THE GROWTH OF CRYSTALS FROM A STREAM OF VAPOUR.

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The mechanism of the growth of crystals from the vapour is a problem which has become of interest since Volmer showed that with mercury the molecules on the surface could be mobile, and since Kossel and Stranski elaborated their theory of crystal growth. The experiments of Alty have shown that in certain cases the rate of evaporation of a crystal mass can be much less than the rate at which molecules strike its surface when it is surrounded by its vapours in equilibrium, consequently there must be a certain difficulty in the transition of a molecule from the crystal lattice to the vapour and vice versa. The present series of quantitative experiments has been made using a rough molecular stream to give thick layers of crystalline deposits on a cooled target in order to obtain in a direct way information concerning the details of the mechanism of steady crystal growth.

Experimental Method.

The essential part of the apparatus is shown in Fig. 1; the whole of it was contained in an outer vessel which was surrounded by liquid air and which could be evacuated. It consisted of a furnace with a small orifice in its lid and a cooled target 2.5 cm. wide situated above the furnace at a distance 2.50 cm. from the orifice. The furnace could be removed and weighed; when it was heated in a vacuum the vapour of the substance in it was emitted from the orifice and a certain fraction of the stream struck the target. In order to use the arrangement to investigate the condensation on the target this fraction had to be known.

As a step towards investigating the nature of this stream, experiments were made with a hollow target fitted with a perforated lid. The ratio of the area of the holes in this lid to the area of its surface was 0.190. If every molecule striking the surface of the target condensed then the

4 Alty, P.R.S., 1937, 161, 68.
ratio of the deposits inside and outside the target should be 0.190, and this occurred with salicylic acid at temperatures below \(-40^\circ\text{C.}\); at these temperatures also the deposit inside the target had the form of sharply defined patches opposite the holes in the lid. At higher temperatures the whole behaviour became irregular and the deposits inside the target diffuse. In the following work it is assumed that all molecules of a vapour reaching a cool enough surface will condense, and that for salicylic acid \(-40^\circ\text{C.}\) is a low enough temperature for the stream densities used.

Experiments with a cold solid target could now be used to investigate the properties of the stream emitted by the furnace for salicylic acid. A series of 21 experiments were made at stream densities of 0.071 to 4.0 mg./min. on the surface area of the target, and the fraction of the molecules leaving the furnace which struck the target was found to be constant and equal to 0.234. A series of five experiments carried out at a stream density below 0.03 mg./min. gave a lower value of 0.224. For a cosine distribution the fraction of the molecules striking the target should be 0.200, hence we may assume that this lower value indicated a tendency to a cosine distribution at the lower rates of emission. All experiments on partial condensation were, however, made at stream densities of 0.1 mg./min. or higher and hence it is the properties of the stream under these conditions in which we are interested. The diameter of the orifice in these experiments was of the order of 1 mm., and the mean free path at the orifice was always small compared with 1 mm. On the other hand, when the molecules reached the target the mean free path had become large compared with 1 cm., and for this reason the deposit was confined to the front of the target and the various lead wires for the heating coils and thermocouples attached to the furnace gave sharp shadows on the walls of the outer tube. Experimentally it was
found that the constancy of the fraction striking the target over a range of stream densities was characteristic of iodine, stannic iodide and mercuric iodide as well as salicylic acid, and only anthracene gave a variable ratio. Finally, it was possible to give a rough quantitative explanation of the constancy of the ratio with the aid of the following assumptions:—

(1) That the point of narrowest cross section of the jet emitted by the furnace is near to the orifice. Hydrodynamic theory indicates that the velocity of efflux is here equal to the velocity of sound in the vapour under the same conditions of temperature and pressure.

(2) That the distance which a molecule had to travel from the orifice before the mean free path became so long that the effects due to collision between the molecules in the stream could be neglected, was so short that it could be assumed that this condition was fulfilled at the orifice itself.

(3) That the distribution of velocities was a Maxwellian one, with superimposed on it a velocity equal to the velocity of sound in the direction of the stream.

