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AGGREGATION AND FLOW OF SOLIDS

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AGGREGATION AND FLOW OF SOLIDS

BEING THE RECORDS OF AN EXPERIMENTAL STUDY OF THE MICRO-STRUCTURE AND PHYSICAL PROPERTIES OF SOLIDS IN VARIOUS STATES OF AGGREGATION

1900–1921

BY

SIR GEORGE BEILBY, F.R.S.

MACMILLAN AND CO., LIMITED
ST. MARTIN'S STREET, LONDON
1921

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PREFACE

THE observations recorded in the following pages filled all my spare hours most pleasantly for many years. It must be admitted, however, that their preparation for publication was always regarded as the least attractive part of the work, except in so far as it secured the friendly criticism and encouragement of other workers. I gladly acknowledge in this respect my indebtedness to the late Lord Rayleigh, Sir William Roberts-Austin, and Mr. F. H. Neville, as well as to Sir Joseph Larmor. To Mr. J. E. Barnard my special thanks are due for his valuable criticism and guidance in all that relates to microscopic technique.

As my main purpose was to follow up the experimental study of matter in the solid state on the lines which I had myself initiated, I had not time to keep in touch with the application of the results of this study to the current problems of metallurgy, though some of the more obvious of these applications were developed in published papers, *e.g.* "The Hard and Soft States in Metals," "The Polishing of Metals and other Substances," and "The Disintegration of Metals under Alternating Stresses."

One result of this course has been that the bearing of these observations on current metallurgical problems has occasionally been misapprehended or altogether missed by other workers.

About two years ago it was represented to me by Sir Herbert Jackson that the more fundamental bearing of

this work had not been recognised in quarters where it would have been of value, and he cited particular instances within his own knowledge in which new researches were being carried out in apparent ignorance of the experimental evidence obtained, and of conclusions which had already been reached by me. He therefore urged that these observations should be put together and presented as a consecutive whole. Owing to the pressure of other duties, it would have been impossible for me to undertake this task single-handed; but, as Sir Herbert was good enough to promise his personal help, and as he was further able to enlist the assistance of Mr. W. D. Haigh, who was prepared to devote a considerable proportion of his leisure time to the collection and arrangement of the existing materials, the work was begun at the end of 1919.

Mr. Haigh had access not only to all my published papers, but to all the original experimental and other notes, as well as to a large collection of photo-micrographs, many of which had not been published. He has, in addition, repeated for himself a number of the experimental observations, and certain new photo-micrographs made by him have been reproduced in Plates XXII. and XXXIV. He took up the work of compilation with enthusiasm and discrimination, and nine months ago it had reached the stage at which its final arrangement in due proportion and perspective could be considered. To this part of the work all my leisure has been devoted for the last few months, always of course in full co-operation with Sir Herbert Jackson and Mr. Haigh. I desire here to record my gratitude to Sir Herbert Jackson, whose promise of help has been most generously fulfilled, and to Mr. Haigh for his untiring devotion to the work. I can unhesitatingly say that without his constructive skill and insight the work could not have been accomplished.

The narrative has necessarily two sides—it is a record

of actual experimental observations, and it sets forth the conclusions reached as to the meaning of the observed phenomena. These conclusions, as they are now presented, are the result of the more mature consideration which has been given to the subject as a whole during the past year. For any readers who are interested in the origin and development of these views, the list of my published papers on this subject may be useful for purposes of reference, though the main facts and figures on which the papers were based are for the most part reproduced in the following pages.

Twenty years ago the electron theory was in its infancy, and we were almost entirely ignorant of the structure of the atom. No attempt had been made at that time to picture the atom, with its nucleus and electron rings, as an entity of definite form and structure. The atom was generally regarded as a minute particle separated from neighbouring atoms by distances which were enormously large in comparison with the dimensions of the atom itself.

During recent years, however, the X-ray examination of crystals has shown unquestionably that atoms are space-filling entities which can be built up into solid aggregates, constituting matter as we know it.

The latest knowledge of crystal structure is in accordance with the view that the atom is a structure of definite size and shape which behaves in effect as an elastic solid. This view has guided my own observations and conclusions from the outset. There appear to be good grounds for the expectation that the further work of Sir William Bragg, Professor W. L. Bragg, and other physicists, will throw new light on the structure of solids not only in the crystalline, but also in the strained or vitreous state.

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See PLATE I.

SECTION I

MICROSCOPIC METHODS AND MEASUREMENTS

Introductory

WITHIN the last half-century a complete science of micro-metallurgy and metallography has grown up, and the minute structural changes which take place in metals and in alloys have, through the reproduction of photo-micrographs, become familiar to students and to readers who have never themselves used the microscope. It is important that the general methods of microscopic research, particularly with regard to illumination, should be understood, in order that the observations to be discussed in what follows may be rightly interpreted. These will, therefore, be briefly described.

Transmitted Light

In the study of rocks and minerals, which are as a rule comparatively transparent, it is usual to examine the specimens by light transmitted by reflection from a mirror beneath the stage, and passing through a lens which condenses it on the object placed on the stage.

Reflected Light, Normal and Oblique

For the examination of opaque objects it is obvious that transmitted light is not available. The alternatives

are to illuminate by normally reflected or by obliquely reflected light. The former is obtained by focussing the image of the illuminant on a small reflecting prism or on a thin parallel plate of glass, placed at an angle of 45° with the optical axis, within the tube of the microscope. The rays falling on the prism or mirror are reflected downwards, and passing through the lenses of the objective are focussed on the specimen, forming a critical image of the illuminant in the centre of the field. With the thin parallel glass plate set at 45° with the optical axis there is a considerable loss of light, owing to the fact that the rays entering the tube of the microscope and falling on the glass plate are partly transmitted by it and partly reflected downwards through the objective on to the surface of the specimen. These latter rays are reflected back through the objective and again pass through the glass plate. In so doing they are in part reflected and in part transmitted, the transmitted portion only reaching the eye.

For the prism illuminator the glass plate is replaced by a small right-angled prism, which gives total reflection. Owing to this it is necessary that the prism should not occupy more than one-half of the area of the microscope tube, as otherwise it will prevent the light reflected from the surface of the specimen from reaching the eye. Of these two forms of illuminators the first is to be preferred, as although it does not give so intense an illumination, it is less liable to produce false or distorted images, and is more efficient in rendering fine detail than the prism method, where only a part of the objective is illuminated.

By the vertical method of illumination there is evidently no limit to the nearness of the objective to the surface of

the specimen, and lenses of the highest resolving power can be used under the most favourable conditions. For this reason, illumination by normally reflected light has been almost universally employed in micro-metallurgy, obliquely reflected light being generally reserved for examination at low magnifications.

Oblique Reflected Light as a Test of Polish

In the examination of opaque objects by reflected light the image which reaches the eye must be produced by rays reflected from the surface of the object. If this surface is perfectly smooth and flat, the only reflected rays which will reach the eye of the observer are those which have struck the surface of the object normally within the field of vision. If no such rays are present the field will appear absolutely black and featureless. Illumination by an intense oblique pencil of light, with the exclusion of all other sources of light, is then an absolute test of the liquid-like smoothness of any given surface. On the other hand, any departure from the perfect blackness of the field shows either that the surface is not perfectly smooth and continuous, or that it is not perfectly opaque. Surface irregularities in an opaque material act as minute reflecting surfaces which deflect some of the incident rays into the optical axis and enable them to reach the eye of the observer. If the material is not perfectly opaque, or if it is covered by a translucent layer, the obliquely incident rays are not completely reflected, when a portion will penetrate below the surface and may give rise to its general illumination either by internal reflection or by refraction.

Discovery of New Features of Surface Structure by the use of Oblique Light

At the outset of these studies the puzzling appearances presented by reflecting surfaces, which were also partly translucent, were forced on my attention, and it was only after long continued observations on metal and other surfaces, and on films prepared in a variety of ways and under varied conditions of illumination, that the structural significance of these appearances was discovered. It was in this way that certain features of the surface structure of solids, which had hitherto escaped the notice of other observers, were proved to be real.

Oblique Illumination must be specially adapted to each of the three Purposes for which it can be used

For the most effective use of oblique illumination it must be recognised that there are three distinct purposes to which it may be applied, to each of which the illumination must be specially adapted. If the purpose is to obtain a magnified but undistorted picture, in which natural lights and shadows bring out the modelling of the surface, the illumination must not be derived from a small source of light, the image of which is focussed on the object by a condenser or reflector, but from a large dead-white reflecting surface or from a bright sky. If a condenser is used it should be placed so as to throw a broad unfocussed beam of wide angle all over the surface of the object. In this way fractures and roughened surfaces are faithfully presented. As this form of illumination can only be applied when lenses of fairly large working distance are

used, the limits of resolution and magnification are relatively moderate.

The 16 mm. apochromat of 0·3 N.A. is the lens of highest resolving power which fulfils the necessary conditions. Its working distance is 8 mm. and this just leaves room for a beam of sufficiently wide angle to reach the field on the surface of the object. With this lens the picture shows little or no signs of breaking down at a magnification of 250, and in special cases may be further magnified without serious damage to its general features.

Many unsuccessful attempts were made to use the 12 mm. apochromat of 0·65 N.A. for this purpose, but the angle of the illuminating beam was much too acute, owing to the very small distance between the front lens and the surface of the object, and the pictures produced were an unintelligible mass of diffraction patterns.

In the case of translucent films, by the use of transmitted light, obliquity over a wide range can be secured, while lenses of the highest resolving power can be used.

The other purpose for which an oblique beam of light can be used is for the detection of the presence of surface irregularities on an otherwise smooth reflecting surface. By focussing the critical image of a minute, intense source of light on the centre of the field, irregularities only a few molecules in thickness give a pattern built up of diffraction discs. At low magnifications and with moderate intensity of illumination the texture of the surface which is disclosed may bear a more or less close resemblance to the structure which is disclosed by normally reflected or transmitted light with lenses of high resolving power, but when the critical image of the sun or of an electric arc is used, the

appearances obtained must be taken simply as an indication that a structure of some sort is present.

Closely related to the foregoing use of oblique illuminates by the critical image of the source of light is its use for the detection and observation of particles suspended in a transparent liquid. For example, the formation and behaviour of the delicate clouds formed by the meeting of extremely dilute solutions of two reagents, which produce a solid precipitate at the surfaces at which they touch, can be followed with ease. In this way particles and films can be examined which are too thin to be seen by transmitted light. This use is referred to in Section III., in dealing with the formation of solid aggregates.

The " Ultra Microscope " of Siedentopf and Szigmondy was described some years after the above method was first used in my observations.

Positive and Negative Pictures of the same Object obtained by Normal and Oblique Light

It should be remembered that the images produced by normally reflected and by obliquely reflected rays are as negative to positive. The lights of one are the shadows of the other and vice versa. Figs. 5 and 6 are photomicrographs of a surface of frosted silver on which a burnisher mark has been made. On both a certain amount of light is scattered by the general surface, but where the burnisher has pressed the irregularities into a smooth reflecting surface, the blackness under oblique and the brightness under normal rays are well seen. In the latter case, if the surface is not uniformly flat, those parts which are at an angle will reflect the rays outside of the micro-

scope and will be seen as black patches. If oblique rays are turned on an undulating or rippled surface the different parts will appear light or dark according to the particular angle at which they receive the incident rays. If the surface under examination is not perfectly smooth, but has some texture sufficiently fine to scatter the incident rays instead of reflecting them unbroken, it will appear light both by normal and oblique rays; but each light will develop its own appearance of texture as the rays reflected into the microscope by the two kinds of illumination can never give identical pictures.

When the surface is not absolutely opaque the effects of refraction and absorption will affect the appearance by the two kinds of illumination. General absorption of light of a particular wave-length will colour the picture.

The microscopic images produced by rays transmitted through a transparent or a translucent specimen result partly from the total or partial absorption of the rays and partly from their refraction. In interpreting photomicrographs it should be remembered that all these factors are concerned in the production of the picture.

Resolving Power of the Microscope

Though expert microscopists are thoroughly familiar with the fundamental distinction between magnification and resolving power, this knowledge is far from general; it is therefore desirable to refer briefly to this distinction in its bearing on all attempts to follow the minute structure of matter to its furthest visible limits.

The refinement and accuracy of the picture presented to the eye of the observer or recorded on the photographic

plate depends primarily on the lenses of the objective. The refinement of detail is determined by the angle of the cone of rays which enters the front lens and emerges from the aperture of the back lens of the objective. The wider this aperture the greater is the resolving power of the lens. The relative resolving powers of lenses are expressed by their numerical apertures. Numerical aperture is defined as the sine of half the angle of aperture multiplied by the refractive index of the medium between the front lens of the objective and the object. For a certain N.A. the maximum resolution which is possible can be stated, though in any given objective it does not necessarily follow that this maximum will be reached in practice. The magnification of the microscopic picture depends first, on the focal length of the objective; second, on the distance from the objective to the eyepiece, referred to as the tube length, which, however, is fixed for any given objective; and third, on the magnifying power of the eyepiece. The image produced by the objective can therefore be magnified to any desired extent, but this magnification adds nothing to the detail of the picture. Its legitimate use is for the purpose of making the details more easily apprehended by the eye of the observer. If the magnification is pushed too far, the details lose sharpness and the picture becomes "woolly." The resolving power of the lenses used in these observations is referred to in the description of Plate I.

Range of Molecular Attraction and Measurement of Magnitudes

Throughout the paper it will be necessary to refer to magnitudes which are far removed from our everyday

standards. The stage on which the activities of the solid molecules are displayed is bounded on one side at least by the somewhat narrow limits of the molecular attractions.

The arguments to be here advanced are mainly founded on microscopic observations, in many of which the resolving power of the most modern lenses has been pushed to its utmost limit. It will therefore make for clearness if at the outset we pass briefly in review the state of existing knowledge as to the size of solid and liquid molecules and the range of their attractions.

For the clear marshalling of the facts relative to the range of the molecular forces we are indebted to Sir Arthur Rücker, who, in his brilliant lecture before the Chemical Society in 1888, brought together all the best and most trustworthy observations on this subject by the ablest physicists. After careful criticism and argument the results of these observations are summarised in the form of a table, which now forms an invaluable standard of reference for all enquiries on this subject (*Chem. Soc. Journal*, 1888, liii. p. 260).

$\mu\mu$.		
118	Superior limit to ρ.	Plateau and Maxwell.
96-45	Range of unstable thickness begins.	Reinold and Rücker.
59	Superior limit to ρ.	Plateau.
50	Magnitude of ρ.	Quincke.
12	Range of unstable thickness ends.	Reinold and Rücker.
12	Action of silver plate on phase of reflected light alters.	Wiener.
10·5	Thickness of permanent water film on glass at 23° C.	Bunsen.
4-3	Mean distance between centres of nearest molecules in gases at 760 mm. and 0° C.	O. Meyer.
3-1	Thickness of metal films which polarise platinum.	Oberbeck

$\mu\mu$.		
1-0·02	Thickness of electric double layer.	Lippmann and Oberbeck.
0·2	Smallest appreciable thickness of silver film.	Wiener.
0·14-0·11	Diameter of gaseous hydrogen molecule.	O. Meyer and Van der Waals.
0·07-0·02	Mean distance between centres of nearest liquid molecules.	W. Thomson.
0·02	Inferior limit to diameter of gaseous molecule.	W. Thomson.

From this table it will be seen that the superior limit ρ, the radius of molecular attraction, is given by Plateau and Maxwell at 118 $\mu\mu$, and by Plateau and Quincke at 50 and 59 $\mu\mu$. The diameter of the gaseous molecule is given by Exner, O. Meyer, and Van der Waals at 0·11 to 0·14 $\mu\mu$. In an earlier part of the same lecture Lord Kelvin's conclusion is referred to, in which he calculates the diameter of the molecules of Zn and Cu to be probably at least 0·1 $\mu\mu$.

These early estimates of the diameter of molecules have been superseded as a result of the work of recent years. They are, however, retained here as they indicate the state of knowledge at the time when my active interest in the minute structure of solids began.

In the step-by-step exploration of the polished layer on a cleavage plate of calcite, which is described in Section V., the diameter of the calcite molecule was taken as ·31 $\mu\mu$. Professor W. L. Bragg has been good enough to send me the following reply to an inquiry as to the probable dimensions of the $CaCO_3$ molecule as determined by X-rays.

In the crystal structure of calcite, as determined by X-rays, there is apparently no molecule of $CaCO_3$. The structure consists of two kinds of groups, calcium ions, with a double positive charge, and CO_3 ions, with a double negative charge. Each calcium ion is surrounded by six CO_3 groups which are equidistant from it

and vice versa, so that one cannot pair the oppositely charged ions into molecules. One cannot therefore say that the $CaCO_3$ molecule has a definite size as a unit isolated from other molecules. Some dimensions of the crystal structure are:

Distance between centre of calcium atom and centre of CO_3 group . . . . = 3·19 Åu.
(1 Åu. = 10-8 cm.)
Distance between centres of oxygen atoms and carbon atom . . . . . = 1·24-1·30 Åu.
Distance from centre of calcium atom to centre of oxygen atoms, which are its nearest neighbours in the crystal structure . . . . = approx. 2·40 Åu
Distance between successive planes parallel to cleavage face 100 of calcite . . . = 3·030 Åu.

To remove one complete sheet of molecules from the 100 face a solvent would therefore have to dissolve away 0·303 $\mu\mu$ from this face.

In the diagram, Plate I., an attempt has been made to show these and similar magnitudes in their inter-relation by means of a drawing to scale.

The scale used is an unusually large one; it is approximately as 1 : 100,000, that is to say, the objects represented on the diagram are magnified 100,000 times. Take for instance the thickness of a gold leaf, which is about $\frac{1}{280,000}$ of an inch. Its representation on the diagram measures about three-eighths of an inch. Even on this exaggerated scale a single molecule if drawn would be so small as to be quite invisible. The unit of measurement used in the diagram is the micro-millimetre, or the one-millionth part of a millimetre: this is generally written as $\mu\mu$ or as 10^{-6} mm. The advantage of this unit is that it is equally convenient for the expression of microscopic or of molecular dimensions. On the diagram beginning on the left there is a scale of micro-millimetres divided into tens and hundreds; next to this are three bars which represent on the same scale the wave-lengths of mean red, mean green, and

mean violet lights respectively. The centre of the diagram is occupied by a series of seven sections all on the same scale, of leaves or films of thicknesses varying from 1 $\mu\mu$ up to 360 $\mu\mu$. With reference to the three black bars on the extreme right, these represent, still on the same scale, the resolving power of three lenses with which some of the photo-micrographic illustrations were made. The numbers placed at the lower end of the bars are the numerical apertures of the lenses. Taking the third of the series, which is marked as having a numerical aperture of 1·4, its length is about 150 $\mu\mu$. This means that if two lines were ruled on a glass plate 150 $\mu\mu$ apart, they would be seen as two distinct lines by means of this lens. With either of the other two lenses the two lines would merge into one, as the lens would fail to resolve them.

The diagram shows at a glance that an object may be visible to the unaided eye even though one of its dimensions is far below the range of microscopic resolution. For example, the thickness of a gold leaf is about 90 $\mu\mu$, that is to say it is 60 $\mu\mu$ below the resolving power of the lens of 1·4 N.A. Yet we can see the surface of the leaf with the unaided eye, and can examine it microscopically without difficulty. But if we try to see the edge of the leaf we shall fail, for instead of the real edge we shall see an ill-defined line, the apparent width of which will entirely depend on the aperture of the lens used. With the 1·4 lens the apparent width will be 150 $\mu\mu$, with the 0·65 it will be 300 $\mu\mu$, and with the 0·3 it will be 700 $\mu\mu$.

The obvious lesson from this is, that in using the microscope in this region of micro-dimensions we must be careful to keep its limitations and their possible effects always in mind.

SECTION II

SURFACE TENSION FORMS IN LIQUIDS AND SOLIDS

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SECTION II

SURFACE TENSION FORMS IN LIQUIDS AND SOLIDS

Surface Tension Forms in Liquids

For a clearer understanding of the aggregation and surface structure of solids it will be well to refer at this stage to surface tension in liquids, and to certain structural forms which result from it, known as surface tension forms.

Surface tension in liquids is that property in virtue of which a liquid surface behaves as if it were a stretched elastic skin, which completely encloses the mass of liquid within it. The behaviour of this skin has sometimes been likened to that of a thin sheet of india-rubber, and up to a certain point this analogy may no doubt be helpful, but it completely breaks down in one important particular. The contractile force of the rubber skin is not constant, but beginning at zero for the unstretched sheet, it increases as the surface is stretched. In the liquid skin, on the contrary, the contractile force per unit area is constant, not only under all increases of its area by stretching, but also under all decreases by contraction down to the point at which the range of molecular attraction is reached. As the area is increased by stretching, additional molecules pass from below the surface and take their places in the skin. As it decreases, molecules pass from the skin into

the interior, where their attractive force is balanced by that of the surrounding molecules, and they become neutral so far as surface tension is concerned. This idea of an almost indefinitely contractile skin, if once firmly grasped, supplies a clue which enables us to understand the varied and often strikingly unlike forms which result from surface tension in liquids, and as will be shown later in the more minute aggregation of solids also.

In any moderately large mass of liquid the force of gravity keeps the surface horizontal and flat, but when the force of gravity becomes small as compared with the contractile force of the surface skin, as it does when the mass of liquid is very small, the contractile force begins to overpower the gravitational force, and the surface becomes convex. As the mass is further decreased the convexity of the surface increases, till a point is reached at which the whole mass becomes spherical, this being the form in which perfect equilibrium of the skin is reached. The soap-bubble, the raindrop, the dewdrop, the leaddrop, and mercury globule all assume the spherical form under this influence. The effects of gravity and surface tension on small liquid masses can be very conveniently studied in the case of mercury, because mercury can lie on most surfaces without wetting them. If the mass of mercury is sufficiently small, it is perfectly spherical. As the mass is increased the side of the sphere which rests on the supporting surface is slightly flattened; as the mass is further increased the whole sphere is flattened, but the surface still remains convex; but a point is reached at which gravity so completely overpowers surface tension that a truly flat upper surface is developed.

