of the crystal.

One particular characteristic of growth of resorcinol, however, made it possible to obtain oriented crystals that were so thin the top and bottom surfaces were not resolved as two separate lines but rather as a single outline. It was accomplished by lifting the optical cell, containing a resorcinol solution saturated at about 35° C, above the hot stage so that it rapidly cooled toward room temperature of about 22° C. The very rapid drop in temperature resulted in dendritic growth as might be expected. The characteristic of growth that proved helpful was that resorcinol tends to form very thin lath-like crystals when grown dendritically from an aqueous solution. These dendrite laths, although grown quite rapidly, are able to grow with very few visible defects, apparently
Figure 11. Resorcinol crystal (schlieren view).

Figure 12. Resorcinol crystal (schlieren view) showing two stages of growth.
Figure 13. Resorcinol crystal (schlieren view) showing seven stages of growth.
because of the extremely thin nature of the crystals.

The optical cell was then lowered into its place on the hot stage where its temperature began to return to that of the stage. The dissolving dendrite was observed through the microscope and its progress was arrested by slightly lowering the temperature when the dendrite had dissolved back to appropriately small dimensions.

The procedure described above, which could be reproduced at will, resulted in an ultrathin seed which would produce a thin crystal when the temperature of the stage was lowered. Figure 14 shows such a crystal in four stages of growth. Note that only a single outline is seen for each stage of growth. Figure 15 is a different crystal showing ten stages of growth.

The most striking feature of these resorcinol crystals revealed by the multiple exposure schlieren photography technique is the great difference in growth rates shown by opposite ends of the c-axis. The end showing the (011) terminations has a growth rate perhaps as much as one hundred times as great as the end showing a (001) termination. This result is not particularly surprising, as it agrees with an earlier study by the writer of the relative growth rates of larger bulk crystals of resorcinol\(^5\); but it is quite interesting for a number of reasons that were pointed out in the earlier investigation.
Figure 14. Thin resorcinol crystal (schlieren view) showing four stages of growth at one minute intervals.

Figure 15. Thin resorcinol crystal (schlieren view) showing ten stages of growth at thirty second intervals.
Resorcinol is one of the benzene derivatives and has as its nucleus the benzene ring. The benzene ring consists of six carbon atoms arranged in a symmetrical hexagonal ring. All six carbon atoms lie in the same plane and each is bonded to a hydrogen atom. In resorcinol two of the hydrogen atoms are replaced by OH groups in the 1 and 3 positions of the ring, carbon atom positions being numbered consecutively 1-6, clockwise around the ring. The resorcinol molecule, then, can be represented as

\[
\begin{array}{c}
\text{OH} \\
\text{C} \\
\text{H-C} \\
\text{C-H} \\
\text{H-C} \\
\text{C-OH} \\
\text{H} \\
\end{array}
\]

The molecular configuration makes the resorcinol molecule highly polar, the end containing the OH groups being highly hydrophylic and the other end being hydrophobic, like benzene.

The resorcinol molecules are bonded together in two different crystalline configurations, the \(\alpha\) form being stable up to 74\(^\circ\) C and the \(\beta\) form being stable from 74\(^\circ\) C to the melting point of 110\(^\circ\) C. The \(\alpha\) structure of resorcinol was determined by an X-ray study in 1936\(^5\) and the
Resorcinol belongs to the orthorhombic point group symmetry class \( \text{mm2} \) and to the \( \text{Pna2}_1 \) space group. The unit cell dimensions are \( a_0 = 10.53\text{Å} \), \( b_0 = 9.53\text{Å} \), and \( c_0 = 5.66\text{Å} \). There are four molecules per unit cell arranged in spiral chains about the \( 2_1 \) screw axis. Figure 16 shows one perspective of a crystal structure model of resorcinol where cardboard of the proper shape and size was used to represent the planar resorcinol molecule with the OH group positions being marked by black circles.

It is obvious upon inspection of the model that the benzene-like ends of all of the molecules are pointed toward one end of the \( c \)-axis while the hydroxyl ends are facing the other. It would be expected, then, that faces terminating one end of the \( c \)-axis would have a completely different surface chemistry from those faces terminating the other end. A large difference in growth rates between the two ends would, therefore, not be unexpected. The point group symmetry class, \( \text{mm2} \), of resorcinol also indicates that there would be no reason to expect the growth rates to be equal.
Figure 16. Resorcinol Model.
Comparison of Results with Crystal Morphology Theories

It was shown in the earlier work\textsuperscript{50}, however, that the prominent theories of crystal morphology, the Law of Bravais, the Donnay-Harker Law, and McLachlan's Theory of Laminarity, would all predict that opposite faces on a crystal grow at equal rates. Although the terminations on the resorcinol crystals shown in the schlieren photographs do not correspond to opposite faces, larger bulk crystals are terminated with \((011)\) and \((0\bar{1}1)\) faces on one end of the \(c\)-axis and \((0\bar{1}1)\) and \((0\bar{1}1)\) on the other, and the investigation showed a similarly large difference in growth rates.