With these assumptions the probability that a molecule with a given thermal velocity would have a resultant velocity in such a direction that it would strike the target could be calculated. This probability was then summed over a Maxwellian distribution curve and the ratio of the area of the curve so obtained to the area of the original Maxwellian curve gave the fraction of the molecules striking the target.*

This calculation was carried out in the case of iodine and the result obtained was that the fraction of the molecules striking the target should be independent of the stream density and equal to 0.233. The experimental value was 0.230. Here the agreement is much closer than the approximations in the calculations would lead one to expect; it should be noted that the only property of the substance that is important in the above calculations is (the ratio of the specific heats). In the case of iodine was taken as 1.30, for salicylic acid, however, we should expect that and in this case the ratio striking the target should be 0.220 as compared with the experimental value 0.234. This method of calculation always gives values to the ratio which are constant with stream density and, in accordance with the experimental results higher than that given by the cosine distribution, a fact which gives support to our general picture of the nature of the stream emitted by the orifice. In the case of anthracene, however, the fraction striking the target varied from 0.290 at 0.2 mg./min. to 0.230 at 3 mg./min., these results were not so easily reproducible as with the other substances, but the variation with stream density was always there. It should be noted that in the case of anthracene the molecular weight is of the same order as those of the other substances used but the collision area is much larger; we should therefore expect that collisions in the stream would be more important with anthracene than with the other molecules. Scattering in the beam would account for the decrease in the fraction of molecules striking the target at high stream densities, but the explanation of the high value of 0.290 is not clear.

All these experiments on the fraction of molecules striking the target were made with the target at a sufficiently low temperature to ensure the complete condensation of all the incident molecules.

* Lamb, Hydrodynamics, p. 25.

* A correction had to be applied for the molecules with a resultant downward velocity. For these molecules it could be assumed either that they are not emitted by the furnace and their number subtracted from the stream, or that in reality they move downwards from a point above the orifice so as to strike the lid of the furnace and to be reflected upwards with a cosine distribution. In the case of iodine these two assumptions give the results of 0.235 and 0.231, respectively, so that the difference is unimportant from the present point of view.
Both furnace and target were fitted with heating coils and thermocouples, and with the aid of these it was possible not only to vary the rate of emission of the furnace but also to make measurements at higher temperatures where complete condensation of all incident molecules did not occur. Such measurements were made in the following way:

The target was heated to its appropriate temperature and the apparatus evacuated, the furnace was then heated to the correct temperature, the experiment continued for a suitable period and then stopped by admitting air into the apparatus. A series of experiments for different times but with the same temperature of furnace and target yielded a series of measurements of the deposition of the target all at the same stream density, and from these a curve could be plotted showing the weight deposited on the target as a function of the weight emitted by the furnace as shown in Fig. 2. The relationship obtained was, as would be expected, linear, but the line did not go through the origin; one reason for this was that the deposition of the first layers on the target was not smooth but the subsequent deposition, and it was necessary to cover the target with a thin deposit before making an experiment. This uncertainty at the beginning of the experiments did not affect the results since they were always obtained from the slopes of these lines, which divided by 0.234 (in the case of salicylic acid), give the ratio \( D/v \) where \( D \) was the rate of collection on the target in mg./min.\(^{-1}\) and \( v \) was the amount falling on the target also in mg./min.\(^{-1}\). In all cases these quantities were calculated for the whole area of the target, \( \pi \times 1.25^2 = 4.9 \text{ cm.}^2 \) and mg./min.\(^{-1}\) and they could be reduced to mg./min.\(^{-1}\) cm.\(^{-2}\). Therefore \( v \) could be regarded as a measure of the stream density; it was always obtained from the average of the stream densities of the points constituting a graph such as that shown in Fig. 2.