Oil Film on Water

When an oily liquid is allowed to spread on the surface of water a new element requires to be considered. If the oily layer is of sufficient depth the force of gravity will be in the ascendant and the upper surface of the layer will be flat and parallel with the water surface. But if the thickness of the oily layer is sufficiently reduced, the effect of gravity practically disappears, and surface tension becomes the main controlling force. Now it is not alone the surface tension of the oil which must be considered, but also that of water. The latter acts normally to the surface, and its general tendency is, therefore, in the same direction as that of gravity, namely to draw the oil over the water surface in a uniform layer. As the thickness of the oil film is reduced the equilibrium between the surface tension of the water and that of oil becomes unstable, and a state is reached in which the oil is partly pulled over the surface of the water by the surface energy of the water, and partly drawn up into drop-like forms by its own contractile energy. This condition of instability lasts for a considerable time, during which the forms assumed by the oil film are both interesting and beautiful.

Sequence of Typical Forms

When a water surface is touched with a needle which has been dipped in an oily liquid, a film shoots out over the surface in all directions. At first this film appears quite continuous, but presently it becomes punctured all over with small round holes caused by the retraction of the oil under the contractile force of its own skin. As the retrac-

tion proceeds the holes become larger and the film between them becomes thicker. The larger holes as they extend their area swallow up the smaller holes which they encounter in their extension. As the holes enlarge, the spaces between them become mere connecting ridges. Presently the ridges show signs of irregular thickening at certain places, and of thinning at others. This continues until the thick portions have grown at the expense of the thinner parts, and finally the ridge divides at a thin place by the drawing up of the oil into the thickened parts at either side. The separated portions assume the form of rods with rounded ends, which gradually approach more and more to the circular form. This is a very much simplified history of what actually occurs, but if the changes are closely watched with a magnifying glass, they are seen to be complicated by the fact that on every portion of the film surface there are changes proceeding which are a repetition, on a much smaller scale, of those occurring on the film as a whole. The recognition of this feature, the repetition of these changes of structure on a smaller and smaller scale, is of importance, as it supplies a valuable clue to the origin of certain structural forms which are to be found stereotyped in films produced by the direct aggregation of solids. The Figs. 1, 2, 3, and 4 show, diagrammatically, four steps in the film changes: first, the perforation of the film by small holes; second, the enlargement of these holes and the gathering up of the film into mere ridges between them; third, the dividing of the ridges into separate pieces; and fourth, the final state in which the oil is gathered into isolated discs, or flattened droplets.

Eosin Films

By allowing thin films of a solution of eosin in water, to which a little gum has been added, to dry slowly on glass plates, most of the steps in the passage of the continuous film to the final stage, when the film has collected in discs or flattened droplets, can be stereotyped in a convenient form for reproduction as photo-micrographs. Two specimens of these are shown in Figs. 7 and 8. The openings in the films are of all sizes and shapes, from small round perforations to the large openings surrounded by ridges. These ridges also show thick and thin portions, and some of them have already divided, the separated portions having drawn themselves into more or less circular forms. At the sides of the photograph, Fig. 7, the film is granular and unperforated. This granular texture is here seen to be a stage which precedes the actual perforation. The granulation is caused by the heaping up of the substance in tiny ridges round central depressions. The photograph was made by transmitted light, so that the bright spots are thin places, and therefore depressions in the film. A number of these depressions nearer the centre of the plate have actually perforated, showing the clear glass below. This granular film structure is of peculiar interest, and will be referred to later when the structure of thin metal films is being considered. The ridges round the large holes also show the granular structure. Their presence illustrates what was said as to the repetition of smaller and smaller forms on the larger elements of structure.

It is to be noticed that though the greater part of the substance has been drawn up into the bolder forms, yet a thin transparent film still remains on the

surface, and in this the structure is repeated on a smaller scale.

Influence of Surface Tension on Films of Paint or Varnish

The various forms assumed by liquid films under the influence of their contractile skin are thus seen to range from a minute pitting or granulation, which can be of great uniformity even over a large surface, to the bolder open-work patterns, in which the liquid has been drawn up into comparatively massive ridges.

Before passing on to consider the surface structure in solids one other illustration of the effect of surface tension on liquid films may be given. When a brush, charged with ordinary oil paint, is drawn over a smooth horizontal surface, the coating of paint left on the surface shows the brush marks; that is to say, the points of the bristles of the brush draw little parallel tracks in the paint. If the paint is not too thin, and if it sets quickly enough, these tracks remain in the solidified paint as slight ridges and furrows. If the paint sets slowly, the ridges and furrows disappear, leaving the surface smooth and liquid like. If the brush were charged with melted tallow instead of with paint, the coating left on the smooth horizontal surface would set almost instantly, and the brush marks would be deeper and more sharply defined. The viscosity of the liquid layer and the length of time for which the liquid state persists are the factors which determine the nature of the surface which is produced.

In the case of the paint or the melted tallow, we see surface tension at work on a comparatively large scale. A thin layer of paint or varnish will not measure more than

25,000 $\mu\mu$ in thickness. Taking that portion of the layer which is under the influence of surface tension as being 100 $\mu\mu$ thick, we have the ratio of 1 : 250 between the elastic skin and the layer which it covers.

It is obvious that as the thickness of the total layer is diminished this ratio will become more and more favourable to the influence of surface tension. In the case of the surface film on solids, we are often dealing with thicknesses which are well within the range of the molecular forces.

Surface Tension Forms in Solids

Having considered in some detail the effects of surface tension on the aggregation of thin mobile liquid films, we will now pass on to a study of the corresponding forms which have been discovered in thin films of metals in the solid state.

Surface Tension Forms developed in thin Metal Films

While studying the appearance and structure of surface films on metals in their more massive forms, it was thought that considerable light might be thrown on that subject by a parallel study of the behaviour of translucent films supported on glass or mica, as these present the great advantage for microscopical examination in that they permit of the use of transmitted light. It is not necessary here to describe the various methods by which the metallic films were deposited on glass or mica ; it will be sufficient to say that films of gold, silver, and platinum were obtained in thickness which ranged from a few millionths of a millimetre up to several hundred times that amount. These

films being firmly adherent to glass or mica can be regarded as in a condition analogous to that of a thin oil film on the surface of water, or to the eosin film on the glass surface, but with this fundamental difference, that while the water-oil combination was throughout in the mobile liquid condition, the metal glass combination was supposed to be in a condition of solid immobility. The mobility which was found to have occurred in the metal films was produced by heating them in an air bath to temperatures ranging from 250° to 400° C.

These temperatures are far below the melting-points of the metals, as well as of the mica and glass supports.

Figs. 13, 14, 15, and 16 are photographs, at an original magnification of 440 diameters, of gold films of three degrees of thickness. The first was thicker and the second about as thick as ordinary gold leaf, and before annealing showed the usual rich olive green translucence by transmitted light. The other two were considerably thinner than these, and were blue, not green, by transmitted light. The thicker films, Figs. 13, 14, and 19, after annealing, show very plainly that surface tension has been at work, and we are therefore obliged to conclude that the molecules have been in a state of free movement under the influence of this force. The forms assumed by the gold are remarkably like those which were taken by the eosin solution, Figs. 7 and 8, or like the more transient forms which are seen in an oil film on water. As with the eosin so with the gold, there is a structure within a structure. The drawing up of the opaque and more massive figures has left a thinner film of gold on the glass, which in its turn has been drawn into perfectly transparent reproductions of the same type of figures on a rather smaller scale. In

the next film, Fig. 15, which was less massive, the opaque figures are much smaller, and show that the final stage in aggregation under the influence of surface tension had been reached, the aggregates being mainly in the forms of rods or rounded patches.

The transparent part of the film is peculiarly interesting on account of the sinuous interlaced pattern which has been developed, no doubt, under the combined attractive force of the supporting glass surface on the one hand, and that of the more massive gold aggregates on the other. The fourth and thinnest film, Fig. 16, is free from massive opaque aggregates; it was entirely transparent and completely covered the surface of the glass. As a whole it is very much more uniform, and is much more typical of the thin film structure than the other three films are. Fig. 25 shows a similar structure developed on a thin platinum film, which has been fully annealed.

The structure of even the thinnest of the gold films is sufficiently bold to show distinctly by transmitted light. The silver film shown in Fig. 17, though of very fine texture, is sufficiently thick to show the granular structure and its surface tension origin very distinctly even by transmitted light. By obliquely incident illumination the silver film, Fig. 18, shows a structure which corresponds very closely with that of the previous photograph. While the more prominent mounds or granules which have caught the light appear as ill-defined discs, their more shallow neighbours are fairly well defined. In this photograph a line has been scraped across the film so as to show the torn edges against the dark glass surface. The continuity of the film over the whole surface is thus made clear; it is a film, not a disjointed collection of mounds.

The tendency of oblique illumination to exaggerate the details of structure can be distinctly seen in this photograph.

The foregoing illustrations show that an increase in the mobility of the molecules of a solid, which is still far short of the freedom of the liquid state, is sufficient to enable the force of surface tension to assemble the molecules of a thin film into new forms of aggregation.

The molecular mobility which occurs at the moment of the partial solution of a solid surface may be seized by the forces of surface tension, with the result that the forms of structure which are due to these forces are found on surfaces which have been slightly etched by solvents. At the surfaces of solids and liquids alike these potential forces are always present, and ready, as it were, to take advantage of any increase of the mobility of the molecules to impress their characteristic forms of aggregation upon them.

Surface Tension Forms due to Action of Solvents

The solvent whose effects we will first consider is mercury. When a surface of gold is exposed to mercury, the latter at once forms a thin film of alloy. If the gold is gently heated, so as to volatilise the mercury, the surface of the gold is left in a frosted condition.

The micro-structure of the surface now reveals the very interesting fact that the mercury in volatilising has not left behind it a sponge of gold as might have been expected, but that the gold is now in the form of transparent granules of a deep gold colour, which give little or no metallic reflection from their surface. The explanation appears to be that at the moment of their separation from

the mercury by heat, the molecules of gold are in a state of freedom which permits their mutual attraction to draw them together into granular or drop-like forms, Figs. 20, 21, and 22.

This phenomenon is even more plainly seen when mercury is allowed to act in the same way on metal films supported on glass. In this case, by the use of transmitted light, the micro-structure is seen to consist of granules and rounded forms.

If a film of gold on glass is exposed for an instant to mercury vapour, the minute globules which condense on the surface spread with great rapidity through the gold, forming a transparent alloy. The structure of this film of alloy under high magnification is shown in the micrograph, Fig. 23.

By gentle heating the mercury is driven off, and the gold is left in the form of a continuous film dotted thickly over with slight thickenings or mounds, which mark the points at which the alloy has been drawn up into aggregations.

When a minute globule of mercury is placed on a gold leaf laid upon glass, the mercury may be watched by the microscope as it spreads between the many folds and laminations of the leaf.

The difference between the laminated texture of the leaf and the closer and more horn-like texture of compact films deposited by chemical agents is made very obvious when the behaviour of mercury on one and on the other is watched by the microscope. In the leaf, thin streams of mercury may be seen shooting rapidly in all directions till the whole surface is converted into an alloy. In the compact film the mercury creeps slowly and almost un-

obviously from point to point. In the one case the mercury molecules move in a body from point to point, in the other they seem to diffuse through the substance of the gold.

Comparison of the Etched Surfaces of Gold and Glass

To illustrate further the effect of solvents in producing sufficient molecular mobility among the undissolved molecules on the surface to permit of their aggregation under the influence of surface tension with the development of characteristic forms, the behaviour of two widely different substances will be referred to — gold and glass. The polished surface of a plate of pure gold was very lightly etched with chlorine water, so lightly indeed that the surface appeared to be only slightly dimmed where the solvent had acted ; but when examined by a lens of high resolving power under normally reflected light, Fig. 9, the originally smooth surface was seen to have given place to a fairly uniform structure of exactly the same type as that seen in the thinnest annealed gold film, Fig. 16. The fire-glazed surface of a glass slip was lightly etched by exposing it to the action of hydrofluoric acid gas mixed with air, Figs. 10 and 11, and as was the case with the etched gold, the surface appeared to be only slightly dimmed, but on examination by the same lens and by transmitted light a surface structure was disclosed, so remarkably like that developed on the gold plate that it would be very difficult to distinguish the two photographs, Figs. 9 and 10. By continuing the etching so as still further to remove the surface layers, the crystalline structure of the gold was disclosed ; in this case it happens to be a broken and dis-

torted structure, as the plate had been prepared by beating it out to four times its original area, Fig. 90. The glass surface also was more deeply etched, and in this case, also, a different structure was disclosed, Fig. 12, which is probably a compromise between a surface tension form and a crystalline form. Microscopists are familiar with compromises of this description, which are seen when very thin films of salt solutions are allowed to crystallise on a glass slip. If the film of salt solution is below a certain thickness, the forms assumed are purely those due to surface tension. As the thickness of the film is increased, the crystallic force gradually overpowers the surface tension, and the deposit becomes more and more sharply crystalline. Observations have shown that there is a definite limit for each substance, below which the crystallic force is completely controlled by surface tension.

SECTION III

THE VARIED WAYS IN WHICH AGGREGATION TAKES PLACE

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See PLATES VIII., IX., X., XI.

SECTION III

THE VARIED WAYS IN WHICH AGGREGATION TAKES PLACE

The Characteristic Feature of the Solid State is Rigidity

THE formation of solid aggregates is primarily due to the mutual attraction of the molecules. It may be assumed that this attractive force is at its maximum at the absolute zero of temperature, and that, as the temperature is raised, the molecular vibration caused by heat tends to weaken or counterbalance the attractive force of the molecules.

In the solid state the attractive force is still so strong that the molecules adhere to each other, or at least retain fixed positions relatively to each other, so as to produce a structure which has and retains a definite form. This quality of the molecular aggregate is most conveniently defined as "rigidity." It is sometimes referred to as "hardness"; but this term has been used in so many different senses that its use in any particular case involves further definitions or explanations. This indefiniteness is partly due to the fact that "hardness," like "softness," is most frequently used as a term of comparison. It is true that "rigidity" is to some extent open to the same objection, and, from that point of view, it is not quite

an ideal term for the most fundamental property of the solid state. For this purpose "solidity" naturally suggests itself; but "solidity," like "hardness," is already used in various senses. To most minds, for instance, "solidity" suggests density and mass, as well as rigidity; but density and mass are the common properties of matter in all its states, and are not specially characteristic of the solid condition.

In what follows, then, we shall regard "rigidity" as being that fundamental property of the solid state which results from the retention by the molecules of fixed positions relatively to each other, so that energy has to be expended in altering these fixed relations.

Changes of State result from the Addition or Abstraction of Heat

All the elements and many of their compounds can exist in the three states: solid, liquid, and gaseous. The step from solid to liquid occurs when the temperature is reached at which the attractive force of the molecules is so far counterbalanced by the vibration due to heat that they acquire a degree of freedom and mobility which enables them to move independently. Under this new condition they can no longer retain each other in fixed positions, and cannot therefore build up a permanent rigid structure. In the liquid state the molecular attraction is, however, still sufficiently strong to enclose the aggregate with an elastic bounding surface or skin, through which only a relatively small number of molecules can escape into the gaseous state.

The step from liquid to gas occurs when the boiling-

point is reached. The molecular attraction is now so far overpowered by the heat vibration that the surface tension skin can no longer keep the molecules from freely escaping in the gaseous state. Sufficient of the molecular attraction, however, still persists to influence the movements and encounters of the liberated molecules, which do not therefore fulfil the ideal conditions of a perfect gas. This final stage is only approached when the temperature is raised very much above the boiling-point.

A tentative hypothesis under which the interplay between the two forces, cohesion and the molecular vibration caused by heat, can be conveniently visualised, is described in Section IX. For our immediate purpose it is sufficient to emphasise that the primary influences which determine the formation of molecular aggregates are cohesion and the vibration of the individual molecules.

In the passage of a substance directly from the liquid to the solid state, aggregation is due to the reduction of the kinetic energy of the liquid molecules by the withdrawal of heat to the point at which it no longer overpowers the molecular attraction, so that the molecules come to rest in contact with each other, either in the orderly homogeneous arrangement of the crystal, or in the more heterogeneous arrangement of the amorphous vitreous state. In the case of pure substances which solidify in the crystalline state, the solidifying-point is one of the most constant of their physical properties.

When aggregation of a solid takes place from solution, either through cooling, or by the slow evaporation of the solvent, a new factor is introduced by the presence of the highly energised molecules of the solvent, which may exercise an influence on the structure of the resulting

aggregate. Similarly, when aggregation takes place from the gaseous state, the presence of the highly energised gas molecules may influence the form and structure of the aggregate.

In both gases and liquids the outward forms of the aggregates which are separated may be very much affected by moving currents and eddies. In smoke clouds produced by the imperfect combustion of hydrocarbons, by the combustion of metals like magnesium or sodium, or by the combination of gases like ammonia and hydrochloric acid, the forms assumed by the solid aggregates are profoundly affected by eddies and currents in the medium in which the aggregation has taken place.

Before describing the experimental observations on this branch of the subject, it will be well to consider generally the influences which determine aggregation in its various forms.

Solidification directly from the Liquid State

The simplest and most normal form of aggregation is that which results from the cooling of a liquid to its solidifying-point, and continuing to remove the heat of liquefaction as solidification proceeds till the whole liquid is converted into a solidified mass of crystals. As the heat of solidification has to be removed by cooling from the surfaces of the mass, the element of time comes in, and the size and disposal of the crystals in the mass are to some extent affected by the size and shape of the vessel and by the rate at which the heat is removed from its surfaces. Broadly, however, it may be taken that the aggregate is a closely packed mass of crystals, which represents the

substance in its densest form. The mass, however, is not a homogeneous solid as a single crystal is; it is a structure of a definite kind with a "texture" of its own. As will be seen later, this "texture" may be considerably varied without the introduction of foreign molecules, and without altering to more than a trifling extent the volume of the space occupied by the molecules of the substance. This aspect of the subject is dealt with in Section VII.

Crystallisation from Solution

Next in order of simplicity is the separation of crystals from a saturated solution in some suitable solvent by cooling the solution, or by the removal of the solvent by evaporation. When, as is most frequently the case, water is the solvent, complications are introduced by the fact that in some cases water combines with the substance as water of crystallisation, and the crystals as aggregates no longer represent the substance in itself.

When a solvent is used which does not combine with the substance, the method lends itself admirably to the production of well-developed single crystals, in which the molecular arrangement is strictly homogeneous.

The crystal is the simplest as well as the most dense form of aggregation in which the molecules are in close formation. In other forms of aggregation which will be described, great openness of packing is found; but before describing these it may be well to consider generally what influences are likely to make for open packing.

Influences which cause Aggregation in Open Formation

Consider first the kinetic energy of the molecules themselves, as it exists in the form of vibration or pulsations due to heat. At high temperatures this energy can completely neutralise the effects of molecular attraction and cohesion; but this neutralisation takes place in two well-marked steps, the first at the liquefying-point and the second at the boiling-point of the substance. Between and beyond these points the neutralisation proceeds more gradually, and is indicated by the expansion of the solid, the liquid, and the gas as the temperature is raised.

This is a purely thermal operation, which in its application to the elements, as well as to many of their compounds, is perfectly reversible; for, on the withdrawal of heat by cooling, the heat energy, which had been expended in neutralising the molecular cohesion, is completely restored on the return of the substance to its initial temperature.

It follows that, when this heat cycle is worked on normal lines, it is not likely of itself to be the cause of changes in the mode of aggregation.

Starting from the solid state somewhere within the temperature range of crystallisation, the substance may be raised to the state of a perfect gas by the addition of heat. By the removal of this heat, it will be brought back to its original form of aggregation in the crystalline state.

There are, however, two qualifications of this general law which must be noted. The first is that, when the removal of heat energy in the passage from the liquid to the solid state is not slow and uniform, but is greatly accelerated by sudden chilling before the crystalline arrangement of the molecules has fully taken place, some

of the substance is stereotyped in the vitreous amorphous state, and the aggregate retains a structure which is different from that of the normal crystalline state. This subject is more appropriately dealt with in Section VII., in connexion with the hardening of metals by chilling.

The second qualification to the general law is that surface tension and cohesion play a leading part in controlling the forms and micro-structure in layers and films of a thickness of at least 100 $\mu\mu$. It follows, therefore, that in dealing with the aggregation in dimensions of this order, the general law does not hold, and the crystalline state does not inevitably result from aggregation by the removal of heat energy.

It is to be noted, however, that the effect of these qualifications is to make it less rather than more probable that the intrinsic heat energy of the molecules is an influence which is likely to make for openness of packing in aggregation. We must therefore turn our attention in other directions if we are to discover these influences.

A general indication has already been given that the outward form of aggregates may be profoundly influenced when they are produced in a liquid or gaseous medium.

As regards gases, it may be accepted that their influence, added to that of the heat energy of the molecules, invariably leads to openness of texture in the aggregate. Not only the highly energised condition of the gas molecules, but also the fact that, in many cases, they form loose combinations with the aggregating molecules, lead to very remarkable effects. In certain cases which will be described, metals in their crystalline form, when submitted to the action of gases which form loose combinations with the metal at a temperature far short of the liquefying-point,

are so completely disintegrated into molecules or minute molecular units, that they lose all their recognised properties as metals. These disintegrated units are so minute that they are beyond the range of resolution by the microscope, so that we can only conjecture as to the details of the open-work structure.

Disintegration of Silver and Copper by Gases leads to Aggregation in Open Formation

Faraday found that, when a silver leaf is spread on glass or mica, and exposed in a muffle furnace to a temperature of about 350°, it becomes white, lustreless, and translucent. Fig. 105 shows a piece of silver leaf which has been treated in this way. The photograph is by transmitted light, and it will be seen that the leaf has become almost as transparent as the glass on which it is spread. The micro-structure of this leaf is shown in Fig. 17, and is described in Sections II. and X. The conclusion from many direct observations was that the transformed leaf, though porous to gas molecules, formed an optically continuous layer over the surface of the glass.