Another prominent theory of crystal morphology, the Gibbs-Wulff Theorem, was also considered in the previous work and will be reconsidered here. In 1878, J.W. Gibbs\textsuperscript{8} stated that the equilibrium shape of a crystal would be such that the total surface free energy would be a minimum for a constant mass or volume of crystal. The total surface free energy is defined as \(\sum_j \gamma_j O_j\) where \(\gamma_j\) is the surface free energy per unit area of the \(j\)th face and \(O_j\) is its area. The assumption is made that the edge and corner surface free energies are negligible compared to the total surface free energy. The surface free energy is equal in magnitude and equivalent in units to the surface tension in the case of liquids. The units of
surface free energy are energy/cm² = mass/sec², and the units for surface tension are force/cm = mass/sec².

Wulff⁹, in 1901, extended the work of Gibbs as follows. Consider Figure 17 where vectors are drawn from a point inside a crystal normal to each face. The length of the vector to face j is hj and the area of the jth face is O_j. Wulff suggested that for a crystal at equilibrium the vector length hj would be proportional to γ_j, the surface free energy of the jth face; i.e., hj = k γ_j where k is a constant depending on the size of the crystal. Several mathematical proofs have been offered since Wulff's publication, including those of Hilton⁵³, Liebman⁵⁴, and von Laue⁵⁵.

An approximation to the surface free energy, γ, is obtained by calculating the surface energy, ε. The surface energy and surface free energy are related as follows:

\[ ε = γ - T \left( \frac{∂γ}{∂T} \right)_P \]

It is known from studies of the variation of surface tension of liquids with temperature that the term \( \left( \frac{∂γ}{∂T} \right)_P \) should be quite small and negative so that ε is slightly greater than γ. The surface energy, ε, may be calculated, approximately, for a particular face, say (011), as follows. Imagine the crystal to be sliced in two along a (011) plane. The change in potential energy of the crystal
Figure 17. Gibbs-Wulff.
will be approximately equal to the potential energy of the bonds broken, which in turn will be equal to the surface energy of the fresh surfaces formed, neglecting relaxation of the surface area after formation. This procedure produces two surfaces, a (011) surface and a (011) surface. The energy of the bonds broken per unit area will clearly be the same for both surfaces and so likewise their respective surface energies. It seems certain, then, that the surface free energies of opposite faces on a crystal cannot be appreciably different, and hence, according to Wulff, neither should be their growth rates.
III. INTERFACIAL FREE ENERGIES

In the presence of anything other than a vacuum, however, it is the interfacial free energies that should be considered rather than the surface free energies. If a concentrated liquid solution is present, the interfacial free energy may be only a fraction of the surface free energy, because many of the loose surface bonds will be satisfied by bonding with molecules of the solute and solvent of the solution. In addition, the interfacial free energy of opposite faces on a crystal can clearly be quite different as the interaction of a crystal surface with the surrounding solution will be a strong function of the specific chemical nature of the surface presented to the solution. The concentration of the solution, at equilibrium, can even be expected to be different at different faces of the crystal and is related to the lowering of interfacial free energy upon addition of solute by the Gibbs adsorption isotherm, which may be written for this case as:

\[ d\gamma_{sl} = -RT\sigma_s d\ln c_s \]
where $\gamma_{si}$ is the interfacial free energy of the face $i$ of the crystal in the solution, $R$ is the gas constant, $T$ is the temperature in degrees Kelvin, $T_s$ is the concentration of solute adsorbed at face $i$ of the crystal, and $a_s$ is the activity of the solute in the solution which for an ideal solution would be equal to the mole fraction.

Apparently, then, although there would not be an appreciable difference in the surface free energy of opposite faces on a crystal, there could be very large differences in the interfacial free energies due to a difference in adsorption on the two faces.

Unfortunately, there is no way at present to measure solid-liquid interfacial free energies or even to calculate or estimate them with any degree of accuracy.