In addition to these experiments, measurements were also made of the rate of evaporation of a deposit into a vacuum by finding the loss of mass from the target in a definite time. A series of results for this type of experiment is shown in Table I, and the average of several experiments

### Table I. Evaporation Experiments with Salicylic Acid at 7° C.

<table>
<thead>
<tr>
<th>Weight (in mg.) on Target</th>
<th>Time (min.)</th>
<th>Rate of Evaporation mg./min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Expt.</td>
<td>After Expt.</td>
<td></td>
</tr>
<tr>
<td>22.3</td>
<td>13.2</td>
<td>110</td>
</tr>
<tr>
<td>20.3</td>
<td>6.05</td>
<td>135</td>
</tr>
<tr>
<td>14.3</td>
<td>8.9</td>
<td>56</td>
</tr>
<tr>
<td>6.2</td>
<td>4.1</td>
<td>25</td>
</tr>
<tr>
<td>Average ( E = \frac{0.092 \text{ mg.}}{\text{min.}} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Graph showing deposition on target against emission of furnace for salicylic acid. Temperature of target +7° C., furnace 106° C.](image)
will give \( E \) the normal rate of evaporation of a deposit in mg./min. for a target of diameter 2-50 cm.

The estimation of the deposits, which were of the order of 10 mg., was made by titrating in the case of salicylic acid and iodine; for the other substances a target with a removable lid was used and the deposits were weighed.

It will be seen that the measurements above yielded three quantities at a given stream density and temperature \((D, \nu, \text{ and } E)\). It was convenient to define a quantity \( A \), which was called the adhesion ratio, by the relation:

\[
A = \frac{D + E}{\nu}
\]

This adhesion ratio had no direct theoretical significance, but it is a measure of the difficulty of transition from vapour to crystal phase. A high adhesion ratio means that an incident molecule stands a small chance of re-evaporation before it is attached to the lattice or is adsorbed in an energy position not greatly differing from that of a molecule in the lattice.

**Experimental Results.**

In Fig. 3 the adhesion ratios of a number of substances are plotted against \( \log E \). As \( E \) is approximately exponential with temperature, its logarithm serves as an approximate temperature scale for each substance, and for comparing different substances it is more convenient to use a scale of \( \log E \) than a scale of temperature. It will be seen from this figure that as \( \log E \) decreases \( A \to 1 \), and that further, the probability that a molecule striking a crystal surface will fail to condense there does not become appreciable until the probability that a molecule fixed in the crystal lattice will evaporate into the gas phase becomes measurable. The figure does not show the total range temperature variation over which the measurements were made, but it varied between 8° C. for iodine and 30° C. for salicylic acid, and within a temperature range of this order \( A \) always rises sharply to unity from fractional values; this suggests that neither reflection nor elastic collisions with molecules on the crystal surface play an important part in the mechanism of crystal growth. We should hardly expect that either of these processes would be sharply dependent on the temperature of the condensing surface, and it is clear that neither of them can occur at temperatures only slightly below those at which the condensation experiments were made. This evidence is in accordance with the views that have been expressed by...
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others, *e.g.* Eucken, who considered that spectral reflection does not occur from crystal surfaces since the reflected streams are always diffuse. It is assumed in the subsequent discussion that all the molecules striking the surface of a growing crystal are adsorbed in one way or another though they may not necessarily be attached to their appropriate place in the crystal lattice.

**Salicylic Acid.**

It will be seen from Fig. 3 that, of all the substances used, salicylic acid shows the smallest values of $A$ and in particular that with it the fall in $A$ occurs at much smaller values of $E$ than with other substances. Now, only experiments made where $A$ is less than unity are of interest: also if $v$ becomes of the same magnitude as $E$, condensation may cease and evaporation set in, hence in this region steady deposition experiments cannot be made; in general the best results are obtained when $v$ is large compared with $E$. On the other hand, there is an upper limit in the neighbourhood of $v = 3$ mg./min. where the mean free path of the molecules at the target becomes of the order of 2 cm. and hence collisions between target and furnace can no longer be neglected; therefore the range of stream densities in which interesting experiments can be made is $v \sim 3$ mg./min. to $v \sim 2E$. If $A$ does not fall below unity until temperatures are reached at which $E$ is large then the range of stream densities at which experiments can be made is restricted. With salicylic acid, however, this difficulty hardly arises and experiments can be made at $0^\circ$ C. with stream densities of 3.0 to 0.1 mg./min. in all of which partial deposition takes place. Also the temperature range over which measurements can be made is greater than for other substances.