Faraday regarded this phenomenon as if it were entirely due to the action of heat. I must admit that I also accepted this view at first, being mainly concerned in attempts to resolve its structure by the microscope. A useful light was thrown on the subject in "Transparent Silver and other Metal Films," by Professor Turner,[1] when he described experiments which seemed to prove that the active agent in the disintegration of the silver was the oxygen of the atmosphere in which it had been heated.

[1] *Royal Society Proceedings*, vol. 81, No. A. 548.

In view of the well-known fact that molten silver absorbs oxygen, which is given off again as the temperature falls, it is natural to suppose that oxygen is the active agent in the molecular disintegration which so completely changes the properties and appearance of silver leaves which have been annealed in the presence of air.

The frosting of silver by heat, which is so commonly practised by silversmiths, is only another example of the same phenomenon.

The Action of Ammonia on Metals at High Temperatures

Many years ago, while engaged in developing an industrial process which involved the passing of large volumes of ammonia gas through metal tubes at a red heat, some striking observations were made. In the first place, the statement of Ramsay and Young,[1] that ammonia is decomposed into its elements with great rapidity by red-hot iron was amply confirmed. When a current of ammonia at the rate of 4 litres per minute was passed through an iron tube 12·5 mm. in diameter and heated at 810° for 300 mm. of its length, only 27 per cent of the ammonia escaped decomposition, 73 per cent, or nearly three-fourths of the whole, being decomposed. The velocity of the current through the heated part of the tube was about 1·5 metres per second, so that the ammonia molecules were only exposed to the hot metal for one-fifth of a second. Various observers had found that, for equal surfaces, copper has much less action on ammonia than iron. Experiments were accordingly made, using a solid drawn copper tube instead of an iron one. Under

[1] *Trans. Chem. Soc.*, 1884, xlv. 88.

similar conditions of temperature and ammonia current, the quantity of ammonia decomposed by the copper tube in a given time was only about one-third of the quantity decomposed by the iron tube. This result was, so far, encouraging, and an attempt was made to use copper tubes for the industrial operation. However, after exposure to ammonia at a temperature of 800° for a few hours, the tube became so short and brittle that it could not bear its own weight without breaking. The next step taken was to strengthen the copper tube by slipping over it a sleeve pipe of iron, which fitted tightly and gave the necessary strength to resist bending or breaking. Thus protected, the copper tube could not break or crumble away, but it was soon found that it tended to close up until only a very small amount of gas could pass through it. Examination showed that the walls of the copper tube had become very much thickened, and being unable to expand outwards, owing to the sleeve of iron, had expanded inwards until the bore of the tube was nearly closed. Observation with the microscope showed that the copper had become spongy and disintegrated throughout. It retained its colour, and, to a certain extent, its metallic lustre, but it appeared as if it had been in the fluid state, and blown up into a sponge by innumerable minute gas bubbles. Not only was the copper acted on, but the iron sleeve pipe had been reached and penetrated by the ammonia molecules. The iron pipe had become as brittle as hardened steel, so that it could be shattered by a blow with a hammer, and showed a bright, silvery fracture. Under the microscope the iron also exhibited a spongy structure.

At this time a number of other metals and alloys

were experimented with, in the hope that something might be found which would resist the action of ammonia at a high temperature. Nickel, silver, platinum, gold, as well as a variety of alloys, were tried, but in every case the metal acquired the same spongy structure, and its strength and tenacity became seriously deteriorated. No metal which was tried was able to resist the attack of the ammonia molecule at a high temperature. To the already long list of the formidable properties of the nitrogen atom must now be added this power of attacking and disintegrating the most massive and refractory of metals, not even the noble metals being proof against its assaults.

In the case both of the iron and the copper tubes, it was found that under uniform conditions the quantity of ammonia decomposed remained fairly constant. While the continued action of ammonia tends to disintegrate the copper more and more, the greater surface thus exposed does not appear to add sensibly to the decomposition of ammonia by a given mass of metal. During the whole life of the protected copper tube (about 150 hours), the amount of ammonia decomposed did not vary much from 1 gram per minute. On the total life of 150 hours, this amounted to 9000 grams. This quantity of ammonia was many times the weight of the copper which decomposed it. It was evident, therefore, that the amount of ammonia decomposed was not in any way limited to what would be required to form a nitride or a hydride of copper. Examination of the decomposed gases showed that, on the average, the nitrogen and hydrogen were present in the proportion of 1 : 3 by volume. On the other hand, the appearance of the metals after exposure to ammonia clearly indicated that the melting-point of the metal had

been lowered by the action, and, therefore, that chemical combination between the metal and one or other of the gases had taken place at some stage in the operation. To produce a spongy mass, the metal must have been, at any rate, in a plastic or semi-fluid condition, but the structure rather suggested that the metal had been suddenly cooled while in the act of boiling, bubbles in every stage of formation and bursting being fixed in the solidified metal. A spongy state may be produced in a material which is merely plastic, but this appearance of boiling could only be found in a material which had been fairly fluid. The temperature of the experiment was far below the melting-point of copper or iron, therefore at some stage in the operation a more fusible compound must have existed. As everything pointed to the continuous formation and decomposition of some compound of the metal with ammonia or one of its constituent elements, some preliminary experiments were made to ascertain how far combination was taking place. Rolls of fine wire gauze of copper and of iron were heated in a porcelain tube at 800°, and a current of ammonia at the rate of 6·5 to 7 litres per minute was passed through the tube for 70 minutes. The following results were obtained. Weight of copper gauze before treatment, 42·04 grams; after treatment, 43·92 grams—a gain of 1·82 grams, or 4·47 per cent. Weight of iron gauze before treatment, 18·87 grams; after treatment, 20·02 grams—a gain of 1·15 grams, or 6·09 per cent. The iron gauze had become so brittle that it could not be bent without breaking. Its colour was bright silvery-grey, and under the microscope the spongy structure was very well marked. The copper gauze had become equally brittle. Its colour was a bright

pink, and its surface was so completely disintegrated that metallic lustre had disappeared. Under the microscope the bubble structure was very obvious. With both metals, the diameter of the wires had increased two or three times.

As already stated, a number of other metals were exposed to ammonia at a red heat. Although the energy of the action varied to some extent, all without exception were attacked in the same way, and became spongy and disintegrated. Even in the case of those metals, for example, gold and platinum, which did not show any obvious increase in weight through absorption of nitrogen, the appearance under the microscope was the same, and indicated that the action of ammonia had produced a certain degree of fluidity. This was shown in an interesting way when wires of different metals were twisted together and then heated in a current of ammonia. In many cases it was found that these metals had flowed together; thus, iron and copper, iron and gold, gold and platinum, gold and silver, became fused together. In the case of iron and gold, the gold sometimes flowed over the surface of the iron, forming a complete plating at temperatures not exceeding 800°.

For our present purpose the main interest of these observations is as illustrations of the important part which may be played by gases in the disintegration and re-aggregation of metals in open formation.

One of the most significant features is the clear demonstration that a metal may be locally liquefied by the passage through it of minute bubbles of gas at temperatures many hundred degrees below its melting-point. Gold and platinum when acted on by ammonia at 800°

do not combine with nitrogen, but their spongy appearance shows that they must have been in a state of local fluidity. This can only have been caused by the passage of gas bubbles.

A remarkable microscopic observation on the actual issue of gas bubbles from copper at the ordinary temperature is referred to in Section VII.

The Escape of Gases through a Planished Gold Surface at a Temperature Several Hundred Degrees below the Melting-Point of the Metal

A plate of pure gold, the surface of which had been frosted by amalgamation with mercury followed by heating, was planished by beating it on a polished steel surface till a smooth continuous reflecting surface was obtained.

Fig. 26 shows the surface of the planished plate. This and the three following figures are direct photographs without enlargement, by normally reflected light, with a 3 mm. oil immersion apochromat of 1·4 N.A. The magnification is ×1500.

Fig. 27 is the same plate after heating to between 700° and 800° for 10 minutes. The surface film has become detached and broken up, evidently by the escape of air which had been imprisoned by the planished film. The surface has a viscous appearance, and the holes made by the escaping gas add to this effect.

Fig. 28 is the same plate after further heating for an hour. The surface film appears to be aggregating and subsiding into the mass of metal below.

Fig. 29 is the same after further heating for an hour.

In this case, as exactly the same spot has been photographed as in the preceding figure, it is possible to trace the further subsidence and disappearance of the original surface film.

Fig. 30 is another specimen of planished gold after heating for one hour. The ruffled surface again shows the effects of escaping gas.

In Fig. 31, after a further hour's heating, the final subsidence and the viscous flow of the surface are clearly seen.

Aggregation in Open Formation brought about by the Action of Solvents

In the arts the frosting of metal surfaces by the use of solvents has long been known and practised. The present observations have shown that the frosting is due to the production of a film of metal in open formation. In many cases the films so produced are indistinguishable from similar films produced by gases at high temperatures. In some cases the open formation is brought about by the solution of the portions of the metal which are present in the vitreous state, because the metal in this is more soluble than in the crystalline state. This is well seen when gold leaf is floated on the surface of a solution of potassium cyanide. The solution of the vitreous metal, which has been produced in the operation of gold-beating, can be all dissolved away, leaving a transparent film without metallic lustre and of very open texture. This texture is more distinctly seen when the transparent film is lifted from the solution on a glass slip and allowed to dry. It can be wetted and dried any number of times without altering its appearance and behaviour.

Films of this type are regularly produced when polished surfaces are etched. In etching gold with *aqua regia*, these open-work films are often beautifully coloured in shades ranging from red to purple and blue. (See also Section X.)

When the action of the solvent gives rise to a gas, as is the case with *aqua regia* and nitric acid, the opening up of the undissolved molecules is carried to a much further extent than when no gas molecules are set free. The selection of an etching agent for micro-metallurgical purposes is generally made by a process of trial and error, till the solvent is found which brings out most distinctly those features of the structure which it is desired should be emphasised. Sometimes this results in the production of a coloured open-work film over the surface of one constituent, and at other times the different constituents are so easily distinguished by this intrinsic colour and form that the presence of these films would be unnecessary or undesirable. In perfectly crystallised specimens the films left by the partial solution of the flowed surface layer which is produced by polishing may actually obscure the crystalline surface beneath, and deep etching is resorted to so as to remove this layer completely. In specimens in which the crystals have been broken down by flow, and metal in the vitreous state has been freely formed, the difficulty of producing a clear, well-defined structure by etching is greatly increased; and if at all possible, a solvent which does not liberate a gas should be used, in order to minimise the production of open-work films.

Figs. 100, 101, 102, 103 illustrate the etching of gold, both in the highly strained and in the fully crystallised states.

Crystalline Arrangement in Open Formation

Owing to the readiness with which its molecules can be thrown into open formation by solvents and gases, pure silver is a difficult metal to etch satisfactorily. An interesting phenomenon was, however, discovered while attempts were being made to develop a satisfactory structure on the end of a $\frac{1}{4}$-inch rod of pure silver which had been hard rolled. It was just possible to distinguish the distorted remains of the original grains by very careful polishing and etching with nitric acid. The polishing was being carried out for the purpose of producing a perfectly regular smooth surface layer over an under surface, which was as free as possible from concealed furrows left by rubbing on the finest French emery-paper. The etching agent was nitric acid, in which a good deal of silver had been dissolved, and it was warmed to about 80°.

It had been found after many trials, that the longer the silver was left in contact with the acid, the more spongy and open did the texture of the etched surface become, and each fresh trial was made with a shorter period of contact. In this way a point was reached when only the surface of the polished layer was attacked; and, on washing the specimen, an entirely new crystalline structure was disclosed. After a little practice, it became possible to produce this effect at will, and the photograph shown in Fig. 34 was obtained from one of the most successful specimens.

This new structure was entirely confined to the surface layer; for, if the specimen was again dipped in the acid, however briefly, it disappeared, and the distorted crystals underneath were disclosed. This surface crystallisation

had no obvious connexion with the deformed grains underneath, which were very much smaller and distributed with the utmost irregularity. In general type it is akin to the surface crystallisation on a frosted window-pane, or on a thin film of stearin which has been melted on glass and allowed to cool.

The stage at which this structure was produced was when the action of the acid had removed the surface tension skin over the polished surface, and had set free, but not dissolved, the minute particles of crystalline metal in the flowed layer. These freely moving particles, being themselves crystalline, were instantly marshalled in radii from centres of influence which may have been supplied by the larger grains underneath, or from surviving nuclei in the polished film. The two chief requirements for crystalline arrangement are: freedom of movement of the molecules, and the directing power of a crystal. The directing power in this case clearly proceeded from the centres, for radial growth from each centre has extended outwards till it meets the growth from other centres. The necessary freedom of molecular movement was secured by the action of the solvent.

The structure was quite visible to the unaided eye, and the magnification in the figure is only ×10. The microstructure under higher resolving power was essentially of the open-formation type; it had none of the compactness and solidity of a regular crystal.

At first this was regarded as an unique example of the occurrence of crystalline direction and growth in an aggregate in open formation; but this possibility having been once recognised, the phenomenon can be traced in many cases of surface etching in which films of open forma-

tion are deposited on some crystals and not on others, evidently under definite crystalline direction.

To the numerous examples of the influence of surface tension in aggregation in open formation, this case of crystalline direction must be added. It follows, therefore, that in the study of aggregation in open formation both of these directing influences must be taken into account.

Frosting produced by Mercury as a Solvent of Gold

A spot on the surface of a gold plate was amalgamated with mercury, which was then driven off by a gentle heat. The surface was " frosted," the colour of the part at which the mercury had penetrated most deeply was darker and more red, and metallic reflection had disappeared. Where the mercury had not penetrated so deeply, there was some metallic reflection. Fig. 20 is a photograph by normally reflected light at a magnification of 250 diameters.

On the light part of the surface the mercury has acted very slightly, and the lustre of the original surface is not much diminished, though there has been sufficient action to bring about aggregation in rounded forms. On the dark part the action has gone deeper, and in consequence the amount of light which has escaped absorption has been insufficient to disclose the details of the structure. Figs. 21 and 22 are photographs of the light and dark parts at a higher magnification by the 3 mm. objective. In Fig. 22 the spots of light on the dark background are reflections from the tops of transparent or translucent granules of rounded form.

Gold leaf on glass was exposed to mercury vapour, and then heated sufficiently to drive off the mercury. By

transmitted light the dark patches were deep green, and the clear parts between them were colourless. Fig. 23 is a photograph of the leaf by transmitted light, and at a magnification of 440 diameters.

The final effect of this treatment is similar to that obtained by heat annealing. There is the same granulated transparent film covering the glass, while the brown-green aggregations form a skeleton outline of the ribs and markings of the original leaf.

Having illustrated and studied aggregation under the influence of heat, of gases, and of solvents, we shall now consider the forms of aggregation which result when a solid is produced by the interaction of substances in the liquid state, as when a precipitate is produced by the mixture of solutions of two soluble salts.

Precipitates from Mixed Solutions

When solutions of silver nitrate and sodium chloride are mixed, silver chloride separates as an insoluble precipitate. When moderately strong solutions are used, a bulky white precipitate is produced, which on shaking aggregates in flakes or clots.

Quincke has made a lifelong study of the forms assumed by relatively large aggregates produced by precipitation, and has emphasised the part played by surface tension in the development of the outward form assumed by the aggregates. From these studies it is evident that surface tension is only one of the influences which determine these forms. The relative motion of the two liquids and their relative masses and surfaces are important factors. Under these influences drop-like forms may become transformed

from spherical and drop-like to ovoid, cylindrical, or ring-like.

The purpose of the present inquiry was, if possible, to trace the aggregation of precipitates from the earliest possible stage in their production, and to watch not only their initiation, but their early development by the microscope.

One of the methods used was to prepare solutions of silver nitrate and sodium chloride so dilute that, when mixed in equal volume, only a slight cloud of silver chloride was produced. The microscope having been arranged, as described in Section I., for the focussing of a critical image of a Nernst filament on the field of vision of a glass slip on the horizontal stage, single drops of each solution were placed on the slip, just so far apart that, when they had flattened out to thin films, they would meet as near as possible to the middle of the field of vision. The lens combination used was the 16 mm. apochromat for a 10-inch tube-length, and either the 6 or 12 compensated eye-piece. With a little practice it was possible to make all the adjustments so quickly that the film of precipitate which formed at the common surface of the two liquids as they spread could be picked up and its developments followed.

The first visible step is the formation of an extremely thin film, which is not of uniform thickness, but is covered with minute lens-like thickenings. With the forward movement of the two liquids, the film tends to break up, and these lens-like units are set free, being set in Brownian movement by the highly energised water molecules. The broken-up film is immediately replaced by a fresh film at the common surface. If the solutions are rather more concentrated, the films formed are thicker and more

robust, so that they break up into pieces which contain a number of the lens-like units. These pieces, when they touch, build up into larger aggregates, and form clouds which ultimately aggregate and settle down on the surface of the glass slide as granules.

In the earlier papers on this subject these minute lens-like units were referred to as " spicules," and they were then believed to be definite units of structure. They were first observed as a surface phenomenon by obliquely reflected light, under which they are in danger of being confused with the diffraction discs which are always produced when an intense beam of oblique light is directed on any slightly roughened surface. The reality of the " spicular " structure was, however, clearly proved by the exhaustive examination of thin metal films by normal light, both reflected and transmitted, and with lenses of the highest resolving power. Fig. 17 is a thin film of annealed silver by transmitted light at a magnification of 1000 diameters, in which the structure is seen to be real. Fig. 18 is another silver film by obliquely reflected light of low intensity. Part of the film has been scraped off so as to show the contrast between the film and the bare glass underneath. The film is continuous, and is covered with little mounds or spicules. The same type of structure is shown in the transparent parts of the annealed gold films shown in Figs. 13, 14, 15, 16, and 19.

In the case of the thinnest film of silver chloride which was deposited at the common surface of the two solutions, the lens-like units were only visible when they happened to turn so as to catch the light and reflect it into the optical axis of the microscope. They were therefore not spheres, but minute plates or scales.

The Pellicle of Calcium Carbonate formed on the Surface of Lime Water

Lime water is a saturated solution in water of hydrated calcium oxide. When its surface is exposed to the air, the carbonic acid of the air unites with the calcium oxide, forming calcium carbonate, which is insoluble. This insoluble substance forms a thin film or pellicle, which covers the surface of the liquid. This pellicle may be formed more quickly by breathing over the surface of the lime water. Though the carbonate of calcium is insoluble in water, the bi-carbonate, or calcium hydrogen carbonate, is soluble to a limited extent. A familiar experiment to illustrate this is to blow through a tube into lime water in a beaker or test-glass. The carbonic acid in the breath at once forms a precipitate of calcium carbonate. If the blowing is continued till sufficient carbonic acid has been dissolved in the lime water to convert the carbonate into bi-carbonate, the whole of the precipitate is re-dissolved. These reactions are referred to here, as they have a direct bearing on the formation and behaviour of a pellicle of calcium carbonate on the surface of lime water. As will be seen from what follows, these operations supply a most fascinating subject of microscopic study. They can be carried out on a film made by allowing a few drops of lime water to spread naturally on an ordinary micro-slip; or the lime water may be contained in a shallow, flat-bottomed cell. The latter is the more satisfactory arrangement. The stage of the microscope should be horizontal, and the oblique illumination must be carefully arranged as already described, so that the critical image of a small source of light is focussed on the centre of the

field, in order to give the effect of dark ground illumination. This mode of illumination must be maintained from the surface of the liquid down to the glass surface of the slip or cell. It is then possible, merely by focussing the microscope upwards or downwards, to follow all that goes on from the surface of the pellicle down to the surface of the glass bottom.

With fresh undiluted lime water a thick pellicle forms so quickly that it is not easy to follow the earlier stages of its formation. By diluting the lime water to about half its strength, most of the steps in the development of the pellicle can be followed; but even greater dilutions may be used with advantage for the study of the earliest stages of pellicle formation.

The pellicle may be started by lightly breathing on the surface after the film is in place on the stage. If all the conditions are favourable, the pellicle will first appear as an extremely thin continuous film, built up of the minute lens-like swellings which will be here referred to as "spicules." If the stage of the microscope were absolutely free from vibration, the film would no doubt continue unbroken and would grow in thickness till all the dissolved lime was converted into carbonate. The spicules would thicken till they became granules, and the granules till they became crystals. Had this been the case in the earlier experiments, it is probable that the most interesting of these observations would have been entirely missed. Fortunately, from this point of view, the room in which the observations were made adjoined a fairly busy street, and its floor was carried on wooden joists, so that every passing vehicle caused a tremor on the stage of the microscope and in the liquid under examination on the stage. These

periodical tremors tended to break up and make gaps in the pellicle, and thus led to the discovery of the activities of calcium carbonate from its first aggregation as a thin spicular film, till it reached the stage of fully developed, doubly refracting crystals of calcite.

When the break-up of the film takes place while it is still extremely thin, though considerable patches of pellicle continue to float on the surface, large numbers of spicules are set free, and dart about with Brownian movement under the bombardment of the highly energised water molecules. If two spicules have an encounter, they at once coalesce, and the enlarged unit proceeds to fresh encounters till its mass becomes so large that it sinks to the bottom as a granule, and rests there. Its power of absorbing other spicules having increased with its mass, it now acts as a centre of attraction to the still active spicules which play round it with swift to-and-fro movements, ultimately darting into it and being absorbed. It was possible to watch this operation by focussing on the bottom of the cell, and the granules were seen to grow till they took the outward form of rhombs.

As these observations were made in 1903, and were only orally described at the meeting of the British Association of 1904, it seems well to describe them here in the exact words of the records which were made during their actual progress.

The general description of the method of operation which is given in the preceding pages will enable the reader to fit the working record of the experiments into its proper setting, and will help to place the different steps in their proper perspective.

Record of August 24, 1903

In lime water exposed to the carbonic acid of the air or of the breath, the various steps in the building up of definite crystals can be watched from the first appearance of an extremely thin surface pellicle which readily breaks up into scales or spicules through a granular or globular to the definitely crystalline stage, at which the individual units act distinctly on polarised light.