**Solid-Liquid-Vapor Contact Angles**

Some information concerning interfacial free energies may be obtained by the angle of contact that a liquid makes with a solid. If a drop of liquid is placed on a solid surface, it may spread and cover the surface completely; or, more commonly, it may gather up into a lens. The edge of the lens is a three-phase contact line, and the angle that the liquid makes with the solid surface is dependent on the relative interfacial free energies of the
respective phase interfaces in the following manner. Consider Figure 18 which represents an end view of the contact line. In order for the forces to balance parallel to the solid surface

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

where $\gamma_{SV}$, $\gamma_{SL}$, and $\gamma_{LV}$ are the interfacial free energies of the solid-vapor, solid-liquid, and liquid-vapor interfaces respectively and $\theta$ is the contact angle measured in the liquid phase. Credit for this relationship is given by some authors to Young, who stated the principle in words, and by some to Dupre, who set it down as an equation. Thermodynamic considerations of the minimization of surface free energy of the solid-liquid-vapor system, treating the lens as a portion of a sphere in the absence of gravity, yields the same result.

The liquid-vapor interfacial free energy is easily measurable as the liquid surface tension by a number of methods including the capillary height method, the capillary pull method, the maximum bubble method, the drop weight method, and the drop weight volume method. The angle of contact, $\theta$, is likewise measurable by a number of different methods which will be discussed in detail later. The measurement of solid-liquid-vapor contact angles should, therefore, provide a simple and inexpensive method for obtaining information concerning interfacial
free energies.

The purpose of this part of the investigation, then, was to determine the feasibility of using solid-liquid-vapor contact angles to learn something about the interfacial free energies between crystal faces and their saturated solutions.

**Sessile Drop Method**

The earliest and most obvious way of measuring the contact angle is referred to as the sessile drop method. A drop of liquid is placed on the solid and the angle of contact is measured directly from the silhouette as shown in Figure 19. Preliminary measurements of this kind on crystals of alum, rochelle salt, ammonium dihydrogen phosphate (ADP) and resorcinol were encouraging. A non-zero contact angle was noted on all of the above crystals and the substance of greatest interest, resorcinol, showed a much larger contact angle on the (111) terminated end than on the other. This result is what was expected on the basis of the highly polar nature of resorcinol. One end was expected to be hydrophobic, like benzene, and the other end was expected to be hydrophylic, or water wetting. The angles observed varied widely, however, and it was known that before reliable reproducible results could be obtained it would be necessary to build an apparatus
Figure 19. Sessile drop.
capable of accurate measurements while maintaining the vapor surrounding the crystal at saturation.

A logical extension of the sessile drop method is what might be referred to as the sessile drop diameter method. If the volume of the sessile drop is constant, then the radius or diameter is a function of the contact angle.

Consider Figure 20. Let R be the radius of curvature of the drop and r be the radius of the base of the drop segment or lens as indicated in the figure. Turning the figure around and labeling coordinate axes X, Y, and Z as shown in Figure 21, the equation of the extended sphere is:

\[(X-R)^2 + Y^2 + Z^2 = R^2\]  

The area (a) of the base of the sphere segment (and the base of the lens) is:

\[a = \pi r^2\]  

and

\[r^2 = Y^2 + Z^2\]  

Substituting (3) into (1)

\[(X-R)^2 + r^2 = R^2\]  

Now the volume of the slice (V) can be seen from Figure 22 to be

\[V = \int_0^b \pi r^2 dX = \int_0^b \pi r^2 dX\]
Figure 20. Sessile drop calculations.

Figure 21. Sessile drop calculations.
From (4) above
\[ r^2 = R^2 - (X-R)^2 = R^2 - X^2 + 2XR - R^2 \]
\[ = 2XR - X^2. \]  
(6)

From (5) and (6)
\[ V = \int_0^b \pi (2XR - x^2) dx = \pi (b^2R - b^3/3) \]  
(7)

From Figure 23
\[ b = R - s \]  
(8)
\[ s = R \cos \theta \]  
(9)
\[ b = R - R \cos \theta = R(1 - \cos \theta) \]  
(10)
\[ \frac{r}{R} = \sin \theta \]  
(11)
\[ R = \frac{r}{\sin \theta} \]  
(12)

From (10) and (12)
\[ b = \frac{r}{\sin \theta} (1 - \cos \theta) = \frac{r(\cos \theta)}{\sin \theta} \]  
(13)