The variation of $D/v$ with log $v$ is shown in Fig. 4, and it will be seen that this ratio is not constant, as it would be if there were a constant condensation coefficient. An explanation of the variation of $D$ with $v$ can be given in terms of the hypothesis of the existence of a mobile layer, but the relationships obtained between these two quantities can be more conveniently illustrated by other figures, which are shown with the theory that we now discuss.

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Theory of Variations with Stream Density.—Crystals of salicylic acid growing under a microscope can be seen growing as needles almost entirely at their pointed ends. They grew into needles of a similar shape under experimental conditions, hence, if there was no surface mobility of molecules adsorbed on the crystal surface, the fraction of the incident molecules which could condense would be extremely low. However, the experimental results give values generally over one half; so that the assumption of surface mobility in an absorbed phase appears to be necessary. We may regard the growing face of the crystal as a number of fixed energy holes into which molecules can fall and out of which they can jump as a result of their vibrational energy. Let the concentration of mobile molecules (i.e. molecules not yet fixed in their final positions in the crystal lattice) on the growing face be $c$ and the concentration on other crystal faces be proportional to $c$. Suppose these molecules react to give bimers, then the rate of formation of such bimers is $k \cdot c^2$.

Let the concentration of these bimers which can dissociate with an energy of dissociation $Q$ be $n$. Then the rate of dissociation is given by $k'ne^{-Q/RT}$. Also if the crystal grows by the adhesion of bimers then rate of growth will be given by $k'n$. Therefore the equilibrium condition for bimers is

$$k \cdot c^2 = k'n \cdot e^{-Q/RT} + k'n.$$

If we now neglect $k'n$ which occurs only on the growing face in comparison with the other two processes which occur on all the faces we may write approximately,

$$n = \frac{k}{R}e^{Q/RT}$$

and hence the rate of crystal growth is

$$K_1c^2e^{Q/RT}.$$

Here it is suggested that the bimerisation takes place in the mobile layer, but the same equation for the rate of growth is obtained if we assume, instead, that the formation of bimers takes place when the molecules attach themselves to the crystal surface. The essential point is that molecules in the mobile layer cannot start to behave as part of the crystal until they have been attached in pairs.

Therefore $D =$ measured rate of deposition

$$= \text{rate of growth} - \text{rate of loss from crystal}$$

$$= K_1c^2e^{Q/RT} - K_2e^{-X/RT} - K_3e^{-Y/RT} \quad \ldots \quad (1)$$

where $K_2$ and $X$ refer to the transition from a fixed position in the crystal lattice to the mobile layer, and $K_3$ and $Y$ refer to the transition from a position in the lattice to the vapour directly.

On the other hand, since the concentration of mobile molecules on different crystal surfaces is assumed to be in a constant ratio, the rate of evaporation from the mobile layer and the crystal is given by:

$$v - D = K_4e^{-Q'/RT} + K_5e^{-Y/RT} \quad \ldots \quad (2)$$

where $Q'$ is the energy of absorption into the mobile layer of a molecule from the vapour. Now for salicylic acid at $0^\circ$ C., the rate of normal evaporation is only 0-03 mg./min., hence the term $K_5e^{-Y/RT}$ cannot be
greater than this and actually should be much less. Also Neuman\(^7\) has shown theoretically that if a mobile layer plays a part in crystal growth then very few molecules will pass directly into the vapour phase without first passing through the mobile layer.

If we neglect this direct transition from the crystal to the vapour then, by eliminating \(c\), the concentration in the mobile layer about which we know little, the relationships (1) and (2) can be reduced to the form

\[
D = k_1(\nu - D)^2 \cdot e^{\frac{Q + 2Q'}{RT}} - k_2 e^{-\frac{X}{RT}}.
\]

This is a theoretical equation describing the growth of crystals of salicylic acid.

Equation (3) can now be applied to the experimental results. If we take the values of \(D\) at different stream densities for the two temperatures \(0^\circ\) C. and \(7^\circ\) C. we can plot \(D\) against \((\nu - D)^2\) and so get the two straight lines shown in Fig. 5 in which the points for \(\nu = 0\), i.e. when \(D = -E\), are included.