The formation of the surface pellicle may take place in such a way that it forms a continuous film which grows rapidly in thickness, or spicules may form singly or in groups on the surface of the liquid. The single spicules, if they becomes submerged, move about with great energy in the liquid till they come within range of each other's attraction, when they unite to form more massive units. These larger units become more powerful centres of attraction, and quickly pick up so many other spicules that they sink in the liquid and settle on the bottom of the vessel. Here they continue to attract such of the moving spicules as come within their range, and thus grow till they pass from the granular to the definitely crystalline stage.

The collections of spicules which float on the surface also attract the other moving spicules on the surrounding surface or from the liquid below. Those gathered from the surface tend to extend the area covered by the group, while those gathered from below increase the mass of the spicules or granules already composing the group or film.

When the conditions are favourable, individual spicules or groups of these floating on the surface in open formation grow by the attraction and absorption of spicules from the

liquid till they become granules or crystals. When the latter stage is reached the floating groups show their mutual attraction in a very marked way, and the surface is rapidly cleared of individual crystals by their becoming attracted to and uniting themselves with the groups. Sometimes two individual crystals come within range of each other's attraction and rush together violently; but naturally the larger groups are the centres of attraction for all wanderers. The crystals on the surface measure about 6000 $\mu\mu$. The attraction is seen to take effect slowly, at a distance of 25,000 to 30,000 $\mu\mu$ (0·03 mm.), but when the distance becomes reduced to 12,000 to 15,000 $\mu\mu$ the smaller crystal or mass rushes into the larger and becomes attached to it. Sometimes, however, the smaller crystal does not come to rest at the first point of contact, but moves round as if to settle in a firmer contact.

Record of January 3, 1904

Water of extreme dilution was tried, but, while the growth of granules and of crystals from spicules was observed, the movements were not so interesting as when a certain amount of pellicle is formed on the surface of the water. This evidently requires a fairly strong solution of $CaOH_2O$. Old lime water which had deposited a good deal of lime on the sides of the bottle was used undiluted. In this case a fairly thick pellicle formed quickly, that is to say, before the slip was adjusted on the stage of the microscope. The pellicle gave good spicular reflections by oblique light, and was just thick enough to show its structure by transmitted light. There were breaks in the pellicle, which left lagoons or sheets of water surrounded

by the rough edges of pellicle, portions of which projected into the lagoons, giving a much indented coast-line.

The pellicle was firmly knit together, and though occasional movements, due to pedetic activity, took place among a few of the enclosed spicules, these did not alter the general compactness of the sheet. By focussing for the lower depths of the water at one or other of the lagoons, it was seen that a moderate number of actively moving spicules were floating about.

In the course of ten or fifteen minutes it was noticed that one of the lagoons was dotted over with granules varying from 2500 to 5000 $\mu\mu$. These were spaced with fair regularity 10-12,000 $\mu\mu$ apart. Each granule was executing a gentle dance-like movement, not exactly in time with its neighbours, but the movement of the company as a whole was smooth and even. Occasionally a granule would, without any apparent cause, make a complete change of place; but, as a rule, each granule confined its movements to the place proper to itself, never approaching within a certain distance of any of its neighbours.

Where the granules came from was not observed on the first occasion; there was so much to watch in the movements of the company that it was only incidentally noticed that, on a small lagoon adjoining that which was immediately under observation, and connected with it by an open channel, another company was gradually marshalling. This, which consisted of more uniformly sized units (these being nearer 2500 than 5000 $\mu\mu$), was more rhythmical in its movements and arrangement than the first and larger company. By the time that it had nearly filled the lagoon, it assumed a rounded outline, and the granules were arranged in lines with fair regularity. The

swelling of this company by additions from without coincided with a drawing closer to each other of the units. When this reached a certain degree of nearness—probably from 5000 to 7000 $\mu\mu$—the units ran together, and their individual movements ceased. Sometimes a united pair continued to move about till it was attached to another group. Sometimes individual units remained free, and even wandered off to groups forming outside the main combination. Meantime the company on the larger lagoon was drawing closer and closer, till the greater part of the units became fixed. Here, also, there was greater freedom both of movement and of selection of partners. After a few minutes the final adjustments had taken place in both companies, which attached themselves to the pellicle surrounding the lagoons.

In passing the other parts of the film under the field of vision, it was seen that other lagoons contained even larger companies of granules, some having come to rest and others still in course of formation.

Attention was now arrested by the general absorption which was going on of the pellicle by the larger granules and crystals, which were growing with great rapidity. The growth took place in two ways. In the first of these the crystal shot quickly into and along the edge of the pellicle, apparently absorbing the spicules, and growing obviously by this process. In the second case two or more large granules ran together, and then continued to feed unitedly on the spicules of the pellicle. Crystals as large as 20,000 to 40,000 $\mu\mu$ were formed with great rapidity. The complete absorption of the pellicle in this, as in a former operation, was a matter of comparatively few minutes.

When the surface was cleared of pellicle, it was seen

that the glass surface under the water was sprinkled thickly over with well-defined crystals. The larger groups of these remained floating on the surface, being made up of crystals of all sizes from 40,000 $\mu\mu$ down to 2500 $\mu\mu$.

Films produced by the Action of Gases on Metal Surfaces

The tarnishing of polished metals in a town atmosphere is due to the formation of a surface film generally of oxide or sulphide. These films always show a spicular or granular micro-structure. That they are aggregated in open formation is proved by the fact that they continue to grow in thickness so long as the surface is exposed. This means that the molecules of oxygen, water, and sulphuretted hydrogen can penetrate through the film and reach the metal surface below. Several features of interest were disclosed by the microscopic study of the formation of coloured films in tempering steel.

Oxide Films on Tempered Steel

The colours assumed by polished steel at gradually increasing temperatures were determined by floating small pieces of thin strip steel on the surface of a bath of mercury, the temperature of which was controlled by a high-temperature mercury thermometer. The temperature corresponding with each colour was first determined. These were :

235°	Straw colour.	290°	Purple-blue.
260°	Brown.	300°	Deep blue.
270°	Brown-purple.	305°	Bright blue.
275°	Deep purple.	307°	Pale blue.

At 235° a deep straw colour was reached in five minutes,

and no very obvious darkening occurred in thirty minutes. At 275° a deep purple was reached in ten minutes, and this changed to blue from the margin inwards during a further period of twenty minutes. At thirty minutes there was only a small patch of purple left in the centre, the rest of the surface being watch-spring blue.

It appears, therefore, that when the temper colours are used as an indication of the temperature of the steel, the element of time must be taken into consideration. The watch-spring blue, which is supposed to represent a temperature of about 300°, could actually be produced by continued heating at 275°. The oxygen molecules from the air continue to pass through the open formation of the film.

The straw-coloured films produced at about 235° are so thin and transparent that they act like a coloured lacquer, through which light is reflected from the polished metallic surface below. At 260° the film is still transparent all over, but it is now thicker, and its natural colour by transmitted light is a deeper red. At 270°-280° purple patches begin to appear. In these patches there is a blending of blue reflections from the surface of the thicker parts of the structure with the red light which is transmitted from below. When the whole film has become so thick that the transmitted light is cut off, only the pale blue reflected by the oxide is seen.

In Phillips' *Mineralogy* it is stated that specular iron ore, Fe_2O_3, is blood-red in thin lamellae, and in greater thicknesses has metallic lustre and a dark steel-grey colour by reflected light. The foregoing observations confirm this, and show further that the aggregations are in open formation, also that from the outset the structure is of the "spicular" type developed by surface tension.

Smoke Clouds and Films

The conditions of aggregation when a precipitate is formed at the common surface of two gases are very similar to those which prevail at the common surface of two liquids which form a solid precipitate when they meet and mix; but the much greater mobility of the gases makes it impossible to study the steps in the aggregation. If the smoke from a cigarette is watched as it rises in still air, and is illuminated by a beam of sunlight at right angles to the line of vision, the effect of convection currents and eddies on the forms assumed by clouds can be studied, and some idea may be formed of the effect of these rolling and vortex movements on the structure of the minute solid aggregates. For the microscopic examination of these aggregates it is necessary to resort to the films deposited on glass or other surfaces exposed to the clouds at the earliest stages in their formation.

This can readily be done by using the familiar method of preparing smoked glass by passing a warmed slip of glass back and forwards through the flame of a candle. Films of any thickness can be obtained in this way.

A film prepared in the manner indicated, which was of a clear uniform brown colour by transmitted light, was lightly scratched with a needle. At some points the scratch looked like a tear in a lightly felted fabric which had been built up in layers. The depth of the film, measured by focussing for the surface and then for the glass below, was 2300 $\mu\mu$.

Absolute alcohol was run over a part of the film drained off, and the film dried. The effect of this treatment was to shrink the film, and by oblique light it became more

brightly spicular, while by transmitted light it was more crisply granular. The shrinkage, measured at the dividing line between the shrunk and the unshrunk portion, was 2300 $\mu\mu$. The shrunk portion was too thin to measure by the focussing method, even with the 4 mm. lens. The granules in the shrunk portion measured about 1500 $\mu\mu$ in diameter with this lens. The elements of structure of the unshrunk film measured 800 $\mu\mu$, but these units had none of the solidity or depth of colour of the larger granules of the shrunk portion.

Fig. 35 is a photograph of the meeting-point of the shrunk and unshrunk portions by transmitted light, at a magnification of $\times 700$.

Neither from direct observation nor from the photograph is it possible to say definitely what is the nature of the openwork structure of these films. Careful examination of the scratched or scraped film suggests that the film is built up of superimposed layers of an openwork fabric. They are formed by allowing the luminous hydrocarbon flame to impinge on the relatively cool surface of the glass slip, which is covered with a condensed layer of air. The combustion gases roll over this surface, and in so doing are quickly cooled, depositing a thin open-work layer, which in turn becomes the condensing surface for another layer, and so on as long as the glass is passed backwards and forwards in the flame.

Magnesia Smoke Films

While these films are evidently in some sort of open formation, their appearance is very different from that of the smoke films. They also appear to be built up of

spheroidal elements, but the spheroids are of a more solid appearance, and their size is varied. Consider the formation of these films. The metal is raised to the ignition temperature, and continues to burn, thereby keeping up a temperature at which the metal is volatilised. Magnesium vapour encounters the mass of air which rushes into and past it. Here we have the formation of a solid magnesium oxide at the common surface of two masses of gas which are rapidly moving over each other and we may suppose that the solid particles are set in rotation; but in this case the conditions are different from those which exist in the gas smoke, for here the solid is produced at the highest temperature, and its separation does not depend on cooling. The effect of the rotation will therefore be more simply one of aggregation by accretion from without. Hence the varied size of the granules, which is no doubt determined by the length of time each particle has been in rotation before it is arrested at the condensing surface. The texture of a thin magnesia film by transmitted light is similar to that of an annealed silver or platinum film, and it appears just as continuous. The appearance of texture is caused by regularly distributed slight moulds or spicules. More or less thickly dotted over the surface there are more fully developed spheroidal granules which are sufficiently massive to appear dark by transmitted light. By the 12 mm. objective the small (relatively) dense granules measure about 1500 $\mu\mu$. The thinner units of spicular texture are rather smaller.

SECTION IV

COHESION AMONG MINUTE SOLID PARTICLES AND BETWEEN THESE PARTICLES AND FLAT SURFACES

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See PLATES XII. and XIII.

SECTION IV

COHESION AMONG MINUTE SOLID PARTICLES AND BETWEEN THESE PARTICLES AND FLAT SURFACES

Introductory

In the previous section it has been shown that cohesion and surface tension play a leading part in determining the form and texture of solid aggregates. This is the case not only in connexion with the transient production of a liquid or mobile phase by the flow resulting from mechanical disturbance [as in polishing and in the cold working of metals], but also in the precipitation of molecular aggregates at the surfaces of contact of gases with gases, gases with liquids, gases with solids, liquids with liquids, and liquids with solids. These effects of cohesion and surface tension have in some cases been demonstrated in aggregates so minute as to be on the limits of microscopic resolution.

The experimental observations described in this section are concerned with the effects of cohesion on relatively large molecular aggregates, the volume and weight of which can be measured or estimated with a fair degree of accuracy. If the preliminary conclusions from these observations are confirmed by further study, they may lead to a useful extension of the existing knowledge on this subject.

These observations and the photo-micrographs by which they are illustrated were made many years ago, the earliest notes being dated July 1908. A short paper on the subject was drafted in November 1911, but was held over till some further observations had been made.

The outbreak of war in 1914 led to the practical abandonment of all work on this subject, though a few observations were noted in January 1915. During the preparation of the present work the subject has been carefully reviewed, and the observations are now published for the first time.

Cohesion is the most Fundamental Endowment of Matter

During the past twenty years enormous strides have been made in the study of the ultimate structure of the atom, and in particular the experimental study of the disintegration of the radio-active elements has thrown an entirely new light on inter-atomic energy. This energy is now known to be of so high an order compared with the molecular forces as previously known, that many physicists have come to regard these latter as merely residual effects of the inter-atomic energy. However true this may be, the fact remains that in matter as we know it and as it affects our daily lives, cohesive force must always remain its most fundamental endowment.

Metal Filings adhere to the File and to the Mass which is filed

To metal workers it is a matter of everyday experience that when steel is being filed the filings become magnetic and tend to arrange themselves like a fringe along the edges of the file or of the piece of metal. When filing

pieces of gold and silver with a fine watchmaker's file, it was noticed that some of the filings adhered to the metal and to the file. Examination with a lens showed that the adhesion was quite general over the surfaces and edges, and did not in any way suggest the existence of magnetic polarity in the filings or metal. The metals being good conductors and well earthed, any electrical explanation of the phenomenon was also ruled out.

A few trials showed that only filings below a certain size adhered to the metal, also that gold and silver were quite interchangeable, and indeed that any kind of filings, if fine enough, would adhere not only to the surface of any metal but to glass or porcelain.

Fig. 36 is a polished silver plate, on which silver filings had been sprinkled. The plate was then turned upside down, so that the filings here shown had all been left adhering to and suspended from the polished surface.

Fig. 37 shows gold filings adhering near the point of a steel needle. The needle and the filings had both been freed from grease by washing with pure benzene.

Filings being of very irregular shape and size were quite unsuitable for a more careful study of this phenomenon, and attempts were therefore made to find some kind of particles more suitable for the purpose. Zinc dust, which is the fume condensed in the distillation of zinc, was examined under the microscope, and was found to consist of minute spherical globules like lead shot, but of a great variety of sizes. Attempts were made to separate the different sizes by levigation in absolute alcohol or benzene. This was only partially successful, as cohesion among the globules led to their aggregation in mixed masses made up of a variety of different sizes.

Zinc Globules adopted for more Accurate Observations

Fig. 38 shows the zinc globules left on a glass micro-slip, on which the levigated dust had been sprinkled, the slip being then turned upside down. The photograph was taken with the slip again reversed, so as to bring the groups of globules to the upper side. The illumination was from above by obliquely reflected light, and from below by reflection from the sub-stage mirror. Some of the globules were in direct contact with the glass surface, but a considerable proportion were only in contact with each other; the groups were therefore built up to a height (or depth) of several globules.

Under visual observation it was possible to follow the arrangement of the groups by focussing from top to bottom and by varying the incidence of the illumination from above and below. For the photograph, however, the best that could be done was to focus so as to give a moderate degree of sharpness from top to bottom.

In Fig. 39 the zinc globules were picked up on the edges of a thin steel blade. Fig. 40 is a direct photograph of a portion of the upper edge of the blade at a higher magnification. In the groups it is seen that the largest globules are not always in direct contact with the steel edge, but are linked up quite indifferently with their smaller neighbours. The diameter of these globules ranged from 0·033 mm. to 0·005 mm.

These photographs show the important part played by cohesion among comparatively large particles, even though their contacts with each other can be little more than point contacts. Each globule is a spherical aggregate of an enormous number of zinc molecules, the unbalanced cohesive

force of which is uniformly spread over the whole surface, so that when two spheres touch, or come within the range of the cohesive force, they adhere at the point of contact.

The Adhesion of Small Particles lends itself to open Packing

This obviously lends itself to the packing of the spheres in very open formation and throws light on the part played by the cohesive force in producing the great openness of packing, which is well recognised as a feature in fine powders.

It also throws light on the methods of aggregation in open formation, which are discussed in Section III., if it may be assumed that the individual molecules or small aggregates act under the influence of cohesion, as the globules do, and adhere when they touch at any point on their surface.

Powders produced by the grinding or precipitation of transparent substances do not lend themselves well to microscopic examination. Their irregularity of form and the absorption and scattering of light due to their transparence make it impossible to produce, either visually or in photographs, pictures which give any real indication of the state of aggregation of the particles.

Metal globules, on the other hand, are well adapted for the experimental study of this subject, owing to their opacity and to the fact that their diminutive size may permit gravity to be outweighed by cohesion, though still sufficiently large to be well within the resolving power of lenses of moderate magnification.

For the Measurement of the Cohesive Force Larger Globules of Gold and Silver were used

The zinc dust contained only a few particles which were too heavy to hang suspended from the glass surface, and these were of irregular form and could not be used to find the maximum size of globule which would hang suspended by cohesion. For this purpose gold and silver globules were made by melting fine filings distributed through calcined magnesia. In this way a proportion of the globules was obtained as well formed spheres. In January 1915 copper globules were obtained by spraying molten copper in a chemical works spraying burner. These globules were too small for final suspension tests, but their dimensions are included in the following table, in which are given the diameters of all the gold, silver, and zinc globules which were used in these experiments, and opposite each it is stated whether or not it hung suspended from the underside of the glass slip.

MEASUREMENT OF GLOBULES BY EYE-PIECE MICROMETER

Zinc.	0·033 mm.	Hung from glass surface.
	0·015 mm.	,, ,, ,, ,,
	0·007 mm.	,, ,, ,, ,,
	0·005 mm.	,, ,, ,, ,,
Gold.	0·222 mm.	Did not hang.
	0·193 mm.	,, ,, ,,
	0·165 mm.	,, ,, ,,
	0·113 mm.	Hung from glass surface.
	0·100 mm.	,, ,, ,, ,,
	0·088 mm.	,, ,, ,, ,,
Silver.	0·313 mm.	Did not hang.
	0·165 mm.	Hung from glass surface.
	0·132 mm.	,, ,, ,, ,,
	0·110 mm.	,, ,, ,, ,,

Silver.	0·094 mm.	Hung from glass surface.
	0·082 mm.	,, ,, ,, ,,
	0·077 mm.	,, ,, ,, ,,
	0·072 mm.	,, ,, ,, ,,
Copper.	0·099 mm.	Hung from glass surface.
	0·082 mm.	,, ,, ,, ,,
	0·055 mm.	,, ,, ,, ,,

The largest gold globule which hung suspended from the glass surface had a diameter of 0·113 mm.; its volume therefore was 0·000756 mm.^{3}. Assuming the density of gold to be 19·5, this globule would weigh 0·0000147 gram.

Measurement of Cohesion between Globules and Glass Surface

The cohesion tests were made by placing the globules on a glass micro-slip, which had been carefully cleaned and polished. A few drops of pure benzene were flowed over the globules and the glass, and were rapidly drained off by absorption with filter-paper. After the benzene had completely evaporated, the slip was slightly warmed to ensure that no moisture had condensed during the evaporation of the benzene. The slip was then turned upside down on the open stage of the microscope. The globules which remained in suspension were examined through the glass slip by objectives of various powers, and were measured by the eye-piece micrometer. Even with lenses of the highest resolving power no surface of optical contact between the metal and the glass could be detected.

Assumptions as to Area of Contact

To calculate the cohesive force between the gold and the glass some assumption has to be made as to the area

over which the cohesive force is acting. For this purpose four different areas of contact have been assumed, namely, 10,000, 2500, 1000, and 400 $\mu\mu^2$, or circles of approximately 113 $\mu\mu$, 56 $\mu\mu$, 36 $\mu\mu$, and 23 $\mu\mu$ diameter. The weight supported per mm.^{2} is obtained by multiplying the weight of the globule by the ratio of the area of contact to the area of 1 mm.^{2}. Taking the weight of the globule as 0·0000147 gram, the weight supported in each of the four cases would be equivalent to :

1. 1·47 kilograms per sq. mm. or 0·93 tons per sq. inch.
2. 5·88 ,, ,, ,, ,, or 3·72 ,, ,, ,, ,,
3. 14·7 ,, ,, ,, ,, or 9·33 ,, ,, ,, ,,
4. 36·75 ,, ,, ,, ,, or 23·32 ,, ,, ,, ,,

Cohesion of Gold based on Tests of Tenacity

Though the tensile strength of gold in the massive state is known, the absolute cohesion of its molecules is not known. In the ductile metals, fracture under tensile stress is always preceded by flow of the molecular units over each other as in a viscous liquid, and the fractured ends of the test-piece always show that this flow persists till the actual parting takes place. This subject is dealt with at considerable length in Section VII., and it is shown that, even after a wire has been drawn down till the crystal grains have been reduced to fine fibres embedded in metal in the vitreous or hardest state, flow still occurs at the point of fracture, Fig. 96.

In this condition the tensile strength of pure gold at 15° C. was found to be 15·6 tons per square inch.

When the temperature during the test was reduced to −180° C., the tenacity rose to 22·4 tons per square inch, but the fractured ends still showed that flow had occurred

at the point of fracture. From this it is evident that the latter figure still falls short of the direct cohesive force which would be exercised if all the molecules in the cross section were axially in touch, and were all pulled apart at the same moment, as is the case when hardened steel is pulled apart. It seems probable, therefore, that the molecular cohesion of gold is of a higher order than is indicated by ordinary tensile tests.

It must be borne in mind, however, that in these experiments the cohesion is that between gold and glass. This combination was used mainly because of the convenience for observational purposes of a transparent suspending plate, but there were indications during these inquiries that the cohesion between metal and metal was higher than between metal and glass.

Effect of Films of Condensed Gas on the Cohering Surfaces

Further experiments are needed to show whether, and to what extent, the effective contact area is affected by the presence of the layer of condensed gas which always exists on clean, dry, solid surfaces. It is believed that actual moisture on the glass and on the globules was got rid of by heating the glass slip with the globules immediately before the suspension tests. In some cases a temperature of 200° to 300° C. was used, which would also drive off or seriously reduce the layer of condensed gas. The glass slip on which the copper globules were tested was heated on an electrical hot plate to 200° C., and was turned upside down while hot. Some of the globules remained suspended from the underside, the diameter of the largest of these being 0·083 mm.