Substituting (13) into (7)
\[ V = \pi \left[ \frac{r^2(1 - \cos \theta)^2}{\sin^2 \theta} - \frac{r}{\sin \theta} + \frac{r^3(1 - \cos \theta)^3}{3 \sin^3 \theta} \right] \]  
(14)
\[ V = \frac{\pi r^3}{\sin^3 \theta} \left[ (1 - \cos \theta)^2 - \frac{(1 - \cos \theta)^3}{3} \right] \]  
(15)

Equation (15) above, when expanded, yields
\[ V = \frac{\pi r^3}{3 \sin^3 \theta} \left[ \cos^3 \theta - 3 \cos \theta + 2 \right] \]  
(16)
Figure 22. Sessile drop calculations.

Figure 23. Sessile drop calculations.
Then
\[
\frac{3V}{\pi r^3} = \frac{\cos^3 \theta - 3 \cos \theta + 2}{\sin^3 \theta}
\]

A graph may be drawn of \( \frac{3V}{\pi r^3} \) vs. \( \cos \theta \) and is shown as Figure 24.

Now the volume of the drop \( (V) \) is known, as will be explained later, and in this case was equal to \( .0003 \text{ cm}^3 \) so that
\[
\frac{3V}{\pi} = .2865 \text{ mm}^3
\]

A table was then prepared of the radius of the drop vs.
\[
\frac{3V}{\pi} = .2865 \text{ mm}^3.
\]

A third column could then be added to the table of \( \cos \theta \) by using column two and the graph of Figure 24. A final graph could then be drawn, as shown in Figure 25, of the radius of the drop in mm. vs. \( \cos \theta \).

The diameter of the drop was measured by viewing the crystal on a microscope stage through a filar eyepiece. The microscope was fitted with an above-stage mirror so that reflected light could be used. The filar eyepiece contains a calibrated traveling crosshair so that accurate measurements of the diameter are possible.

The volume of the drop was kept constant by using a microdropper which was constructed from a standard
Figure 24. \( \cos \theta \) vs. \( \frac{3V}{\pi r^3} \) graph.
Figure 25. \( \cos \theta \) vs. drop radius.
laboratory medicine dropper as follows. A small hole was made in the rubber bulb and a small circle of rubber was cemented across the other end of the dropper. The rubber circle was pierced by a pin in preparation for the insertion of a small glass capillary tube about one inch in length.

The glass capillary tube was prepared by drawing glass tubing after heating. Several capillaries were also prepared for spares. The glass capillary was then inserted through the small hole pierced in the rubber circle.

When the end of the capillary was immersed in a liquid while the hole in the bulb was open, the liquid would rise to the top of the capillary and stop. The measured quantity could then be forced out by squeezing the bulb while covering the hole. The microdropper was calibrated by weighing and averaging several totals of ten drops of distilled water.

This method has a strong advantage that it becomes more sensitive as the contact angle approaches zero. Some disadvantages also became apparent, at least in regard to the measurement of the contact angle of a saturated solution with a crystal face. It is difficult to deposit the drop perfectly normal to the solid surface. The drop, therefore, was nearly always somewhat elliptical in outline rather than circular as was desired. A problem
peculiar to this investigation was that it still proved to be difficult to maintain the vapor surrounding the liquid at saturation. It was first thought that a current of saturated vapor could be played over the surface while a measurement was taken. The vapor, however, cannot be saturated with pure water, because the vapor pressure of pure water is higher than the water vapor pressure of a saturated solution, of resorcinol, for instance, and condensation would occur on the crystal surface. Enclosing the microscope stage area, containing open containers of saturated solution, was reasonably successful but quite awkward to work around.

One fact became obvious, however. As success was more nearly realized in keeping the vapor saturated, the contact angle became much smaller. It was difficult to find large enough surface areas on the crystals void of irregularities so that the drop remained nearly circular. This would not be a problem if one were working with polished surfaces, but it was a serious problem when working with laboratory grown crystals.

**Inverted Bubble Method**

It was apparent at this time that the requirements for an apparatus capable of yielding consistent and accurate measurements of the contact angle of a crystal face
and its saturated solution must include the conditions that the crystal face be absolutely clean and that the air be completely saturated with the vapor of the saturated solution. An apparatus that ideally meets the above conditions was designed and constructed.

In use, the crystal is completely immersed in its saturated solution so that the slightest growth or dissolution creates a new surface. A small air bubble, which quickly becomes saturated with the vapor of the saturated solution, is brought into contact with the crystal face being tested.