The fact that straight lines can be obtained in this way shows once again that any attempt to describe the condensation of salicylic acid in terms of a single condensation coefficient is unsatisfactory. In fact the condensation coefficient \(f\) as defined by Alty\(^4\) can be expressed in terms of the above symbols as \(f = E/v_{eq}\) where \(v_{eq}\) is the stream density falling on a crystal surface that is surrounded by its vapour at equilibrium. The values of \(f\) so obtained (at \(0^\circ\) C.: 0·54; at \(7^\circ\) C.: 0·56) are less than unity though rather higher than the value of 0·29 found by Alty in the case of benzoic acid.

From the ratio of the slopes of the lines at \(0^\circ\) C. and at \(7^\circ\) C. we obtain \(Q + 2Q' = 22·900\) and from the intercepts * on the \(D\) axis we get

\[\text{Fig. 5.—Graph of } D \text{ against } (\nu - D)^2 \text{ for salicylic acid at } 0^\circ \text{C. and } 7^\circ \text{C.}\]

\[0^\circ \text{C. and } 7^\circ \text{C. we can plot } D \text{ against } (\nu - D)^2 \text{ and so get the two straight lines shown in Fig. } 5 \text{ in which the points for } \nu = 0, \text{ i.e. when } D = -E, \text{ are included.}

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\[\text{7 Neuman, Z. Elektrochem., 1938, 44, 474.}\]

\[\text{* The ratio of the intercepts is, of course, not so accurate as the ratio of the slopes, but it can be obtained much more accurately than Fig. } 5 \text{ would suggest by plotting out the points nearest to the origin on a larger scale. The percentage errors do not vary very greatly over the different points on these lines.}\]
$X = 24\,000 \text{ cal.}$ Since $X$ refers to the energy of transition from a fixed point in the lattice to the mobile layer we should expect it to be less than the latent heat of sublimation; actually it is rather greater since the latent heat is measured by Hirsbrunner 8 is only $19\,500 \text{ cal.}$ This is probably due to the molecules jumping from the lattice into the mobile layer in pairs.

**The Variation with Temperature.**—All the experimental evidence in support of equation (3) has so far been taken from measurements of the condensation of salicylic acid at different stream densities at the two temperatures of 0° and 7° C. In addition to these results it is also possible to make experiments at other temperatures which give values of $E$ and $D/\nu$ at a stream density of 3 mg./min., and hence we can derive values of $A$ at these other temperatures. Such a curve showing the variation of $A$ with temperature is plotted in Fig. 6, curve I. If we now make use of the energies of transition found from the measurements at 0° and 7° C. it is possible to calculate values of $D$ at other temperatures.

![Fig. 6.—Adhesion ratio for salicylic acid against temperature.](image)

Curve I. Observed values with $D/\nu$ for comparison. Curve II. Calculated Curve.

and to obtain a calculated curve showing the variation of $A$ with temperature (see Fig. 6, curve II), the two points at 0° and 7° C. being of course the same for curves I and II. The agreement between these two curves is not quantitatively accurate but they both have the same form. One interesting point may be noted: at 24° C. two experimental values of $A$ were obtained, one near $\nu = 2 \text{ mg./min.}$ and the other near to $\nu = 4 \text{ mg./min.}$; under these conditions it is the higher stream density which gives the lower value of $A$—quite the reverse of what occurs at lower temperatures; this reversal also occurs in the calculated points.

**The Crystal Structure of Salicylic Acid.**—These experimental results may be taken as supporting the bimolecular hypothesis as far as the growth of crystals of salicylic acid is concerned, and it seemed possible that some bimolecular arrangement would be present in the crystal structure. Salicylic acid was therefore examined by Mr. G. Knott of the Crystallographic Laboratory, Cambridge, who found, on the basis of a packing model, that the molecules were probably packed together in pairs as is common with other carboxylic acids. He also showed that these double molecules lay in planes inclined at an angle of 40-50° to the $c$ axis. There were four molecules to the unit cell.

The Size and Shape of Crystals.—The crystals deposited on the target consisted of a felt of small needles, whose size was larger at high than at low temperatures. This is in agreement with the results obtained by G. Haas, who found that the size of crystals for deposits of silver and antimony was larger in the case of deposits formed at high temperatures than with those formed at low temperatures. In the case of the deposits of salicylic acid there was no well-defined variation of crystal size with stream density.