With the object of getting rid of the surface gas film, zinc globules were heated till they began to volatilise, and were immediately submerged in pure benzene. Under the microscope the submerged globules still stuck together and tended to pile up in open formation, though not to the same extent as in air. This reduced effect is not surprising, as the interposition of the mobile liquid molecules of benzene seems likely to reduce the effective cohesion between the globules among themselves.

Brass Filings under Benzene so as to exclude Air Films

To exclude the possibility of the minute metal particles being covered by a gas film, a new watchmaker's file was thoroughly cleaned by benzene, and was then completely submerged under benzene in a shallow open tray, and brass filings were produced by rubbing the edge of a strip of the metal over the surface of the file. As the filings were produced under the benzene and completely out of contact with air, it is justifiable to conclude that the possibility of gas films had been eliminated. The filings, still completely submerged, were swept by a fine sable brush into a small glass bottle, which had been completely filled with benzene. The finest of the filings still adhered to the sides and bottom of the bottle. The larger filings, which would have adhered in the dry, hot state to the glass surface, did not adhere, so that in this case also the presence of the benzene evidently reduces, but does not do away with, the effect of cohesion.

SECTION V

POLISH IS THE RESULT OF SURFACE FLOW

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See PLATES XIV., XV., XVI., XVII., XVIII., XIX., XX., XXI., XXII., XXIII.

SECTION V

POLISH IS THE RESULT OF SURFACE FLOW.

HAVING studied in some detail the influence of surface tension on the aggregation of molecules of various conditions of mobility, the particular kind of mobility which is conferred on the molecules of a solid by various forms of mechanical disturbance, *e.g.* cutting, grinding, and polishing, will now be considered.

The "Scratching Test" of the Mineralogist as a General Means of classifying the Resistance of Solids to Surface Disturbance

A surface may be disturbed in various ways when a moving point, made of some material harder than itself, is passed over it. The surface of the greater number of solids can be "scratched" or "ploughed" by the point of a hardened steel needle, and the number of substances which cannot be scratched or ploughed by a diamond point is exceedingly small. To the mineralogist the scratching test conveys a great deal of information by which he is enabled to classify mineral substances of every type. "Softness" combined either with tenacity or with friability, at one end of the scale, and the corresponding qualities associated with "hardness" at its other end, can

provide a sufficiently extensive series of pigeon-holes for the reception of every kind of mineral, from metallic gold or soap-stone at one end of the scale, to the diamond or corundum at the other.

The New Theory of Polishing applies to Most Types of Solids

In every one of these substances, if it is sufficiently homogeneous to be polished at all, the fundamental principles on which polishing depends are absolutely identical. This may be supplemented by another statement: *The polished surface on a solid substance is as truly due to the presence of a surface tension skin as is the surface of a liquid.*

These two propositions on the theory of polishing are based on observations which have been made on the effects of mechanical disturbance on the surface structure of a great variety of solids. The evidence justifying these statements will now be considered.

Action of Files and Cutting Tools on Metal Surfaces

When a soft metal like silver is filed, even a very casual inspection of the surface shows that it has been ploughed into ridges and furrows by the projecting points of the file. If the file cuts are fine, there is nothing in the appearance of the surface to show that any abrupt breaks in the regular removal of the metal have occurred. But, if a coarser file is used, there is evidence of the tearing out of metal in irregular pieces, and the ridges and furrows are far from smooth. The ridges and furrows on a cut surface of lead are shown on Fig. 32, Plate X.

The ploughing effect in soft metals is so familiar that

it might readily pass without arousing any special interest or any idea that its existence called for a more intimate explanation. The convenient statement that softness and toughness are intrinsic properties of these metals, and that ploughing and smearing are, therefore, a natural response to the mechanical treatment by tools or abrasives, does not necessarily strike us as unsatisfying, but this as an explanation is bound to appear less and less satisfactory if the attempt is made to apply it to hard and brittle substances, in which the qualities of softness and toughness are conspicuously absent.

Speculum Metal

Speculum metal gets its name from the fact that it was found to be a peculiarly suitable material for the manufacture of mirrors for telescopes and other optical appliances. It is an alloy of copper and tin, and it is so hard and brittle that it cannot be worked by ordinary tools. In some states it is as brittle as glass, and can easily be shattered by a blow with a hammer, yet it is a remarkably easy substance to polish. Herschel, who had great experience in the grinding and polishing of mirrors for astronomical telescopes, believed that these two operations were identical, polishing being merely a finer kind of grinding. His idea was that the essential feature of polishing was the gradual flattening of the surface by the removal of material. This is an exact description of the operation of grinding, but the essential feature of the polishing operations is left out. What this essential feature really is will be made clear by the following illustrations.

Fig. 41, Plate XIV., shows the surface of a block of speculum metal, across which a scratch had been drawn with the point of a very fine needle; the width of the scratch was about $\frac{1}{75}$ of a millimetre, or the $\frac{1}{1800}$th of an inch. The surface was then polished on the finest emery-paper across the scratch. The scratch has acted as a trench, in which the shavings ploughed out by the emery have been intercepted and are seen in a heap, the top of which nearly reaches the surface level, and is in fairly good focus. It is seen that these " shavings " are really rounded bodies, which are more like drops than like shavings or turnings.

Fig. 42 shows the effect of polishing the speculum metal on rouged leather across the line of the emery furrows. This is somewhat striking. The extremely fine particles of rouge appear to have gripped the surface layer all over simultaneously, and to have flowed and dragged it across the emery furrows, partly filling them up and partly bridging them over. The flattening of the surface brings into view the outlines of the crystalline grains of which the metal is built up.

Fig. 43 shows the effect of further polishing, still in the same direction, on the rouged leather. The emery furrows have now been completely flowed away, and a smooth layer has spread over the whole surface. Owing to their greater hardness, the crystalline grains have been left slightly in relief, the intergranular spaces containing a softer eutectic having been worn down to a lower level.

Fig. 44 shows the same surface, after treatment with a solution of potassium cyanide, which has dissolved away the flowed layer and fully disclosed the crystalline structure

below. The next photograph, Fig. 45, shows the surface layer again restored by polishing.

This series of photographs demonstrates very clearly the spreading of a definite layer over the surface by polishing and its removal by a solvent.

The extreme readiness with which the surface of speculum metal can be flowed, in spite of its hard and brittle character, at once explains why this alloy lends itself so admirably to the making of highly polished mirrors.

Speculum metal being an alloy, it might be supposed that in its case the effects of flow to some extent depend on the presence of the eutectic in which the crystalline grains are imbedded. That this is not the cause of surface flow in the crystalline metal was clearly shown when the foregoing experiments were repeated, using instead of speculum metal a piece broken from a large crystal of pure antimony.

Antimony

For the polishing experiments a portion from a well-developed crystal of antimony was selected. One of its faces was smoothed by rubbing it to and fro on a very fine file, but the metal was so brittle and fragile that it splintered very badly during the filing. It was then rubbed on the finest emery-paper, and, while it still splintered, some portions of the surface were ploughed with comparatively smooth furrows. Fig. 46 shows the antimony surface as it was left after polishing on emery. The larger of the pits left by the splintering are still visible as rough angular gaps, but the outlines of the smaller pits are closing in and rounding under the surface flow caused by the emery. The specimen was next rubbed across the line of the emery

scratches on a polishing block covered with wash-leather sprinkled with the finest rouge. Fig. 47 shows the surface at this stage. As in the case of speculum metal, the rouged leather appears to have seized the upper layer of molecules and pulled it over the surface like a skin. The remarkable effect of roofing over the ridges and furrows is well seen. In some cases the line of the furrow can only be traced by the row of holes in the covering film. The forms and dispositions of the holes in the layer exactly resemble the holes which one would expect to find in spreading a viscous paint or varnish over an irregularly furrowed surface. The smoothing of the surface in the antimony is mainly due to this roofing over effect of the viscous layer, while in the speculum metal the whole of the substance of the ridges appeared to be ultimately flowed down, and the furrows were really obliterated, not disguised.

When this surface was etched with a solution of potassium cyanide the surface skin was removed, and the furrows and ridges were again exposed (Fig. 48). The impression conveyed by the preceding photograph, Fig. 47, is confirmed, namely, that the ridges and furrows had been covered over, not entirely levelled down or removed.

Flowed Surface Film covers Pits

In examining the specimen under the microscope, the attention was arrested by a curious appearance presented by two of the pits on the surface, which appeared as if covered over with a film of greatly diminished reflecting power as compared with the rest of the surface. A search over other parts of the surface disclosed a number of

similar pits, which showed the covering film with greater distinctness. A group of these pits is shown on Fig. 49, in which the surface markings can be traced across the film over the pit. The photographs, Fig. 50, show a very large pit on an unetched part of the surface in process of being covered over by the flowed surface layer. The viscous appearance of the film as it spread out from the edge of the pit is in harmony with the equally suggestive appearances of the other photographs. It is difficult to believe that the flowing metal could be carried across the pits from side to side without the help of some support from below, yet evidence has been obtained that, in the case of the smaller pits at all events, the film is carried across the pits without any support. Figs. 52 and 53 are enlargements of Figs. 49 and 50.

It may safely be predicted that any one seeing these photographs for the first time, and knowing nothing about their origin, would without doubt believe that he was looking at a layer which had been painted across a surface while the material was in the condition of a viscous fluid. If this observer was told that the viscous-looking surface layer was in reality a substance (antimony) so brittle and fragile that it could easily be reduced to a fine powder in an ordinary pestle and mortar, and that it could not be filed with the finest watchmaker's file without splintering, he might be justified in considering that he was being treated to some ingenious paradox, and it would only tend to heighten this sense of paradox if he were further shown that this viscous-looking layer was even harder than the original material, so that it formed an enamel-like protective coating over the more fragile material below.

The paradox appears to have only one possible solution,

namely, that what *appeared* to have happened really *had* happened, and that we must take it as established that the surface layer had for a brief period been in the liquid condition. Further, as the surface film in its final state differed most markedly in its physical properties from the original crystalline antimony, it must be accepted that, in the metal in its final form, this flowed film is to be regarded as in a perfectly distinct state or condition from the original substance. If these conclusions are correct, then the observations on surface flow have led us to recognise that a crystalline solid can by mechanical disturbance be made to pass through an intermediate mobile state into a vitreous or non-crystalline state. So important a conclusion could hardly be made of general application till it had been proved experimentally with a great variety of substances; but these observations have been repeated in a variety of ways on many different substances, so that now it can be stated with confidence that the above conclusions can be applied quite generally.

Transparence of the Surface Film in Metals

When the foregoing experiments were made in 1903, it was suggested that the diminished reflecting power of the film covering the pits probably indicated that it had become translucent, but no direct evidence of this translucence was afforded by these particular observations. Neither could it be established from these experiments whether the film was carried across the pits on a support provided by small granules or flakes, which had filled up the pit to the level of the general surface, or whether the film was carried across without any support from below. The

following experiments on copper made in 1914 definitely show:

(1) That the film which covers the pits is transparent, or at any rate highly translucent; and

(2) That in the case of the smaller pits the mobile film has been carried across the empty pit without any support from below.

In the casting and working of copper, unless certain precautions are taken, the metal is always more or less spongy, owing to the presence of gas bubbles. When the surface of this metal is ground and polished, some of the gas bubbles are laid open and appear on the surface as tiny pits. If the cast metal has been subjected to cold working, by rolling or otherwise, the larger bubbles are distorted and take elongated and other varied forms. By any method of polishing which will give a fair surface the pits are flowed over and obliterated, but by carefully regulated etching it is possible to remove the surface layer step by step, and the film covering the pits can be reduced to extreme thinness. Through this thin film one seems to be looking right into the pits.

In polishing metal surfaces the amount of the metal which is removed by the polishing agent can be varied through wide limits under certain conditions. By suitable methods the skin developed on the surface may be raised to a maximum thickness or reduced to a minimum. For the present purpose it was desirable that the skin produced should be as thin as possible.

The copper used in these experiments received its final polishing on fine linen stretched over a hard flat surface and moistened with one of the ordinary commercial brass polishing liquids. On the copper surface prepared in this

way the pits, as seen under high magnification, appear as blue spots on a pale rose-coloured ground of the solid metal. While some of the film-covered pits appear uniformly blue, others show patches of red at various parts of their surface. When these red patches were first noticed it was supposed that they indicated a thickening of the film at these points to the extent necessary for normal reflection. More careful study has shown that the red patches are due to reflections from the inner concave surface of the pit. The beam of light from the vertical illuminator behind the back lens of the object-glass of the microscope passes through the film covering the pit, strikes the concave metallic surface, and is reflected back through the film to the object-glass and thence to the eye-piece. The reflecting surface of the pits is evidently far from optical perfection, and the reflected beam is therefore more or less broken up by its irregularities.

By the use of autochrome plates it has been possible to obtain high-power photo-micrographs in natural colours of pits on a copper surface. Four of these transparencies have been reproduced by the three-colour process and are shown in Figs. 54, 55, 56, and 57.

Figs. 54 and 55 are at a magnification of 800 diameters, and Figs. 56 and 57 at 1800 diameters. In Figs. 54 and 56 the pits are covered with a blue film, but show patches of red on the blue. Figs. 55 and 57 show the same pits after the film has been dissolved and removed by a 10 per cent solution of ammonium persulphate, acting for 20 to 30 seconds. On comparing the members of each pair, 54 with 55 and 56 with 57, it is seen that the red patches in 54 and 56 correspond with the spots of light reflected from the concave surfaces of the uncovered pits, as shown in 55

and 57. It is clear that the pits which show these reflections from the under surface must have been practically empty when they were covered by the film, so that the film during its flow was quite unsupported from below.

The thickness of the films covering the pits is probably of the order of 10 to 20 micro-millimetres.

Surface Flow in Calcite

The following observations deal with surface flow in a substance of a totally different character from the metals or alloys. Calcium carbonate occurs in nature as the beautiful crystalline mineral calc-spar, or Iceland-spar. These crystals are familiar to the optical physicist, to whom their doubly refracting property, combined with their transparence and freedom from colour, has made them invaluable. For other reasons calc-spar has been of great value in researches on surface flow. By careful selection it is possible to find crystals which, by cleavage, can be made to give surfaces of high natural polish, and, as the operation of cleavage can be carried out so as to avoid any rubbing of the cleft surfaces, it is possible in this way to obtain surfaces which are crystalline close up to their outside layers of molecules. It is obvious that surfaces of this description are very valuable for purposes of comparison with those which have been artificially polished or otherwise prepared. Further, calcite is anhydrous and infusible, so that there can be no question that the fluid condition of the surface molecules is neither due to their solution in water of crystallisation, nor to the reduction of the melting-point of the substance by pressure.

Structure disclosed by etching a New Cleavage Surface before and after Gentle Polishing

A crystal of Iceland-spar was split so as to present a fresh smooth face which had never been touched or rubbed in any way. A small drop of very dilute hydrochloric acid (containing about 0·2 per cent of HCl) was placed on this fresh face, and after 10 to 15 seconds was removed by touching the spot with a torn edge of soft filter-paper. The liquid tends to spread over the face in all directions, no doubt owing to the perfect freedom from dust and grease of the surface ; but, as far as possible, it is desirable to confine the etching action to one spot, so that a comparison between the etched and unetched portions may be more readily made. Slight etching resulted from the treatment, but the etched surface, though slightly undulating and irregular, showed no new structure or markings. When the experiment is repeated a number of times, it is generally found that the surface, though slightly lower where the acid acted, is otherwise unaltered. A fresh cleavage face of the crystal was now firmly stroked a few times in one direction with the point of the forefinger covered with clean soft wash-leather. Under the microscope and illuminated by an intense oblique beam, no change could be detected. The surface remains to all appearances unaltered. A drop of dilute acid was placed on a part of the stroked face. The drop flattened to a hemisphere, but did not spread. After 10 to 15 seconds it was removed as before. The pit produced had well-defined edges, and the flat bottom was covered with furrows and ridges running in the direction of the strokes with the finger. Fig. 51, Plate XV., shows a crystal which has been treated in this way. Two etched

pits are shown, the larger of which was about two millimetres in diameter. The magnification is very small, as the object of this photograph is only to show the general appearance of these pits in relation to the crystal face as a whole. This experiment was repeated in a variety of ways, and on all of the three parallel sets of faces. The direction of the strokes was varied, so as to make a number of different angles with the cleavages. In every case the result was the same, even a single stroke showed unmistakably on the etched surface. Fig. 58, which is at a magnification of 215, necessarily takes in only a small portion of the unetched surface, close to the edge of the etched pit. The unetched portion has a smooth glass-like surface ; only a few faint scratches being visible under the most searching examination. Faint cleavage lines crossing the face indicate that the stroking had not been parallel with any of the natural cleavages. Fig. 59 is a photograph of a portion of the same surface at a higher magnification. The number and depth of the flow lines are influenced by the amount of the stroking and by the pressure exerted by the finger. Flow lines were distinctly developed by a single stroke in which, it was roughly estimated, the pressure exerted did not exceed 4 lb. per square inch. In this case the flow lines were obviously fewer than they were when a number of strokes had been given.

Some indication of the depth to which the molecular disturbance has penetrated is given by the additional time required for the acid to dissolve and remove all traces of the disturbance. If the acid is left on the surface for a sufficiently long time, for instance with the acid in question, for 30 to 60 seconds, no trace of the flow lines remains, and the etched surface presents the same appearance as the

etched surface of an untouched face, the limits of the disturbance having been reached. The depth to which the disturbance penetrates is not much affected by continued stroking. The influence of the stroking is therefore limited to a very thin surface film, but within this limit it is quite unmistakable. If a stroked and etched surface is further stroked, its details become rounded and glazed over.

The evidence of surface flow afforded by these experiments on calc-spar is even more striking than that derived from the similar experiments on metals. Not merely the slightness of the mechanical disturbance which causes the flow, but the nature of the material in which the flow is caused, impart to this experiment a special interest and value.

In the case of calc-spar we may fairly suppose that the number of molecules which are removed on the polishing leather is small compared with the number which compose the mobile surface layer. In polishing metals there is often a considerable quantity of the metal removed by the polishing agent, as, for instance, even the finest emery becomes quickly clogged with metal removed from the surface, while rouged leather becomes discoloured from the same cause. In the case of the emery, the tool edge, or the file, it seems probable that the flowing is caused by the seizing of the metal of the surface by the metal which is lifted by the tool, or ploughing agent, and moves over the surface with it. When the final polishing stage is reached, the whole, or at any rate a large part of the surface, is flowed at the same instant, otherwise it would afterwards show striation or rippling. A freedom of movement has been conferred on the molecules which enables

them to behave like liquid molecules. This freedom lasts only so long as the molecules are moving over each other under the action of the polishing agent. When the movement ceases, we must assume that the freedom also ceases, but not before the molecular attraction has drawn the surface into a continuous covering skin, comparable in smoothness with the surface of a liquid. In the case of the calc-spar rubbed by leather, the under surface revealed by the etching shows unmistakable signs of furrowing, but the unetched surface is perfectly smooth, with the smoothness of a liquid surface. It has been proved that the finer furrowing is caused by fibres of the leather, but it seems likely that the deeper furrowing is caused by minute fragments detached from the crystal and carried along through the liquid-like surface film; *in either case it is equally certain that the surface layer can only close over and mask the effects of the furrowing if it has been in a state of complete fluidity for a measurable depth and for a finite period after the externally caused movement has ceased.*

We may form a mental picture of the operation at the moment when the external movement ceases and the unopposed molecular attraction assumes command, maintaining the movement till the molecules have reached the more stable equilibrium of a continuous surface skin. Where the ploughing action has extended deeper than the range of the molecular attraction, the ridges and furrows remain, only their surface being covered with a film left by the moving molecules. In the case of a brittle metal like antimony, the liquid layer probably carries along with it such portions of the metal as have themselves escaped the flowing action, and have remained therefore as aggregates of solid molecules. Any considerable mixture of

such solid aggregates will make the flowing layer more pasty and less perfectly fluid.

Two distinct facts are brought out by these observations. The first is that, by mechanical disturbance, a considerable amount of freedom of movement is conferred on the solid molecules. The second is, that the molecules, when in this state of freedom, are under the control of the molecular attraction which determines the forms assumed by the mass of freed molecules at the moment when their freedom is about to cease, through the withdrawal of the externally applied force. The forms assumed by the surface are determined, as in a viscous fluid, by surface tension.

Attention has already been drawn to the fact that some idea of the depth to which the disturbance has penetrated, and the thickness of the resulting flowed layer to which it gives rise, can be obtained by the time required for the acid to dissolve and remove all traces of this layer. As experience was gained in the exploration of surfaces by means of step-by-step etching it was felt that this method was capable of considerable development, and that it could be used to determine the thickness of this surface layer with a fair amount of confidence.

Exploration of the Surface Layer by means of Step-by-Step Etching

In the method which was adopted small drops of uniform size, and containing known quantities of hydrochloric acid, were placed on the polished surface, and were allowed to remain there till the acid had dissolved all the calcium carbonate it could take up. The drop was then washed off, first with water and then with absolute alcohol.

The weight of the calcium carbonate removed was calculated on the assumption that the whole of the HCl in the drop was converted into calcium chloride. The density of the calcium carbonate was taken to be that of calcite -2·75—though it is probable that the density of the polished layer is considerably greater than this. The area of the surface acted on by the drop was measured, and from this the thickness of the layer dissolved by the acid was calculated. Microscopic examination showed that, with all but the most dilute solutions of acid, the amount of carbonate removed was fairly uniform over the whole area over which the drop spread. The strength of the acid used ranged from 0·2 to 0·000125 per cent HCl; the weaker acids were made directly by dilution from the stronger. It was noticed that the more dilute acids lost a part of their solvent power if they were left standing overnight in glass flasks or bottles; the tests were, therefore, always made with freshly prepared dilutions. It seems probable that the errors involved in this method all tend to cause the calculated effects of the removal of calcium carbonate to be in excess of the actual effects, the error being greater as the higher dilutions are reached. This is of special interest in connexion with the determination of the minimum depth of disturbance which could be detected by the microscope, as in this case the calculated thickness of the layer removed is practically certain to be a maximum figure. Experiments were made by applying successive drops of acid to the same spot on the polished surface, and some interesting observations were made in this way, but in the most complete series of experiments the drops of the different dilutions were placed on fresh parts of the surface. The pits so produced were carefully explored by

the microscope, using objectives of various resolving powers, and with different means of illumination.