A.F. Taggart used a bubble method for contact angle measurements of minerals to determine their amenability to the flotation process of ore separation. Taggart, with his method, brought a bubble down to the surface being tested, and if the contact angle was large enough, the bubble would adhere to the surface when the bubble holder was removed.

With the present method, the crystal face is horizontal and above the air bubble so that the bubble is held against the crystal face by its own buoyancy, regardless of the contact angle. The relationship of the interfacial tensions at the three phase contact line is shown in Figure 26 and is similar to that for the sessile drop.
Figure 26. Bubble contact.
Resolution of forces again yields the result of

\[ \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \]

Present Instrument Design

The apparatus was constructed according to Figure 27. The planetary device (a) shown in the insert allows any face on the crystal being tested to be placed in position for measurement, i.e., horizontal and facing down. The teflon planetary device then sits on the teflon ring (b) which is the same diameter as the teflon rings making up the planetary device. The crystal is completely immersed in its saturated solution held in container (c) which is fitted with two smooth, flat glass viewing ports located on opposite sides of the container so that light from an American Optical model 651 lamp may enter one port and the silhouetted crystal may be viewed through the other. A microscope fitted with a 40 mm objective lens is used for viewing the crystal face and bubble profile.

Fine adjustment of the orientation of the crystal face for absolute horizontality is achieved by adjustment of the two screws (d) on goniometer head (e). The lateral position is controlled by the small translation screws (f) and the vertical position by the large, vertical translation screw (g). Lateral, vertical and orientation information is transmitted mechanically by the three gold
Figure 27. Inverted bubble apparatus.
plated chains (h) which attach to the teflon ring. The container platform may be raised or lowered by the large vertical translation screw (i). The microscope may be raised or lowered by rack adjust (j).

The bubble generating mechanism consisted of a length of teflon tubing connected at one end to a hand-operated squeeze bulb and at the other end to a glass tip. The glass tip was a half-inch length of flared glass tubing. The teflon tubing passes into the small diameter end of the glass tip and is glued in place with epoxy cement. A small disc of cork is cemented to the larger end of the glass tip. A single small diameter hole was made in the center of the cork disc by piercing it with a needle. Small diameter air bubbles could be generated either individually or as a stream by means of a rapid squeeze on the bulb.

The teflon tubing passes through a glass tube right angle which is held in one corner of the glass container by means of a polyethylene split ring. The glass tip may then be positioned directly under the crystal face by rotating the glass tube for direction and by pushing or withdrawing the teflon tubing for the correct distance from the corner.

In practice, the crystal is first secured to the center of the planetary device with thread. The planetary
device is then set on the teflon ring in a position such that the face whose contact angle is to be measured is horizontal and facing down. The glass container, filled with the saturated solution, is then placed on the platform and the upper assembly is lowered until the crystal is completely immersed in the solution. The microscope is adjusted in position so that the profile of the crystal face is visible. The tip of the bubble generator is then positioned under the crystal face and a bubble is released. The tilt screws are quickly adjusted to prevent the bubble from sliding off the crystal face, and the translation screws are adjusted to center the bubble profile in the field of view. The contact angle may then be measured by rotating the filar eyepiece until the movable crosshair is tangent to the bubble at the three phase contact line, and reading the angle directly from the angular scale. A bellows attachment, fitted with a polaroid-type film pack, was also provided which could be placed against the microscope tube, after the eyepiece was removed, in order to obtain a photographic record. The contact angle could then be measured directly from the photograph.

The inverted bubble method was first used on glass microscope slides immersed in water. Figure 28 is a photograph of the profile of a bubble in contact with a microscope slide as it comes out of the package from the
Figure 28. Bubble on uncleaned glass slide.

Figure 29. Bubble on clean glass slide.
manufacturer. The glass plate has been tilted somewhat from horizontal in order to clarify the photograph. The rather large contact angle is indicative of surface contamination of the slide, probably consisting, in part, of hydrophobic oils remaining from the manufacturing process. Figure 29 shows the bubble profile on the same glass slide after it has been thoroughly cleaned with a mixture of concentrated sulfuric acid and sodium dichromate. The angle of contact of a clean glass surface and water is generally accepted as zero. This photograph would seem to substantiate that finding.

Results from the Inverted Bubble Method

The inverted bubble method was next applied to crystals and their saturated solutions.