Finally, we may note that the growth of crystals of salicylic acid may be observed under a microscope with a hot stage arrangement and the growth takes place almost entirely at the ends of the needles, on a face inclined at an angle of approximately 40° to the long c axis. Under these conditions crystals 5 mm. long and 1/50 mm. wide can easily be grown.

Mercuric Iodide.

This substance gave particularly satisfactory deposits in which the crystals were closely packed together and gave excellent microphotographs, from which three clear conclusions can be drawn.

1. The crystals formed at higher temperatures are larger than those formed at lower temperatures.
2. There is a marked change in crystal size with stream density, the crystals formed at low stream density being much larger than those formed at a high stream density.
3. There is an effect whereby a deposit consisting of large crystals, when it is allowed to evaporate into a vacuum, as in the measurement of \(E\), breaks up into very small crystals.

In the quantitative condensation experiments the ratio of the molecules striking the target was 0.220; however, the mercuric iodide had a tendency to react with the copper of the furnace lid to give a scale of mercuric iodide round the orifice and if this scale was allowed to accumulate then the ratio of the molecules striking the target had a tendency to rise. A reference to Fig. 3 will show that \(A\) falls below unity at a lower value of \(E\) than is the case with the other inorganic substances.

Here it is best to consider the changes in the number of molecules evaporating from the surface with changing stream density, i.e. the curve showing the variation of $(v - D)$ with $D$ as is shown in Fig. 7. The characteristic aspect of these curves is that a certain value of $(v - D)$ must be reached if there is to be deposition and this quantity is not exceeded at high rates of deposition. This means that at a given temperature the deposition curve is influenced by two definite quantities, viz. $E$ or $-D$ when $v = 0$, and $(v - D)$ for steady deposition. These two quantities can be plotted as a logarithmic curve against the reciprocal of the absolute temperature (see Fig. 8) and in this way two straight lines are obtained which correspond to energies of 22,500 and 20,400 cal. for $E$ and $(v - D)$ respectively.* The heat of vaporisation of red mercuric iodide which was the form in which all the deposits occurred is given as 20,100 cal. by Shibata and Niwa;** by extrapolating the vapour pressure measurements of these authors we can find the value of the

![Image](https://example.com/image.png)

**Fig. 8.—Logarithms of $(v - D)$ and $E$ against the reciprocal of the absolute temperature of mercuric iodide.**

Alty condensation coefficient for mercuric iodide, and at 27° C. this comes out at 0.61 and is thus in agreement with the value of 0.53 obtained by Metzger and Miescher.† This shows us that the vapour pressure curve cuts the vertical part of the $D$, $(v - D)$ curves shown in Fig. 7 near the top, in this case therefore we should expect that a crystal of mercuric iodide should grow steadily in its supersaturated vapour. This was shown to be the case by some experiments similar to those carried out by Volmer and Schultze‡ which showed that a crystal of mercuric iodide is quite stable in the form $E$ or $-D$ when $v = 0$, and $(v - D)$ for steady deposition. These two quantities can be plotted as a logarithmic curve against the reciprocal of the absolute temperature (see Fig. 8) and in this way two straight lines are obtained which correspond to energies of 22,500 and 20,400 cal. for $E$ and $(v - D)$ respectively.* The heat of vaporisation of red mercuric iodide which was the form in which all the deposits occurred is given as 20,100 cal. by Shibata and Niwa;** by extrapolating the vapour pressure measurements of these authors we can find the value of the

* A possible explanation of the above phenomena would be that the molecules striking a crystal of red HgI$_2$ go through a surface phase similar to the unstable yellow form. If this was so, then we should expect that the two lines should cut at a temperature of 127° C. the transition point of red to yellow mercuric iodide. Actually they cut at 110° C. and the difference between this temperature and the transition point is well within the experimental error. The disadvantage of this view is that the ratio $(v - D)/E$ is certainly above 2 at 27° C. and this requires an energy difference of 2,000 cal. if the two are to be the same at 127° C.; the heat of transition of red to yellow mercuric iodide is only 600 cal. (Steiner and Johnson, J. Physic. Chem., 1928, 32, 912).