The etching was made in the first instance with solutions in a descending scale of acidity, the series being pushed as quickly as possible towards the farthest point at which any visible alteration of the polished surface could be detected. When a condensed beam of sunlight was used to give the oblique illumination of the surface, it was possible to detect the effect of a drop of acid which contained only 0·000125 per cent of HCl. The depth of the layer removed by this drop did not exceed 0·62 $\mu\mu$. This pit could be seen, though not very distinctly, by illuminating the spot by the critical image of a Nernst filament. Illumination by the nearly critical image of the sun showed the whole surface of the pit brilliantly spicular and of a sky-blue colour. If it is correct to assume that the solvent effect of the acid was uniformly distributed over the whole surface of the pit, then it follows that a roughening of the surface not more than two molecules in depth has been detected.

The results of the step-by-step etching are summarised in tabular form on page 99.

The acidity of the solvent is given in fractions of 1 per cent of HCl.

The depth of the layer is given in $\mu\mu$. $1\ \mu\mu = 10^{-6}$ mm. The diameter of the $CaCO_3$ molecules is taken as approximately 0·3 $\mu\mu$.

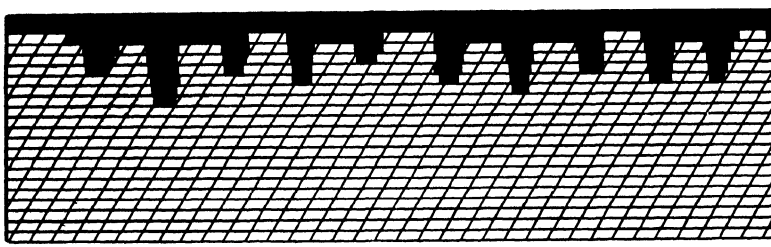
The adoption of the latter figure in 1909, when these observations were first published, is justified by Professor W. L. Bragg's measurements of the atomic groups of which the calcite crystal is built up (Sec. I. p. 12); for he states that, to remove one complete sheet of molecules

from the 100 face of a calcite crystal, the solvent would have to dissolve away 0·303 $\mu\mu$.

HCl per cent.	Depth of Layer in $\mu\mu$.	Number of Molecules in thickness.	Illumination by an intense incident beam at an angle of 30° with the surface.	Illumination by a slightly oblique beam of transmitted light.	Scratches across the Field.
0·000125	0·62	2	Distinct spicular appearance on a deep sky-blue ground.	No visible structure even with an objective of N.A. 0·95 and magnification ×700.	A few accidental scratches
0·00025	1·25	4	The same.	The same.	The same.
0·0005	2·50	8	Brilliant spicular appearance.	The same.	The same.
0·001	5·00	16	The same, but more distinctly granular.	The same.	The same.
0·002	10·00	32	The same; oblong granular, across the flow lines.	Flow lines faintly visible.	The same.
0·005	25·00	80	The same; granules larger.	Flow lines more distinct.	The same.
0·01	50·00	160	The same.	The same, with granular texture.	Regular scratches appear.
0·02	100·00	320	The same; spicular layer disappearing.	Scratches becoming uncovered.	Over 200.
0·05	250·00	800	Spicular appearance only on edge of scratches.	Disturbance confined to scratches.	Over 100.
0·10	500·00	1600	The same.	The same, but fewer scratches.	About 30.
0·20	1000·00	3200	The same.	A few scratches in the undisturbed lamellae, their sides partly etched into rounded forms, and partly broken up and splintered.	

These results show that the mechanical disturbance caused by the polishing agent penetrates to a depth of 500 to 1000 $\mu\mu$. Fig. 60 shows the untouched skin and the under surface at 500 and 1000 $\mu\mu$.

At this depth the disturbance consists mainly of the deeper scratches or furrows which have been ploughed or broken through the thin lamellae of which the crystal is built up. Fig. 61 shows the deeper scratches at a higher magnification. This ploughing has so completely flowed the crystalline substance that the scratches and furrows have been perfectly healed over, and no traces of them are disclosed, even when a powerful beam of light is thrown across the surface. Yet the action of the solvent acid enables us to follow with the utmost minuteness the lines of disturbance and flow. Fig. 62 shows the finer flow-lines



Diagrammatic Section of a Calcite Plate across the line of flow. The flowed material has completely filled up even the deepest scratches.

at a depth of 100 to 150 $\mu\mu$ below the surface. As the surface is approached there is no trace even of the remains of broken-up lamellae, and the appearance is absolutely vitreous and homogeneous, like a coating of varnish or enamel.

The flow-lines on Fig. 62 correspond in size with minute convex projections with which the individual hairs of the wash leather are covered, namely, about 1500 $\mu\mu$.

Increased Hardness of the Flowed Surface

Tested by the loaded needle, the surface is harder and more tenacious than the original undisturbed face of the

crystal. This greater hardness and tenacity became more evident as practical experience in polishing calcite was accumulated. It was found that the resistance of the surface layer to the finer abrasives increased as the polishing proceeded. After a surface skin has been fully developed by polishing, it is able to resist the cutting action of the powders by which the surface had been satisfactorily ground at an earlier stage. It happens not infrequently that the polished surface is spoilt by accidental scratching just when it has reached the final stage. When this occurs, it is useless to attempt to repolish it by going back only a few stages. In most cases there is no alternative but to clear off the whole skin, and to start again from the beginning. When clearing off this skin, one is made to realise how thoroughly its properties differ from those of the natural crystal surface.

The increased hardness and tenacity of the surface skin is believed to be due to the sudden breaking down of the crystalline units into a mobile or liquid state, which immediately congeals into a vitreous solid in which the capacity for further flow is enormously reduced. In this new and harder state molecular movement of the surface still occurs on polishing, but it is confined to a layer only a few molecules in depth, and the flow is so limited that surface scratches and irregularities are no longer obliterated by it. The difficulty of finishing off a calcite surface with a really fine polish is very great, and is largely due to this cause, for the longer the surface is polished the less capable it becomes of flowing into a true liquid-like skin. The most perfect surface microscopically is obtained when a perfectly fresh cleavage face is lightly polished by the finger, covered with a soft chamois leather.

One of the most significant features of this investigation is that the molecular mobility is not confined to a few molecules on the surface, but has followed wherever disturbance has taken place. The deeper scratches can hardly have resulted directly from the passage of the soft fibres of the leather; their appearance suggests rather that they have been made by fragments of crystal dragged along by these fibres. When we come to examine the results of internal deformation in metals, it will be well to keep in mind this evidence that transmitted movements within the mass cause a remarkably free production of mobility. From this we gain an insight into the part which a simultaneous breakdown of a number of crystalline elements of structure may play in this production.

Parallel Growth of Sodium Nitrate on Calcite

The researches of Mr. C. V. Barker on " The Formation of Regular Growths of Crystals of one Substance upon those of another " (*Journ. Chem. Soc.*, 1906, vol. 89, p. 1120) have given a new interest to certain of these observations on the formation and structure of polished surfaces.

He found that, when a cleavage face of calcite was polished by the method already described, it did not interfere with the parallel growth of sodium nitrate crystals on the polished surface. These experiments were repeated, and my observations fully confirmed those of Mr. Barker, for parallel growths were readily obtained, not merely on faces which had been lightly polished by gently rubbing with clean soft chamois leather, but also on faces which had been polished by the more drastic processes of grinding and polishing with abrasive and polishing powders.

These parallel growths of sodium nitrate can be easily obtained as follows. Alcohol is added to a strong solution of the nitrate till a crystalline precipitate separates, and a very thin layer of the mixture is spread on the calcite surface by wiping it with a camel-hair brush, or a fine cloth which has been dipped in the solution. This layer dries rapidly and leaves a thin coating of the salt on the calcite surface. The coated surface is next breathed on, and the crystals dissolve. As the moisture evaporates the sodium nitrate deposits as minute rhombs in parallel order, showing that its molecules are similarly oriented to those of the calcite. Fig. 63 is a general view of the parallel growth of sodium nitrate crystals on a polished calcite surface. Fig. 64 shows a very thin layer of sodium nitrate which has solidified partly under the orienting influence of the crystal and partly under surface tension. Fig. 65 shows the parallel growth on an etched calcite surface on which the deeper flow-lines are still visible.

Observations have shown that polishing develops over the crystal surface a true skin, the substance of which is, in various respects, profoundly different from the crystal substance from which it has been produced. Whatever hypothesis may be put forward as to the intimate nature of this change of structure, there can be no doubt as to the reality of the change. There appears also to be no room for doubt that the liquid-like surface of the outermost layer of the skin, on which the perfection of the polish depends, is due to the fact that this layer has passed through a liquid state, and has solidified under the influence of surface tension. There is abundant evidence to show that the aggregation of molecules at a surface can be so completely controlled by cohesion that crystalline orienta-

tion cannot occur. On this profoundly altered skin, with its smooth liquid-like surface, it has been found that the crystalline influence of the calcite is still sufficient to cause crystals of sodium nitrate to deposit in parallel order, that is, with their molecules similarly oriented to those of the crystal as a whole.

Whether the orienting influence could make itself felt through layers of other indifferent substances was also investigated. Films of gold and of platinum were deposited on cleavage plates of calcite, and on these parallel growths of sodium nitrate were still obtained. But there was always the suspicion that these extremely thin metallic films were not really impervious, and that they might have become soaked with the nitrate solution, thus forming a physical connexion between the crystal surface and the crystallising salt.

More success attended the production of deposited layers of calcium carbonate and oxalate. When a drop of lime-water is placed on a calcite surface, in addition to the pellicle of carbonate which forms over its surface, a fine and fairly adherent layer of carbonate is deposited on the calcite. This layer is translucent, and under high magnification it is minutely granular. With care it can be polished until it becomes almost as transparent as the calcite itself. Films of various thicknesses were deposited and polished, and were then tested with sodium nitrate for parallel growths. The results showed that films could be obtained of sufficient thickness absolutely to stop the parallel growths ; but thinner and apparently equally perfect films were obtained which did not interfere with these growths.

The foregoing illustrations have shown that, alike in the hard non-malleable speculum metal, in the highly

brittle and fragile antimony, and in soft brittle calc-spar, the production of a polished surface involves the liquid-like flow of a thin layer. In some respects glass is unlike any of these materials; it is already mainly in the vitreous state.

Glass—Fire Glaze

In favourable circumstances the natural surface which results from the cooling of glass articles from the fused, or partially fused, condition may approach very closely to the state of perfect polish. In this case the molecular mobility due to fusion, or softening by heat, brings the outer skin under the influence of surface tension. The de-vitrification, to which some kinds of glass are peculiarly liable during prolonged heating, is partly due to crystallisation of the silicates of which ordinary glass is composed, and partly to the decomposition of silicates at the surface by the hot-flame gases which contain oxides of sulphur. The existence of a definite skin on fire-glazed glass can be shown by lightly etching the surface with hydrofluoric acid vapour diluted with air. The surface is only slightly dimmed by this treatment, but the microscope shows that the vitreous reflecting surface has been completely removed, disclosing a fine granulated structure immediately below it. The photographs of etched glass have already been referred to, Figs. 11 and 12.

These illustrations show that fire-glazed glass is covered by a thin surface layer which, in some respects at least, is distinctly different from the substratum over which it is laid. All glass cutters must be aware that this surface skin is very decidedly harder than the body of the glass underneath. When the surface of fire-glazed glass is first

attacked in emery grinding, it resists the action of the abrasive very strongly, and if too fine powder is used parts of the glaze are left on the surface practically untouched. The glass once freed from its surface skin responds more rapidly and with greater uniformity to the action of the abrasive.

Glass is polished by flowing the Surface

From what has gone before, we have seen that the layers of molecules on the surface of various hard brittle substances can be made to flow like a liquid, so that either the smoothest of flow-lines or flattest of liquid-like surfaces may result. Fig. 66 shows that, in one of these respects at least, glass is no exception to this rule. This glass surface was held against a polishing disc armed with the finest emery-paper, with the result that fine flow-lines have been developed all over the surface, while at the point where these flow-lines cross a scratch which had been made previously, there are distinct signs of an attempt to bridge the gap by the flowing glass. In this hard vitreous substance the layer of molecules which can be kept in fluid motion by the polishing agent is, necessarily, much thinner than in crystalline substances, in calcite for instance; but all the observations point quite clearly to the reality of the flow in this case as in the others.

Splintering Scratches, Furrows, and Cleavage Scratches

When glass is marked by the passage over it of a hard point, it may either be scratched, or furrowed, or cleft. A *scratch* is caused by the splintering of the glass along the

track over which the hard body has moved. A *furrow* is ploughed when the tool is so formed and guided that its point or points lay hold of a layer only a few molecules in depth. A certain amount of the glass is shaved off, but the perfectly smooth coating of the groove which is left shows that the surface layer has passed through the mobile or liquid condition. A *cleft* results when a fine wedge-like point is drawn along the surface. The entry and passage of the thicker part of the wedge may result in furrowing or splintering at the outer surface, but these are not essential features of the true glass-cutter's cleaving scratch, which, to be effective, must have forced the glass apart till a cleft is started.

The photograph, Fig. 67, shows a splintering scratch at a low magnification. The conchoidal pits, which are irregularly broken out along the track, are very characteristic, and will be referred to again in connexion with another photograph. Even in this rough scratch, it is not difficult to detect traces of ploughing and flow.

Fig. 68 shows a series of grooves ploughed by drawing the edge of an uncut diamond along the surface under a slight pressure. The magnification in this case is high, about 700 diameters, and the resolution is also good; if reduced to the magnification of the preceding figure, it would only show as a narrow faint trace. The smooth-flowing surface of the grooves is quite comparable in this respect with the flow-lines on speculum and other metals. The lines ruled on spectrum gratings ought to be single, clean furrows of this type, free from broken edges or interruptions of any kind.

The photograph, Fig. 78, shows a single furrow, along one side of which the edge has been slightly broken and

distorted, but without any true splintering. The next two photographs, Figs. 79 and 80, show cleaving or cutting scratches. In Fig. 79 a certain amount of splintering has occurred as the diamond was pressed through the surface layer, but along the track there has been no free splintering of the edges. The broad dark band which follows the cut is the shadow caused by the total reflection from the cleft which has been opened in the substance of the glass below the surface. By focussing for the surface the broad band of shadow completely lacks definition along its outer edge, which is therefore out of focus. By focussing down on the outer edge of the shadow it comes out quite sharply, and it was found by measurement on the fine adjustment that this boundary is 0·1 mm. below the surface. The cleft has penetrated the glass at a slight angle, so that there is almost total reflection from its surfaces; the broad dark band is, therefore, the projection of the shadow of the cleft. In Fig. 78 the furrow made by the diamond appears to have been filled up by flow as the diamond passed along.

From the study of the various ways in which scratching may occur, we are now prepared to pass on to consider the various steps involved in the grinding and polishing of glass. A series of photographs, which are here reproduced, were taken at various stages in these operations. Most of these were made with a 4 mm. objective, having a numerical aperture of ·95.

Grinding is mainly due to Splintering

The large part played by splintering in the grinding of glass at once marks it off from the other examples of polishing which have already been illustrated. Among the

metals the behaviour of antimony most nearly resembles that of glass, for in its case also splintering occurs very freely in the earlier stages of grinding; but in antimony this is, to a great extent, counterbalanced by the freedom with which the metal flows during polishing, thus filling up or bridging over the pits which have resulted from splintering.

While splintering plays a very large part in the grinding of glass, ploughing plays only a small one, at any rate, till the later stages are reached. It has been shown that from the nature of the case only a very shallow furrow can be ploughed in so hard and brittle a material as glass, and there is great danger that splintering may occur even in the final stages of grinding.

Steps in Grinding and Polishing

Fig. 69 is a photograph at a high magnification of a piece of good commercial ground glass. This is merely shown for comparison with the following specimens, which were all hand-ground with emery powders of known degrees of fineness. Fig. 70 shows the first effect, when moderately fine emery is applied between two glass surfaces which are being ground together. The surface is indented in many places by the points of the emery grains, and in some cases it has been splintered and pitted. The greater part of the original skin is, however, still intact. In the next photograph, Fig. 71, the whole of the surface skin has disappeared, and the surface is pitted all over, some of the pits being of very large size. In Fig. 72 smaller pits have for the most part taken the place of the larger ones, though one or two large pits are still visible; definite traces of

flowing action may now be detected. Further results of flow are visible in the next photograph, Fig. 73; the surface still seems to be very irregular, but there are no pits which do not show evidence of partial filling up or covering over. The flowed material is marked by the sinuous surface tension forms which it has assumed. At this stage, as repeated grinding with the finest emery did not appear to produce any improvement in the appearance of the surface, emery powder was abandoned, and fine wet rouge was applied by means of a hard wood rubber.

The next photograph, Fig. 74, shows the remarkably quick effect of the rouge polishing. The rocky-looking texture of the emery surface has disappeared, and has given place to large patches of a structureless viscous-looking material. The larger pits are now brought out with striking distinctness. In Fig. 75 these effects are carried to a further stage, and the number and size of the pits are considerably reduced. The rounded edges of the remaining pits show unmistakably that the flowed surface layer is covering over and masking the irregularities below, just as it did in the case of antimony. The final stage of polishing is reached when all the pits have been covered over. At this stage there is no further structure to photograph.

If, however, a portion of the polished glass surface is lightly etched with hydrofluoric acid gas mixed with air, it will be seen that, as in the case of antimony, the smooth surface layer has been dissolved away, exposing the pits and furrows below, showing that, even in a hard, brittle, and vitreous substance like glass the pits and furrows are filled up and covered over by the flowed surface layer during polishing. Fig. 76 is a photograph of a glass

surface which has been ground with the finest emery powder and then partly polished on the finest French emery-paper (0000), being finally polished with rouge on a rapidly revolving cloth polisher. A part of the surface was then etched with the hydrofluoric acid. The unetched portion is perfectly smooth and liquid-like, but the etched part reveals the original grooves and pits which had been flowed over during the polishing operation.

Emery and Rouge

The emery used in these experiments was prepared by shaking up 15 grams of levigated emery flour with half a litre of water. After settling for four minutes in a cylindrical vessel, the top half of the liquid was run off and settled by itself. The product was set aside as "four-minute emery." The residue in the vessel was filled up with water to the original volume, shaken up and settled for seven minutes, when the top half was decanted and settled, the product being set aside as "seven-minute emery." This set of operations was twice repeated, and the products were set aside as "twelve-minute and twenty-minute emery." A thin film of twelve-minute emery, smeared on glass and dried, showed that it contained crystalline transparent masses up to 0·04 mm. in diameter. After this emery had been wetted and ground between two pieces of glass till its cutting action became very feeble, it was smeared on a glass slip and allowed to dry. The larger angular masses had completely disappeared, giving place to much smaller rounded, gravel-like particles, the larger of which measured about 0·001 mm. Mixed with these was a considerable quantity of glass, which, so far as its structure

could be resolved by the microscope, appeared to be in fine film-like particles.

Attempts have been made to study the structure of fine rouge. It was found that the rouge left in suspension in water, after ten to fifteen minutes chiefly consists of particles small enough to possess Brownian movement. Some of these particles examined by an objective of the highest resolving power appear as transparent red particles of rather irregular shape. Owing to the extreme activity of their movements in water, it is difficult to estimate their dimensions with accuracy, but their average diameter may be taken as from 500 to 800 micro-millimetres. The Brownian movements are not confined to single granules of this size, but groups containing a number of these particles possess activity, though of a lower order than that of the single units. The result of numerous observations goes to show that these visible microscopic particles are really aggregates of very much smaller invisible units, and that the special qualities of rouge, as a polishing substance, largely depend on the hardness of the minutest of these ultimate particles. The visible aggregates are more or less casual associations of these finer units under the cohesive forces. They are not therefore really hard in their collected form; if they were, they would act like emery or other rough powders, and produce furrows and scratches. The flow which is necessarily involved in all true polishing is a molecular operation; the layers of the substance which are involved are in some cases known to be only a few molecules in thickness. It is due to the almost molecular fineness of rouge that the necessary molecular contact over comparatively large areas simultaneously can occur. The seizure of the surface layer of metal or glass in rouge polishing is

something altogether different from the ploughing action of the coarser abrasives.

In the ploughing by emery, or by the point or edge of a steel tool, molecular movement and mobility, often of a considerable mass of the substance, always occur in the immediate neighbourhood of the moving-point, but the essential feature in these cases is that the disturbance is more or less convulsive, the material being turned up from considerable depths judged by the molecular standard. As the moving-point passes on, the disturbed material subsides, as a viscous liquid would, into ridges and furrows of smooth outlines at least in detail.

The complete obliteration of the furrows by the liquid surface layer only occurs when a sufficiently large number of points on the polishing agent and the surface are simultaneously in contact; in other words, if something like a continuous sheet of molecules of the polishing and the polished surfaces are in contact. In polishing the furrowed surface of antimony across rouged leather by hand, there is a perfectly definite feeling of " grip " as the surface of the metal is seized by the rouged leather. This feeling is quite distinct from that produced when the rouged leather is replaced by the finest emery-paper, even though in the latter case more actual force is expended in pushing the metal across the rougher surface.

The finest Emery causes Flow but with less Certainty than Rouge

In the polishing of glass the distinction between the surface flow caused by emery and that caused by rouge is plainly seen. While the finest emery particles undoubtedly

cause flow as they plough through the surface layer, yet the depth to which they penetrate disturbs the under surface and impairs the smoothness of the final surface layer. The rouge particles, it may be supposed, hardly penetrate below the surface, but coming into almost molecular contact with the sheet of molecules on the surface, drag it off like a skin. The fresh molecular layer left by the removal of the skin retains its mobility for an instant, and before solidification is smoothed over by the action of surface tension, thus producing the liquid-like surface which is the necessary condition of a perfect polish.