The contact angles of the prism faces (hko) of rochelle salt, KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6}·H\textsubscript{2}O, were measured and found to be zero. A photograph of a bubble showing the contact angle formed with such a prism face is shown in Figure 30. The contact angle of the (001) face was also found to be equal to zero. A photograph of the bubble in contact with the (001) face of rochelle salt is shown in Figure 31.

The contact angle of the (110) and (111) faces of ammonium dihydrogen phosphate, NH\textsubscript{4}·H\textsubscript{2}PO\textsubscript{4}, was found to be zero. One of the ways in which the contact angle was
Figure 30. Bubble on (110) face of rochelle salt.

Figure 31. Bubble on (001) face of rochelle salt.
expected to change was for it to vary with the degree of supersaturation; therefore, some measurements were also taken under growth conditions. Figure 32 is a photograph of a bubble in contact with a (110) face of ADP under such conditions of strong supersaturation; again, the contact angle was determined to be equal to zero.

The octahedral faces (111) of ammonium alum, \((\text{NH}_4)_2\text{Al}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}\), yielded a zero degree contact angle. The cube faces (100) also gave contact angles of zero.

The finding of a zero degree contact angle for all the developed faces of rochelle salt, ADP and ammonium alum was rather surprising. Resorcinol, \(\text{C}_6\text{H}_6\text{O}_2\), was approached with more confidence, however, because a rather large contact angle had been noticed for the (111) faces of resorcinol when preliminary measurements were made using the sessile drop.

The confidence was ill founded, however, because a contact angle of zero was also obtained for all of the faces of resorcinol.

The angle of contact for all crystals measured with their saturated solutions appeared to be exactly equal to zero degrees. But, whereas the inverted bubble method for measuring the contact angle had solved two very important and difficult problems, namely, the insuring of the saturation of the vapor surrounding the crystal and the
Figure 32. Bubble on prism face of ADP.
perfect freshness of crystal surface for measurement, it introduced the possibility of another.

The angle of contact was obviously very low for the crystals measured, but it was quite possibly not equal to zero for the following reason. There is an energy barrier that must be overcome when the bubble is placed against a solid surface before actual contact between the air and the solid surface takes place. Even though the bubble was left in contact with the crystal face overnight on some occasions, still with an apparent zero degree contact angle, it seemed possible that for very low contact angles the energy barrier may never be surmounted within a reasonable length of time.

Therefore, the decision was made to construct an instrument to measure the contact angle in yet another manner so that the energy barrier problem would not exist.

Goniometer Method

A Terpstra Nedinsco two-circle reflecting goniometer, manufactured by N.V. Nedelandshe Instrumenten Compagnie of Venlo, Holland, was adapted to the tilt plate method of Adam and Jessop\(^5\). The tilt plate method is used as follows. Consider Figure 33. The solid surface whose contact angle is to be measured is partially immersed in the liquid. Some means is available to tilt the
Figure 33. Tilt plate method.
plate relative to the liquid surface while observing the meniscus formed at the line of contact. If the line of contact is observed as a profile, the plate is tilted until the liquid surface remains horizontal right up to the point of contact. The angle of contact is then measured through the liquid phase from the liquid surface to the plate.

In the present modification of the tilt plate method, a collimated light source is used to test that the liquid presents an undisturbed horizontal surface up to the line of contact and also to actually measure the angle of contact when that condition is met.

The Terpstra two-circle goniometer was used to provide the collimated light source, the optical system to view the signal of the collimated beam, and the means to measure the contact angle. Figure 34 is a sketch of the reflecting goniometer as it is generally used to make precise measurements of the angular relationship of the faces on a single crystal.

Two angles may be read directly from the goniometer on an illuminated scale through the viewer (a) as shown in Figure 34. The angle designated as $\phi$ measures the angle of rotation about the $\phi$ axis as labeled in the figure, and the angle $\rho$ measures the angle of rotation about the $\rho$ axis which coincides with the axis of rotation.
Figure 34. Terpstra goniometer.
of the swingout arm (b). The swingout arm carries both the exit signal beam and the telescope for viewing the reflected signal beam. A $\rho$ angle of zero is read when the signal is reflected from a surface normal to the axis. The $\phi$ and $\rho$ axes are at right angles to one another. The exit beam and the reflected beam are actually in a plane normal to the $\rho$ axis, a fact that is not obvious from the view of Figure 34.

When the eyepiece (c) is lowered into viewing position, a magnified view of the crystal or surface being studied is seen. When the eyepiece is raised, an image of the Websky signal is seen if a good reflecting surface is present in the proper orientation.