‡ Metzger and Miescher, Nature, 1938, 572.

‡ Volmer and Schultze, Z. physik. Chem., 1931, 156.
iodide could grow steadily in its vapour which was supersaturated to the extent of 0.43 °C., the experiments being made at a temperature of 100 °C.

**Anthracene.**

Some experiments were also carried out on anthracene, which yielded $D$, $(\nu - D)$ curves of exactly the same type as those shown in Fig. 7. In the case of anthracene the ratio of $(\nu - D)/E$ for the maximum value of $(\nu - D)$ was near to 3 instead of 2 as is the case with mercuric iodide, and consequently anthracene gave lower values of $A$ than did mercuric iodide. The energies obtained from two such curves for anthracene were within the experimental error equal to 17,000 cal., the heat of sublimation.

**Discussion of the Experiments on Mercuric Iodide and Anthracene.**

The interpretation of these experimental results is open to considerable doubt, and it is probable that the results by themselves are not sufficient to form the basis of a complete theory. It is, however, possible to explain them if we assume that thick layers of disarranged molecules are built up on the surface of a crystal on which deposition is taking place. As soon as these layers become thick any increase in the stream density does not affect the condition of the surface or the rate at which molecules will evaporate from it; on the other hand, when a crystal is evaporating the surface exposed to the vacuum is not covered by these thick disarranged layers and consequently the rate at which molecules are given off is lower. A thick layer hypothesis will also cover the decrease in crystal size with increasing stream density observed with mercuric iodide, since at high stream densities the layers will be thicker and consequently the chances that a new crystal germ will be formed will be greater for a given area of crystal surface than would be the case for a thinner layer.

**Stannic Iodide and Iodine.**

The fraction of molecules striking the target was for iodine 0.230 (average of 30 experiments) and for stannic iodide 0.234 (average of 7 experiments).

The curves showing the variation of $A$ with log $E$ for these substances are shown in Fig. 3. It will be seen at once that in these cases $A$ does not start to fall appreciably below unity until very high values of $E$ are reached. To put this in another way, the number of vapour molecules leaving a crystal surface is hardly increased when deposition takes place. This is best shown by comparing the figure of $(\nu - D)$ at $\nu = 3$ mg./min. with the measurements of $E$.

In the case of iodine we have:

| $(\nu - D)$ | $-44.4$ °C. | $-46.8$ °C. | $-52.6$ °C. |
| $E$ | 1.62 | 1.17 | 0.28 mg./min. |
| | 1.23 | 0.87 | 0.27 mg./min. |

Since the technique of the experiment is essentially based on the measurement of differences in $(\nu - D)$, few definite conclusions can be drawn when no considerable variations in $(\nu - D)$ can be recorded.
With stannic iodide measurements were carried out at two different stream densities at a temperature of 7° C.

<table>
<thead>
<tr>
<th>ν</th>
<th>D (−E)</th>
<th>(ν − D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.60</td>
<td>2.28</td>
<td>0.32 mg./min.</td>
</tr>
<tr>
<td>0.51</td>
<td>0.21</td>
<td>0.29 „</td>
</tr>
<tr>
<td>0</td>
<td>0.25</td>
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</tbody>
</table>

The fact that the number of molecules evaporating from the crystal surface is almost invariant with stream density suggests that a molecule striking the crystal surface is quickly adsorbed in a position where its energy state is much the same as that of a molecule attached to the lattice. This may be connected with the symmetrical character of the iodine and stannic iodide molecules, the result of which is that though these molecules may behave in a similar way to mercuric iodide and anthracene, they are able to arrange themselves much more easily into positions appropriate to the crystal lattice.

**Summary.**

Measurements are made on the rate of growth of a crystal mass from a vapour stream of known density. It is shown that in no case can the results be explained on the basis of a constant condensation coefficient. With salicylic acid the experiments are explained by a bimolecular process occurring in a mobile surface phase and this is in agreement with the crystal structure. Measurements are also made with mercuric iodide, anthracene, iodine and stannic iodide, and the results obtained with these substances suggest that thick layers of disarranged molecules may be built up on the surface of growing crystals.

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