Etching and polishing Rock-Crystal

That the surface layer produced on crystalline solids by polishing differs in properties from the original surface is well illustrated in the case of rock-crystal. If a drop of commercial hydrofluoric acid is placed on the polished surface of a lens of rock-crystal, it spreads slightly and then becomes surrounded by what looks like a halo of condensed vapour. Under the microscope it is seen that the halo is caused by the penetration of the acid *under* the vitreous surface layer. The outer or most advanced portion of the halo is minutely granular. As the outer edge of the drop and the inner edge of the halo are approached, the granules become larger till they assume the appearance of minute hemispherical droplets. As the halo steadily grows by the penetration of the liquid, the droplets immediately surrounding the large drop become larger and larger till they encroach on each other and finally coalesce. When the central drop is removed by touching it with the torn edge of filter-paper, the film of liquid which had pene-

trated under the surface layer gradually returns towards the spot which had been occupied by the drop, and there evaporates. With the retiral of the penetrating liquid, the disturbed layer subsides and becomes perfectly flat. At the same time the granules and the droplets disappear, the only trace of their formation which remains being a slight milkiness in the surface layer, which gives the spicular appearance under an oblique beam of light. The space on which the drop lay is marked by an extremely shallow flat-bottomed pit, on the floor of which a little patch of crumpled film shows all that is left of the material whose removal has caused the pit.

The microscopic study of the operation of polishing rock-crystal makes it plain that the course of this operation is strictly analogous to that observed in metals and other substances, due allowance of course being made for the natural effects of the much greater hardness of the material.

Fig. 77 is a photo-micrograph of the polished surface of a lens of quartz, a portion of which has been etched with hydrofluoric acid. This was ground and polished in a similar manner to the glass surfaces already described, and shows clearly that the furrows and pits produced by the emery have been filled in and covered over during the operation of polishing. The experiment with hydrofluoric acid demonstrates not only the existence of a surface layer due to polishing, but also that chemically the vitreous variety of which this surface layer is composed is different from the crystalline, for, had the latter been equally soluble, the acid would have penetrated directly downwards into the unaltered crystal, instead of which it was stopped by this surface, while it could make its way freely at the common surface of the crystalline and vitreous

layers. This confirms the observation on the etching of calc-spar, which showed that calcium carbonate in the vitreous form is more soluble than in the crystalline. Other observations confirmatory of this have been recorded in connexion with metals, but these will be discussed later.

The Vitreous State produced in Powders by Grinding

It has been suggested that the greater solubility of small crystals as compared with large is due to their greater surface energy, and the further conclusion has been drawn that the greater solubility of a substance in the form of powder is due to the same cause. While this suggestion may be justified up to a point, it is clear that, in many well established cases, as in those cited above, there is a difference in the solubility of the two states, the vitreous and the crystalline, which is entirely independent of the outward form or the mass of the substance. Therefore, as any powder which has been obtained from a crystalline substance by grinding must, from the nature of that operation, be to a considerable extent in the vitreous condition, its greater solubility will probably be due to the existence of this state.

The operation of grinding a crystalline substance to powder does not simply consist of its mechanical reduction to finer and finer crystalline fragments, but it necessarily involves the transformation from the crystalline to the vitreous state. A finely powdered substance is vitreous, not because of, or in proportion to the mere fineness of its subdivision, but because of the extent to which the above transformation has been effected by flow during grinding.

The Function of "Flow" in Tabloid-Making

Again, when a crystalline powder is formed into cakes or tabloids by compression, a certain amount of rubbing of the crystalline grains takes place at their surfaces of contact, resulting in the production of mobile layers which pass into the vitreous state and act as a cement which binds the particles into a solid mass.

When a salt or other crystalline substance is to be made into tabloids or briquettes by pressure, the less it is previously submitted to grinding operations the better, because the effect of grinding is to coat the minute particles with vitreous layers, which are much less easy to flow than even a coarser powder still in the crystalline state. The ground powder will require a much higher pressure than the crystalline powder to concrete it into tabloids or briquettes. It is well to remember, as was pointed out when referring to Spring's early work on this subject, that the function of the high pressure is not primarily to press the minute particles closer together, but to produce a rapid and simultaneous movement of the particles over each other throughout the mass. In Section VII., when describing the flow of a minute crystal of antimony under a single blow of the drop hammer, Figs. 87, 88, Plate XXVII., it is shown that "it is the first blow that counts."

General Conclusions

1. The operations of cutting, filing, grinding, or polishing produce on the surface of solids a thin film which is, in many respects, essentially different from the general body underneath it.

2. This surface film results from a certain mobility

which is conferred on a thin layer of the molecules by the tool or polishing agent moving over the surface.

3. While it is in the mobile condition the film of solid molecules behaves like a liquid and is subject to the action of surface tension.

4. The polished surface of a cleavage plate of calcite, even when illuminated by an intense oblique beam, shows no trace of the grave disturbance to which it has been subjected by the operation of polishing.

5. By means of the step-by-step removal of the surface layers by a solvent, the nature and extent of the disturbance of these layers is disclosed, and it is found that ploughing and breaking of the lamellae has occurred to a depth of from 500 to 1000 $\mu\mu$. The complete obliteration of the traces of this disturbance shows that the disturbed substance, as it passed through the mobile to the solidified state, must have extended through the whole depth of the disturbed layers, otherwise the healing of the deeper furrows would have been imperfect, and their traces would have been shown up by the oblique beam.

6. The laying bare of the disturbed layers by the action of the solvent shows that this action is selective, the substance which has been flowed and solidified being first attacked. This has also been shown in the case of the polished surface of rock-crystal. The molecular arrangement of the flowed substance must, therefore, be different from that of the original crystal.

7. The surface layer formed on calcite by polishing is harder than the unaltered crystal surface, and it is equally hard in all directions, which the natural surface is not. The new surface forms a genuine protecting skin over the crystal surface.

8. The presence of this protective skin does not interfere with the parallel growth of crystals of sodium nitrate on the polished surface. Among a large number of experiments with polished surfaces, produced in a variety of ways, no case occurred in which this parallel growth was prevented.

9. By the deposition and subsequent polishing of layers of non-crystalline calcium carbonate and oxalate on the already polished skin, a further skin was interposed between the true surface of the calcite crystal and the deposited crystals of sodium nitrate. Up to a certain thickness this did not interfere with the parallel deposition of the sodium nitrate crystals, but beyond this thickness the deposition was quite irregular, and had no relation to the orientation of the crystal growth.

10. The demonstration that the polish of a lens of rock-crystal has resulted from the formation of a flowed layer of vitreous material on its surface suggests that no crystalline substance is too hard to yield to the mechanical flowing action.

11. The grinding of crystalline substances to powder does not simply consist in their reduction to finer and finer crystalline fragments, but it involves the transformation of, at any rate, a part of the substance into the vitreous condition.

12. When crystalline powders are formed into cakes by pressure the cementing material is the vitreous state which results from flow.

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SECTION VI

THE CRYSTALLINE AND VITREOUS STATES IN SOLIDS

The Phenomena of Surface Flow suggest a New Theory of the Hard and Soft States in Metals

THE discovery that the essential feature of polishing, as distinguished from grinding, is that the polished surface is formed by a true skin of vitreous material, which gives unmistakable signs that it has passed through the liquid state and that, in its final state, it possesses distinctive qualities which differentiate its substance very clearly from that of the unaltered substance beneath it, opens up a new field of study on the crystalline and vitreous states in solids. In following up this study a number of experimental observations were made, the results of which led to the development of a new theory of the hardening of metals by plastic flow during cold working.

According to this theory, hardening results from the formation at all the internal surfaces of slip or shear of mobile layers similar to those produced on the outer surface by polishing. These layers only retain their mobility for a very brief period and then solidify in a vitreous state, thus forming a cementing material at all surfaces of slip or shear throughout the mass.

The physical and other properties of the two states in

metals are so distinct that the existence of a definite stability point has been proved, and from this it is argued that not only must all crystalline substances be capable of existing in the vitreous state, but that, by purely mechanical means, it is possible to transform them into this state.

The Need of a Guiding Principle which could reconcile the many well-known Phenomena of the Two States[1]

When these observations were published in 1904, there did not hitherto appear to have been any serious attempt to arrive at a single guiding principle which would harmonise the many isolated phenomena of the solid state which are met with in the practice of the metal-working arts, and in the systematic testing of materials in physical and engineering laboratories.

The hardening and resoftening of metals in annealing, forging, rolling, wire-drawing, and stamping, as these are practised in the arts; the flow of metals dealt with by Tresca and by Spring; viscosity and elastic fatigue in metals and other solids as observed by Kelvin; mechanical fatigue and disruption in metals exposed to frequent alterations of stresses investigated by Wohler, Baker, Bauschinger, Unwin, and others; the deformation of crystalline grains, and their restoration and growth by heat annealing, studied by Ewing and Rosenhain; and the character of distortion and rupture of iron and soft steel, discussed by Osmond, Fremont, and Cartaud, make a sufficiently varied, though far from exhaustive list of subjects, which in spite of much special study, still remained in comparative isolation from each other.

[1] *Phil. Mag.*, August 1904.

Looking broadly over this wide range of subjects, it is seen that two complementary phenomena stand out prominently, round which the others may be naturally grouped. (1) The deformation of a metal by stresses beyond the elastic limit invariably tends to alter the character of the metal in one definite direction, that is, towards a diminished capacity for being deformed by such stresses. (2) The plastic quality can be restored to the deformed metal by raising it to a suitable temperature.

Hardening and Annealing have been mainly studied as they affect Iron and Steel

In reviewing the earlier researches on the subject of hardening and annealing, it is found that, with very few exceptions, they have had special reference to these phenomena as they occur in iron and steel. This had naturally resulted from the great importance of these materials in engineering and construction, but there can be no doubt that, from the point of view of a broad study of the subject, this choice of the material for investigation had to some extent been unfortunate, inasmuch as the properties of iron and its alloys are very much more complicated than those of any other metal in ordinary use.

In a steel containing a minute percentage of carbon it is possible to identify five or six primary constituents, whose appearance depends almost entirely on the heat treatment to which the specimen has been subjected.

In addition to this it is believed that iron itself can appear in two or three allotropic modifications, each of which has its definite transformation temperature. The student of this subject is therefore confronted with a set of

complicated problems, the elements of which it has been all but impossible to isolate from each other.

For the study of the phenomena which are to be here discussed, it is desirable to detach these as far as possible from complications of the kind above referred to. With this object, while the metals and other substances examined have been of many widely different types, the ultimate reference has always been made to those in which the behaviour is simple as well as characteristic.

It was early realised that accepted Ideas of the Crystalline State could not be stretched to account for all the Phenomena of the Hard and Soft States

At an early stage in this study it was concluded that nothing was to be gained by attempting to stretch our ideas of the crystalline state so that room might be found within that state for all the varied phenomena presented in the mechanical and thermal treatment of metals. A crystalline aggregate must owe its origin to some inherent quality of its molecules in virtue of which *they take up and retain fixed positions with reference to each other.* The molecular theory of magnetism supplies an illustration of a simple form of polarity in which the molecules are arranged end to end to form strings or rows.

The compounds of the asymmetric carbon atom supply a more complete illustration of the direct influence of the molecular polarity on the form of the crystal; for here the definite space relations of the molecule find their counterpart in the geometrical form of the crystal. *The strictness of these molecular and geometrical relations must be regarded as a characteristic feature of the crystalline state.*

Up to its limit of elasticity a crystal may be strained without its ceasing to be a crystal; but when this limit is passed permanent deformation is produced, some of the molecules being moved into new positions relatively to each other, positions which are not in strict accord with the geometrical molecular arrangement.

In considering the transition from the liquid to the solid state we are not necessarily limited to the crystalline form of aggregation. It has already been shown that the forms assumed by the surface layer of a solid metal during annealing are controlled by surface tension rather than by crystallic force. In this case the ordinary forces of cohesion determine the positions taken up by the molecules relatively to each other. Throughout a layer, which is probably many molecules in thickness, the molecules have come to rest in the midst of the activity of the liquid state, their mutual relations in that state being stereotyped at the moment of cooling.

The passage from the liquid to the solid state consists essentially in the arrest or the limitation of the freedom of movement of the molecules relatively to each other. This freedom of movement is determined by the temperature of the substance. When the temperature is reduced by the withdrawal of heat, the molecules must come to rest in the solid state. If the arrest is instantaneous, then the molecules may have no opportunity to arrange themselves according to their polarity, and the solid state which results will be a heterogeneous assemblage of molecules which will bear somewhat the same relation to the homogeneous assemblage of a crystal as a crowd of disbanded soldiers does to the same men in the orderly formation of the company or the battalion. A solid of this type may be likened

to an instantaneous photograph of the molecules in the liquid state; but, while in the photograph there would only be the appearance of fixity, in the congealed liquid the fixity is real.

In addition to the inherent polarity of the molecules, crystalline formation requires time, freedom, and space. Time and freedom are necessary to enable the molecules to turn into the proper orientations, and space may be required if their packing in the homogeneous assemblage is more open than it is in the heterogeneous. The rigidity of the solid state is therefore due to the arrest of the molecular movement either in a homogeneous or a heterogeneous assemblage of molecules. Throughout this paper the term crystalline is applied to the former and vitreous to the latter.

The Passage from the Liquid to the Solid State may produce either a Crystalline or a Vitreous Aggregate

We can picture the transition from the liquid to the vitreous solid state as taking place either by a sudden arrest of molecular movement, or gradually through the increasing viscosity of the liquid phase.

The stability of a vitreous solid, depending as it does on the curtailment of the free movement of the molecules, is obviously determined by temperature.

If that freedom is sufficiently restored by heat to permit the molecules to form into orderly formation under the direction of polarity, the vitreous state will pass over into the crystalline. That this degree of freedom is obtained at a definite range of temperature very much below the liquefying-point is abundantly shown by the observations

which are presented in what follows. The stability of the crystalline state persists from the transition temperature up to the liquefying-point, at which point the movement of the molecules can no longer be restrained, even under the influence of their cumulative polarity.

Some Substances pass naturally from the Liquid to the Vitreous State

The silicates, silica and sugar are all highly viscous in the molten state, and, when they solidify by cooling, they most naturally pass into the vitreous conditions. Glass is thermally stable up to a temperature not much short of its softening-point. By prolonged exposure to this temperature it devitrifies, the silicates of which it is composed crystallise, and it ceases to be glass. In this state it is valueless for any of its usual uses. Pure silica in the vitreous form is now an article of commerce. It is obtained by the fusion of crystalline quartz. Like the vitreous silicates it is thermally stable up to a temperature not far short of its melting-point, but prolonged exposure at this temperature causes it to crystallise, and devitrification results.

Sugar in the vitreous form is in daily use in the manufacture of confectionery. In dry air it is quite stable at ordinary temperatures, but in moist air crystallisation starts on the surface, and in time it becomes completely devitrified.

Viscosity in the Molten State hinders Crystallisation and favours Solidification in the Vitreous State

It seems natural to regard viscosity and the sluggish movement of the molecules which must accompany this

state as the immediate cause of the failure of the molecules to arrange themselves in the homogeneous formation of the crystalline state.

We know that this formation can only occur in these viscous substances over a very short range of temperature after solidification has set in. This range is so quickly passed in ordinary cooling that it cannot be taken advantage of by the sluggish molecules. Another factor has also to be considered. The researches of Ostwald, Lehmann, Miers, and others have shown the very important part which is played by crystalline nuclei in the initiation of crystallisation. In the absence of such nuclei, crystallisation can be almost indefinitely delayed.

This is illustrated by an experiment which was made with sugar. Some crystals of pure sugar were heated on a glass plate till all but a few of the larger crystals had melted into clear drops. In the larger drops a small piece of unmelted crystal was left. The temperature of the plate was now raised to about 150° C., at which it was kept for some time. The drops which contained a crystalline nucleus became crystalline throughout, while the others remained clear and vitreous. Fig. 81 is a photograph of a portion of the plate on which two of the drops are completely crystallised, another which contained a nucleus is partially crystallised, while all the others remain perfectly vitreous.

The Pure Ductile Metals are not hardened by Chilling as are some of their Alloys

The ductile metals, when pure, do not pass into the vitreous state by cooling, because their molecules retain

sufficient mobility to enable them to orient into crystalline rearrangement over a very long range of temperature below the solidifying-point. Gold, for example, solidifies at 1080° C., and its minimum crystallising temperature is somewhere about 230° C. There is thus a range of about 800° C. over which crystallisation can occur. It is obvious that no ordinary method of chilling could carry a mass of metal over this long range so quickly that it could not crystallise.

By the Sudden Solidification of the Mobile Layers produced by Flow the Metal is partly changed into the Vitreous Condition

Though the arrest of crystallisation by chilling the pure ductile metals from the molten state is practically impossible, this arrest can and does occur in the thin layers of mobile molecules which are produced by mechanical flow. The evidence, from observations which have extended over many years, has made it certain that metals can exist in the vitreous form, and that the recrystallisation which occurs when the point of thermal instability is reached is strictly analogous to the similar phenomenon which occurs when other well-known vitreous substances are kept at a suitable temperature in the presence of crystalline nuclei. Although these phenomena occur in masses of molecules which are of microscopic minuteness, they are none the less real, and their cumulative effects are of far-reaching influence in structures which are of an entirely different order of magnitude. Though the films on which this mobility is conferred are of insignificant dimensions when compared with our rough standards of measure-

ment, they are, from the molecular standpoint, relatively massive.

In Section VII. we shall study in more detail the physical and mechanical properties of the two states, crystalline and vitreous, and the conditions under which they are produced.

SECTION VII

INFLUENCE OF THE CRYSTALLINE AND VITREOUS STATES ON THE PHYSICAL AND MECHANICAL PROPERTIES OF DUCTILE METALS

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SECTION VII

INFLUENCE OF THE CRYSTALLINE AND VITREOUS STATES ON THE PHYSICAL AND MECHANICAL PROPERTIES OF DUCTILE METALS

Thermo-Chemical Properties

On thermo-chemical grounds Berthelot regarded hammered, crystalline, and annealed silver as distinct allotropic forms of the metal. He found that the heat of solution of hammered silver in mercury was +2·03 calories, as compared with +0·47 for silver which has been heated to 550°, and +10 calories for crystals of electrolytic silver. These observations show that energy is stored in the passage from the crystalline to the vitreous state. The greater solubility of a substance which is in the latter state also points to this conclusion. If a galvanic couple, consisting of the two states of the same metal, is placed in a suitable solvent, the vitreous dissolves before the crystalline state, which is therefore left as a skeleton of the former mixed structure. This, then, is what occurs when a hard-drawn wire is suitably etched. The vitreous surface layer dissolves first and discloses the granular structure below. In etching hardened or polished metals it is found that solvents act first on the vitreous part, removing it, and leaving the crystalline state exposed. This is exactly the opposite to

what might have been expected to occur under the older view of hardening and polishing as consisting merely in the compacting and smoothing of the material; for the smooth compact surface so produced ought to be more, rather than less, resistant to the action of solvents.

This increased solubility of the vitreous state is well seen when a gold leaf is etched by floating it on a solution of potassium cyanide. The cyanide does not dissolve away the surface uniformly, but it first attacks the vitreous metal and penetrates right through the leaf, so that the film which remains is a skeleton built up of the minute units of the crystalline state which have survived the severe treatment of beating. This observation has an interesting bearing on Faraday's estimates of the reduction of thickness of gold leaves floated on a solution of potassium cyanide, which were made on the assumption that the metal in the thinned leaf is of the same density as in its more massive form. This is evidently not the case.

Reference has already been made to the vitreous surface layer produced in polishing solids such as calcite and quartz, and the increased solubility of this layer has been demonstrated.

It is not too much to say that, but for this difference of solubility in the two states, the present observations could not have been pursued to the definite conclusions which have been reached.

Electrical Conductivity

It has for long been known that the electrical conductivity of a silver wire in the annealed state is 8 to 10 per cent higher than that of the same wire in the hardened

or vitreous state. With other metals also the annealed state has the higher conductivity.

In Mathieson's Electrical Conductivity Tables the differences between metals in the two states are given as: for silver, 8 per cent, for copper, 2·5 per cent, and for gold, 1·8 per cent, the conductivity in the hard state being less by these amounts than in the soft state.

The very marked difference in the case of silver agrees with the well-marked potential developed in a thermo-junction of the metal in the two states, which will be referred to later.

Electro-motive Force

In 1899 Dr. Magnus Maclean made a series of observations on the effects of strain on the thermo-electric qualities of metals.[1] With copper soft and hard the E.M.F. varied from 0·0027 to 0·0264 micro-volts per degree. Steel gave 0·1028, nickel, 0·3784, lead, 0·0076 micro-volt. These observations were not made primarily with the object of ascertaining the maximum E.M.F. between the soft and hard varieties, but to compare the effects of different amounts and kinds of strain; the soft metal was therefore not necessarily in the condition to which it would have been brought by raising it to the transition temperature. The highest temperature used in Dr. Maclean's determinations was 100° C.

Hard and Soft States

The hardening of ductile metals by hammering and cold working of all kinds, and their restoration to softness

[1] *Proc. Roy. Soc.* vol. lxiv. p. 322, and vol. lxvi. p. 165.

by annealing at a suitable temperature, has been known to, and practised by, metal craftsmen from prehistoric times. The fundamental explanation of these everyday phenomena has, however, only been arrived at by the careful observation and correlation of a wide range of physical and mechanical phenomena which accompany this change of state.

General Scheme of Research

After much preliminary experimental work, only a part of which is described here, a stage was reached when it appeared that the physical, mechanical, and microscopic phenomena which accompany the change of state in ductile metals could, with advantage, be simultaneously studied on carefully selected and prepared specimens, with some approach to accuracy of measurement.