The goniometer was mounted on a saddle-like device (f) so that the $\phi$ axis was vertical and the $\rho$ axis horizontal as shown in Figure 35. A small plexiglas mount (g) was fitted to the top of the goniometer head so that a small glass beaker (h) could be inserted which contained the crystal to be measured and the saturated solution. The base of the saddle device was leveled so that when a liquid alone was placed in the beaker, the reflected Websky signal from the horizontal liquid surface could be brought to the center of the crosshairs when the $\rho$ scale read exactly zero.

A microscope slide, fresh from the box and
Figure 35. Terpstra goniometer (side view on saddle).
uncleaned, was introduced to the beaker and allowed to intersect the liquid surface as in the method of Adam and Jessop. The $\phi$ axis was rotated at the milled edge of circle (d) until the line of contact of the glass plate and the liquid surface was parallel to the $\phi$ axis. Eyepiece (c) was lowered into position so that a magnified view of the liquid surface, the glass plate, and the meniscus at the line of contact was visible. An image of the light source, an incandescent coiled filament, could be seen reflected from surfaces where it hit. Translation screws on the goniometer head (e) could be adjusted to move the entire beaker and, hence, the point where the light beam (filament image) would strike the surface. If the light beam struck the surface of the liquid well away from the meniscus, a single clear Websky signal would be seen at $\phi$ equal to zero when the eyepiece was raised. If the translation screws were adjusted so that the light impinged upon the meniscus, a blurry series of Websky signals would be seen at a $\phi$ other than zero because of the curvature and non-horizontal nature of the meniscus.

The plate needs to be tilted so that it enters the liquid at the contact angle and no meniscus is formed. In this case the plate is attached to the beaker and the liquid surface is horizontal due to gravity. The beaker is inserted in a holder at the top of the goniometer head
so that the beaker is tilted as the tilt screws of the
goniometer head are adjusted. The liquid surface remains
horizontal.

If now the series of Websky signals are observed
as the appropriate tilt screw is adjusted, they will be
seen to either spread further apart or approach each other,
depending upon whether the angle the plate makes with the
liquid surface deviates more or less respectively from
the angle of contact. If the tilt screw is turned so
that the contact angle is approached, the blurry signals
will be seen to collapse into a single clean Websky signal.
This indicates that the liquid surface is undistorted and
the plate intersects the liquid surface at the angle of
contact. The eyepiece could be lowered again and the
translation screws again adjusted to make the filament
image fall as close to the actual line of contact as
possible. The procedure could then be repeated to insure
that the liquid surface was horizontal right up to the
line of contact. The $\theta$ angle should still read zero
degrees.

In order to read the actual contact angle, the
translation screw would be adjusted so that the light was
reflected from the surface of the plate. The swing arm
was then rotated so that the Websky signal, reflected from
the plate, coincided with the crosshairs. Fine adjustment
of the $\rho$ knob, shown in Figures 34 and 35, allowed a reading of within a minute of arc. The $\varphi$ angle, read on the illuminated dial, then corresponded directly to the actual contact angle.

The procedure was unchanged for the measurement of the contact angles of crystal faces with their saturated solution except that clear, untextured, transparent polyethylene film was used to completely cover the top of the beaker to insure complete saturation of the vapor.

When sufficient time was allowed to achieve saturation of the vapor, the contact angles of the developed faces of rochelle salt, ADP, alum and resorcinol were again found to be zero, a zero contact angle with this method being characterized by the complete inability to reduce the angle of the meniscus to zero. The crystal face would become horizontal and would then either be out of the liquid or in the liquid and wetted; once wetted the crystal faces would not "unwet."

There was no energy barrier to overcome using this method, so it must be concluded that the contact angle for the above cases is truly zero.
Interpretation of Results

Consider Figure 18, again, which represents the resolution of forces at the three phase contact line. In order to obtain a contact angle of zero, \( \gamma_{lv} \) must be equal to or greater than \( \gamma_{lv} \). Results of other workers in the field of vapor adsorption by solids of large areas provides a basis for making a choice between the two possibilities.

From the study of adsorption isotherms and progressive heat of immersion studies, W.D. Harkins\(^6\) concluded that the film adsorbed on a solid, from the vapor of a liquid which gives a contact angle of zero on the solid, is duplex, i.e., the film is sufficiently thick to give inappreciable (experimentally) interaction between the outermost layer of the film and the solid. Thus the surface free energy of the outer part of the film is supposed to be the same as that of the outer part of the liquid\(^61\). The solid surface, then, when exposed to the saturated vapor, adsorbs a film, of polymolecular thickness, according to Harkins\(^62\), the outer surface of which is indistinguishable from the liquid comprising the vapor. The inner surface of the adsorbed film is said by Williams\(^63\) to be identical to the adsorbed layer immediately adjacent to the solid surface when it is immersed in the liquid solution.
It is clear, then, that the total surface free energy of the solid surface in the presence of the vapor of a liquid with which it forms a contact angle of zero must be equal to the sum of the liquid-vapor and the solid-liquid surface free energies, i.e., $\gamma_{sv}$ equals $\gamma_{sl}$ plus $\gamma_{lv}$ rather than $\gamma_{sv}$ is greater than $\gamma_{sl} + \gamma_{lv}$. Substituting this into the now familiar Young's equation of the resolution of forces

$$\gamma_{sv} = (\gamma_{sl} + \gamma_{lv}) = \gamma_{sl} + \gamma_{lv} \cos \theta$$

and $\cos \theta$ is identically equal to one. Therefore, when a contact angle of zero is obtained, no useful information concerning the interfacial free energies may be determined, except that $\gamma_{sv}$ equals $\gamma_{sl}$ plus $\gamma_{lv}$.

It is also clear why large contact angles could be obtained under slightly less stringent conditions, but contact angles of zero were obtained when rigorous attention was given to obtaining complete saturation of the vapor. At liquid vapor pressures below saturation, the adsorbed film on the solid was not identical to the liquid phase, and a nonzero angle was possible. At saturation, the adsorbed film was identical to the liquid phase, and the result was a contact angle of zero. If the vapor
were not completely saturated, a larger contact angle would be obtained, but it would be impossible to maintain or reproduce, reliably, any vapor pressure other than that of saturation while dealing with a crystal-saturated solution system.

The explanation above applies only to those cases where the liquid exhibits a contact angle of zero against the solid and does not mean that a contact angle of zero will inevitably be obtained. There are many cases of nonzero contact angles being obtained when adequate measures are taken to insure the saturation of the vapor. For instance, the values obtained by Fowkes and Harkins were: graphite and water - $\theta = 85.7^\circ$, talc and water - $\theta = 87.8^\circ$, stibnite and water - $\theta = 84.2^\circ$, and paraffin and water - $\theta = 108^\circ-111^\circ$ depending on orientation.

An extensive investigation was not made using different solvents; however, the contact angle of a resorcinol-saturated benzene solution against all faces of resorcinol was also found to give a contact angle of zero. The solubility of resorcinol in benzene is less than three-tenths of a per cent and that of resorcinol in water is over twenty-two per cent. A broad range of possible degrees of wettabilities is represented by the benzenoid and hydroxyl ends of resorcinol and the solvents, water and benzene. On the basis of this investigation, it
seems very likely that the contact angle of a solid with any liquid in which it is soluble to any practical extent would be zero.

It is unlikely that excluding air from the system could increase the contact angle. The presence of air in the system offers an additional opportunity for the $\gamma_{sv}$ to be reduced enough for the contact angle to rise above zero. It is possible that the use of other types of atmospheres may result in a contact angle other than zero, but the possibility seemed remote and so was not pursued.
IV. SUMMARY

A schlieren-type microscope was developed which allows multiple exposures of a growing crystal or dendrite on a single photograph. Each stage of growth is represented by a bright line around the edge of the crystal at the instant of exposure. Growth rate or morphology change in any direction in the plane of the microscope stage may be measured directly from the single photograph.

The solid-liquid-vapor contact angles of the developed faces of rochelle salt, ammonium dihydrogen phosphate, ammonium alum, and resorcinol against their respective saturated solutions were measured by four different methods. It was hoped that a correlation could be found between the relative rates of growth and the contact angles of the respective crystal faces. It was found, however, that when adequate measures were taken to insure complete saturation of the vapor surrounding the crystal, the contact angle fell to zero in all cases. It seems very likely, on the basis of this investigation, that the contact angle of a solid with any liquid in which it is soluble to any practical extent would be zero.
REFERENCES


38. Wells, A.F., Phil. Mag., 37, 184 (1946).
40. Wells, A.F., Phil. Mag., 37, 605 (1946).
43. Wood, R.W., Phil. Mag., 48, 218 (1901).
45. Dodd, J.D., Microscope, 15, 167 (1966).
56. Young, T., Phil. Trans., 65, 84 (1805).