The metals selected for this purpose were gold, silver, and copper, all in the purest form obtainable. For the conversion of the metal as far as possible into the vitreous state, wire-drawing was the method selected, and, in order that this conversion should be as complete as possible, wires of small diameter were used. Hammering had to be resorted to in preparing specimens for the acoustical tests. Every care was taken to ensure that the history of each wire was known from the stage at which the metal had left the fully crystallised condition. Starting with wires in the hardened state, it was proposed to follow the changes in properties which occurred as these wires were raised in temperature step by step till they were fully restored to the crystalline state. The changes to be observed were :

Crystallisation and micro-structure.

Mechanical stability.

Electro-motive force of couples in the two states.
Elasticity by the acoustical test.

The results of these observations made it abundantly clear that, for each metal, these definite changes in properties and structure all occur over the same short and well-defined range of temperature.

Deformation and Regrowth of Primitive Crystals

Before describing these observations in detail, it may be well to refer to some of the features which distinguish the primitive crystals resulting from solidification directly from the molten state with those which result from raising to the crystallising temperature the broken-down remains of crystals which have become concreted together by vitreous metal in cold-worked wires, strips, and sheets.

When a globule of molten gold solidifies it is seen to be composed of grains. Each grain is a distinct crystal, and is built up of uniformly oriented lamellae. If the globule is flattened by a single blow from a small drop hammer, the etched surface of one of its flat sides shows that the grains have been distorted and extended in all directions, Fig. 82. A cross-section through the flattened globule shows the grains extended longitudinally, while they are thinned out and squeezed together across the section. The original grains retain their identity; they have merely changed their shape to accommodate themselves to the change of form of the mass of which they are units. These primitive grains under distortion by compression show the same general feature of flow as mixtures of ductile metals did in the classical experiments of Tresca. I call these grains "primitive" because they are produced

directly on solidification from the molten state. The crystalline grains which result from the recrystallisation of strained metal are of quite a different type, as are also the crystals which are developed in solid alloys by heat treatment. The flattened globule, after annealing at 300°-350°, now shows the second type of crystallisation, Fig. 83. Instead of a few primitive grains which can easily be counted, there are now as many tens as before there were units, and the rounded and flowing outlines have been replaced by sharp lines and angles. It is plain from this result of recrystallisation that this retention of their identity by the distorted grains *is not a retention of their identity as crystals.* A more searching microscopical examination of the distorted primitive crystals explains the new development, for it shows that their original regularity of orientation has given place to a broken-down and most irregular structure. The well-marked lamellae, which under slight strain show the crystalline steps or "slip bands" of Ewing and Rosenhain, Fig. 84, are no longer found, and a mixed granular structure has taken their place, Fig. 85.

Foam Cell Hypothesis of Quincke

Observations on these primitive grains appear to give some support to the "foam cell" hypothesis of Quincke. According to this hypothesis, the first step towards crystallisation occurs in the liquid state, and consists in the segregation of the pure substance and the throwing out of any eutectic which may be present. In these two liquids differences in intrinsic cohesion cause the pure substance to aggregate in spheroidal masses around which the

eutectic forms in bubbles or " foam cells." The spheroids of pure substance being isolated from each other by the foam cells are free to develop each their own crystalline orientation. This may occur while they are still liquid, or it may only occur on solidification ; but, in either case, the result is the same, and the spheroids solidify as little sacks of uniformly oriented molecules. We have seen how well these little sacks can retain their individuality in the distorted globule, though they have completely lost their individuality as crystals.

An observation made by Dr. H. C. H. Carpenter in the Eighth Report of the Alloys Research Committee is worth referring to in this connexion. In referring to the effect of repeated remeltings of the 9·86 per cent copper aluminium alloy in increasing the size of the grains in the resulting ingot, he makes the suggestion that the phenomenon is of the same class as those which Lehmann discovered in his study of liquid crystals. As Lehmann has proved that some kind of transient aggregation and orientation can occur in certain organic bodies in the liquid state, it is possible that the same phenomenon may occur in metals. Dr. Carpenter goes on to infer that these liquid crystals may somehow survive and increase in size through successive meltings ; but it is not very clear in what way this survival through the mobility of the molten state is ensured, for even admitting the possibility of molecular associations in the liquid, they are almost of necessity transient. Quincke's hypothesis supplies an explanation of the means by which this survival may be secured.

In Dr. Carpenter's experiments it appears quite natural to suppose that, at each successive fusion and solidification,

the units in the foam structure, and therefore the resulting grains, might become larger. By solidification and subsequent crystallisation the cell envelopes are ruptured, and on remelting the metal would be free to run together into larger spheroids. In dealing with liquid foams or emulsions, the most effective, and sometimes the only way to break up the structure, is to freeze one or more of the constituents, and it appears perfectly reasonable to assume that the same holds good in a metal foam or emulsion. This subject has been dealt with by Dr. C. H. Desch in his reports made to the Institute of Metals (1914, No. 1, vol. xi., and 1919, No. 2, vol. xxii.).

In the flattened globule of gold, we have seen that a single blow has completely broken up and destroyed the original crystalline structure. This is shown directly by its micro-structure, and it can be inferred from the entirely new type of crystalline structure which results when the deformed globule is annealed. The new crystallisation has evidently started from a multitude of nuclei which have been supplied by the breaking up of the very limited number of primitive grains. The hardening effect of the single blow has been very marked, as shown by the resistance of the globule to further blows from the hammer. Under repeated blows the rigidity increases or remains constant till the tenth or twelfth; it then diminishes. Even after a number of blows the primitive grains, though they are very much spread and distorted, still retain their individuality, Fig. 86. The structure and properties of the globule flattened by a single blow show that a great amount of flow has occurred throughout the whole mass. It is as if the whole crystalline framework had collapsed simultaneously, and in its fall had produced an almost

general condition of transient fluidity. The instant re-solidification of the mobile mass into a vitreous condition produces the same effect as the sudden chilling of a mass of steel. It would almost appear that a sufficiently quick blow upon a very small globule would bring all its molecules simultaneously into the mobile condition, the mass being thus for an instant a homogeneous liquid. The behaviour of a fragment of antimony under a blow illustrates this effect of the collapse of the crystalline framework even more strikingly than the gold globule. As the first blow develops in the gold globule a new and rigid structure, it is obvious that a second blow can only produce a further deformation, if it is strong enough to break down this structure. If it does so, however, the remains of unflowed crystalline substance are reached, fresh flow occurs, is followed by resolidification, and a new rigid structure results. This set of operations may be repeated so long as the supply of available crystalline substance holds out. When this supply is exhausted the power of self-repair of the broken-down structure will cease. At this stage the effect of further blows is to diminish the rigidity of the mass.

Wire-drawing

These stages can be studied very satisfactorily in wire-drawing. It is well known that the intrinsic tenacity of a metal may be developed to a very high point by wire-drawing, but, if the operation is carried too far, the tenacity instead of increasing begins to diminish. The "flow" hypothesis explains this. It is due to the using up of the crystalline substance and to the loss of the self-repairing power which this substance confers. The broken-down

structure is then liable to open up under distortion, and loss of density and rigidity follows.

Crystal of Antimony flowed by a Single Blow

As is well known, antimony is one of the most brittle and fragile of the common metals, yet it can be made to behave as any malleable substance would. A minute crystalline fragment of antimony, Fig. 87, received a single blow from a small drop hammer weighing a few ounces and falling through about a foot. Fig. 88 shows the result. The surfaces both of the anvil and the hammer were slightly convex, so that the maximum pressure came on the centre of the tiny plate, which is, therefore, slightly concave; the flow from centre to circumference was not quite simultaneous, and the plate was left by the blow in a highly strained condition. Most of the radial cracks by which this strain was relieved appeared during the twenty-four hours after the blow was struck. Immediately after the blow there were only four or five short cracks which did not nearly reach to the centre. The point to be observed is that this brittle fragment, instead of flying into powder under the hammer, has spread into a thin plate as any malleable substance would have done. The parallel lines on the surface are neither slip bands nor lamellae, they are an imprint of the fine flow-lines left by emery polishing on the face of the anvil.

Kahlbaum's Experiments with Platinum

This loss of density was investigated by Kahlbaum in 1904. A platinum bar, 6 millimetres in diameter, was cut

up into short cylinders 32 millimetres long. The specific gravity of these was determined. The rods were rolled and forged, and it is to be presumed that the temperature of forging ensured a complete return to the crystalline condition.

The figures obtained in only one case are given, as the other results are quite concordant.

The specific gravity of the rolled and forged rod of 3 mm. diameter was	21·4314
The specific gravity wire 1 mm. diameter (cold drawn)	21 4136
The specific gravity same wire annealed 3 minutes at white heat	21·4314
The specific gravity wire 0·7 mm. diameter (cold drawn)	21·4181
The specific gravity same wire annealed 3 minutes at white heat	21·4314
The specific gravity wire 0·4 mm. diameter (cold drawn)	21·4142
The specific gravity same wire annealed 3 minutes at white heat	21·4308

No tenacity test is given, but the above results show that the drop in density was related to the amount of work done in wire-drawing. The greatest fall occurred in the wire which was reduced from 3 millimetres to 1 millimetre, which was therefore drawn to nine times its original length. In some experiments made in collaboration with H. N. Beilby in 1904–5, copper wire which had been drawn to five and a half times its length, without further annealing, had a tenacity of 28·4 tons per square inch. A piece of the same wire further drawn to 1·7 times its length showed a reduced tenacity of 27·4 tons per square inch. Experiments with wires of gold and silver gave similar results. We came, therefore, to the conclusion that overdrawing might occur after a wire had been drawn to about five times its length without annealing. Kahlbaum's wires, therefore, were probably overdrawn. Under the flow

hypothesis of the hardening phenomena the reduction in both density and tenacity fall into place quite naturally.

Measurements of Tenacity of Hard-drawn Wires

Tenacity in metals is measured, as is well known, by the tension required to tear asunder a rod, bar, or wire of the material. In ordinary mechanical tests of this kind it is assumed that the tensile stress is uniformly distributed over the whole surface at which rupture occurs ; but this is only approximately true in the most favourable cases, while in many cases it is obviously untrue, as, for instance, when the surface of fracture is large relatively to the length of the specimen, or when the material is not homogeneous. It is not possible to experiment with a chain of single molecules, for even in the thinnest wire its smallest cross-section contains many millions of molecules. It follows, therefore, that only in a perfectly rigid body can all the pairs of molecules be pulled directly apart as they would be in a single chain. Any departure from perfect rigidity must involve that the molecules under strain will move over each other with a certain degree of freedom, as in the liquid state, and the rupture will become to some extent like that of a highly viscous liquid, *e.g.* molten glass, in which the molecules evade any direct pull by slipping over each other.

The changes of state from hard to soft and from soft to hard are effected in the one case by heat and in the other by mechanical deformation or flow. In most, if not all, of the ductile metals the vitreous is the hard state and the crystalline the soft. This is contrary to the usually accepted ideas on the subject, for hardness and brittleness are generally supposed to be specially associated with the crys-

talline properties in metals. In reality the softest metals are those which pass most readily into the crystalline condition, and when in this condition they are in their softest state. This particular softness is due to the readiness with which the crystals can be broken down again into the liquid phase. The crystalline is the state of maximum instability under mechanical disturbance, while the vitreous is the thermally unstable state. The ductile metals may be described as those which pass most readily from state to state: they are equally unstable mechanically and thermally. Mechanical instability and the change of state on which it depends is well illustrated in the stretching of wires under tension. Annealed wires, which are in the crystalline state, stretch when they are stressed beyond their yield point; hardened wires, which are partly in the vitreous state, do not stretch—they break without general extension when their limit of tenacity is reached.

The homogeneous crystalline state as it occurs in a ductile metal, which has been heated above the transition temperature, has no true breaking-point; it yields and stretches when stressed beyond the elastic limit, and in so doing it passes partly into the vitreous state, and when rupture takes place it does so at the breaking stress of the mixed structure. The conditions under which this change of state is brought about may be very different, and the "texture" which results from the mixture of the two states will have an important influence on the mechanical physical properties. A wire, for instance, which has been hardened by simple stretching is less tenacious than one which has been hardened by hammering or by drawing.

The tenacity of the mixed structure which results from plastic yielding that has taken place under favourable

conditions approaches, but never quite reaches, the tenacity of the homogeneous vitreous state. To ascertain the true maximum tenacity of a pure metal it would be necessary to obtain it in this homogeneous condition. For the purpose of this inquiry it was necessary to obtain the metals as nearly as possible in this state.

It had been found that only in the thinnest surface layers—probably from 50 to 500 micro-millimetres in thickness—was it possible to obtain the metal in a perfectly structureless condition. Gold foil when beaten till it covers several times its original area becomes covered with a hard vitreous-looking surface film of extreme thinness, but the lightest of etching on this surface is sufficient to disclose a granular layer of the mixed states, and below this layer further etching discloses the broken remains of crystalline grains and lamellae.

Texture developed by Wire-drawing [1]

By wire-drawing it is possible to destroy all the rougher traces of crystalline structure, such as grains, lamellae, or similarly oriented units, and to reduce the whole substance to a fibrous and granular condition. But in this condition the metal is not reduced to the homogeneous vitreous state; it is still an intimate mixture of the two states.

After a wire has been stretched to four or five times its original length by drawing it through the conical holes of a wire plate, the substance of the metal is entirely reduced to the fibrous granular condition. Fig. 97 *a* is a photograph of a gold wire which has been etched after drawing; the flow-lines near the surface consist of fibres or rows of

[1] *Proc. Roy. Soc.* A, 76, 1905.

granules; *b*, on the same photograph, shows the effect of heating another piece of the same wire to about 400° C. Removal of the surface by etching now discloses the fully developed crystalline grains with their differently oriented lamellae. The thermal transformation from the vitreous to the crystalline state has taken place, and the wire is restored to the soft condition. Figs. 98 and 99 are photomicrographs at higher magnifications, which show the details of structure more fully. Fig. 98 is the granular structure by oblique light at a magnification of 250, and Fig. 99 is the crystalline structure by normal light at a magnification of 700. The granular structure in Fig. 98 is so minute that it absorbs the normal illuminating rays to such an extent that it is not possible to obtain a satisfactory resolution by lenses of high numerical aperture. The granules seen on the photograph are not really the ultimate units, they are only aggregates of these. Fig. 99 shows very clearly the way in which each crystalline grain is built up of similarly oriented lamellae, the orientation in each grain being different.

Heating merely to the lower end of the transition range of temperature, while it starts the change of state and softens the metal, does not develop a well-marked crystalline structure. The steps in the development of this structure as the temperature is raised are fully described at a later stage.

The mechanical stability decreases as the crystalline grains become larger and more fully developed. The yield-point, therefore, varies with the condition of crystalline development.

As the primary object of these experiments was to bring each of the metals used into its highest state of

tenacity, various methods of wire-drawing were tried to find that which would give the best results. It was realised that so long as the actual tension on the wire was accurately observed and its cross-section accurately measured, those results which gave the highest tenacity were the best and most trustworthy. Under these conditions there was no danger of obtaining too high a result for any given metal; indeed, all the chances were the other way. But the purity of the metals was of great importance, for it is well known that minute traces of impurity may seriously affect the mechanical properties.

The metals used were gold of a purity of 9997 parts per 10,000, silver of a purity of 10,000 parts per 10,000, and copper of a guaranteed conductivity of over 100 per cent. It was recognised that the purity of the copper was probably not quite of the same order as that of the gold and silver.

The Method adopted for Testing the Tenacity

The tenacity tests were made by directly loading the stretched wire by a water load, so that the speed of loading and its smoothness could be easily regulated. In the earlier tests which are first described the loading was carried to the breaking-point. Experiments were made at the ordinary temperature and also at the boiling-point of liquid air; in the latter case the wire with both grips was fully submerged in the liquid air during the entire test. The extension was measured after the broken wires were removed from the grips. The diameter of the wires was measured by a micrometer screw-gauge. For each wire the mean of a large number of measurements was taken, the measurements being usually taken in pairs on two

diameters at right angles to each other. All the tenacity tests were made on wires of from 0·38 to 0·55 mm.

After annealing at a temperature rather above the transition-point, the wire was drawn through a series of holes till it reached the desired diameter. The reduction of diameter and the increase of length were as a rule both directly measured. Wires were stretched in this way to as much as 15 times their original length when annealed. The minimum amount of stretching used was 1·4 times.

It was found possible to overdraw a wire so that its tenacity having passed a certain maximum began definitely to fall off. The highest tenacity in gold was developed by drawing it to $3\frac{1}{2}$ times its original length, but by drawing it to as much as 13 times the tenacity was only slightly reduced.

The maximum tenacities recorded at the ordinary temperature were gold 15·6 tons per square inch, silver 25·7 tons, and copper 28·4 tons. At the boiling-point of liquid air ($-182°$) the maxima were gold 22·4 tons per square inch, silver 34·4 tons, and copper 36 tons.

When stressed at the ordinary temperature of 15° C. none of the hard-drawn wires which had been drawn at that temperature showed any general stretching, but on fracture there was a slight extension of from 0·5 to 1 per cent, due entirely to a sharp reduction of diameter at the actual point of rupture. The diameter of the wires after breaking confirmed that there had been no general stretching. When tested at the boiling-point of liquid air all these wires stretched from 11 to 12 per cent. This stretching affected the whole length of the wire between the grips, and the diameter was correspondingly reduced. The tenacity was therefore always calculated on this reduced diameter.

The granular and fibrous texture after this second stretching appeared slightly finer than that of the wires which broke without stretching, and it is believed that this revival of plasticity at the lower temperature is due to the further breaking down of the granules of the crystalline state, which is rendered possible by the increased hardness and tenacity of the vitreous phase. If the second stretching had taken place under the more favourable conditions of wire-drawing, it seemed probable that there would have been a corresponding increase of the maximum tenacity at the low temperature.

Wire-drawing at Low Temperatures

To test this point arrangements were made to draw wires at a low temperature, but as a suitable supply of liquid air was not available a mixture of solid carbonic acid and ether was used as the cooling agent, and the minimum temperature reached was $-80°$ C.

The wire plate was fitted into a solid wooden trough, which was screwed down to the drawing bench. Opposite the particular hole in the plate through which the wire was to be drawn a tube was fixed in the side of the trough. The wire was led through this tube, and then across the trough and through the hole in the plate. The trough and tube could be filled with the mixture of carbonic acid and ether, so that both the wire and the plate could be kept at a temperature of $-80°$.

In carrying out the experiments the wire was drawn through the plate for one-half of its length, while the apparatus was still at the ordinary temperature; the apparatus and the wire were then cooled to $-80°$ by applying the

freezing mixture, and the remaining half of the wire was then drawn through the hole.

In this way specimens drawn at the two temperatures were obtained, which in other respects had been subjected to strictly identical conditions up to the final drawing, so that any differences in the tenacity of the wires could be confidently assigned to the effect of the temperature at which they were drawn.

A gold wire 186 mm. long was annealed at 280°, and was then drawn at the ordinary temperature through successive holes in the wire plate till it measured 352 mm. It was then drawn through the final hole in the way described above; the first half at the ordinary temperature (16°) and the second half at −80°. The extension during the final drawing measured approximately 17 mm. on the first half and 15 mm. on the second. The length was now 384 mm., and the total extension had therefore been 106 per cent.

Our previous experiments had shown that the highest tenacity in gold wire was developed by drawing it, after annealing, to about $3\frac{1}{2}$ times its original length, so that it was not to be expected that the maximum tenacity of 15·6 tons per square inch would be reached in the present specimen, which had only been drawn to little more than twice its original length. This expectation was realised, for the portion which had been drawn at 16° had a tenacity of 14·45 tons, while the portion drawn at −80° had a tenacity of 15·72 tons. The tenacity tests were both made at a temperature of 16°. The gain in tenacity by drawing at the lower temperature was 1·27 tons, or 8·8 per cent.

A specimen of copper wire treated in the same way

showed a gain of tenacity of 6·6 per cent by drawing at the low temperature. The tenacities were :

For wire drawn at	16°	27·2	tons per square inch.
,, ,, ,, ,,	−80°	29	,, ,, ,, ,,

These results show that there is a substantial gain in tenacity by wire-drawing the ductile metal at −80° C., and it seems justifiable to assume that if drawn at the boiling-point of liquid air the tenacity would be correspondingly higher.

It would be quite feasible to carry out this operation on an industrial scale at a moderate cost, and in this way to add substantially to the tenacity of the high conductivity copper wires used for telephone and telegraph cables.

The maximum tenacities recorded by Dewar and Hadfield are : at the ordinary temperature, gold 15·1 tons per square inch, silver 19·5 tons, and copper 15 tons ; at the boiling-point of liquid air, gold 20·1 tons, silver 24·8 tons, and copper 20·1 tons. With the exception of the figures for gold, these tenacities are all considerably lower than those we have obtained. This was only to be expected, for the above tests on copper were made on the metal in the annealed condition. In the case of gold some further explanation appears to be called for. The tenacity of pure gold in the annealed state was found by Roberts-Austen to be 7 tons per square inch, so that the specimen used in the observations by Dewar, if of equal purity, must have been in the hard-drawn, not in the annealed or crystalline condition.

A study of the form and appearance of the fractured ends of the wires used in our experiments reveals several

points of interest. In every case the copper wires showed the cupped formation at the fractured ends. This formation is evidently due to the lower tenacity of the central core, which breaks before the outer skin has completely given way.

The skin, therefore, appears like a sleeve pulled over the fractured ends of the core on both pieces. The weakness of the core is caused by the presence of gases, which no doubt originally appeared as bubbles, but which have been driven into the core by the flow of the metal and there drawn out into fine tubes during the wire-drawing. These tubes appear as minute holes dotted all over the broken ends of the core, and are distinctly visible with a low-power objective, Fig. 89. From the nature of the fracture it is evident that this fibrous or cellular core is a source of weakness, and must considerably reduce the tenacity of the metal. It is possible that the flowing action to which the metal has been subjected may have caused the disengagement of occluded or dissolved gases at the moment of the passage from the crystalline into the vitreous state. A proportion of the gas disengaged would naturally be driven in towards the centre of the wire, as the outer skin must be comparatively impervious.

The silver wires occasionally showed a slight cupped formation, but in this case the structure appeared due to the presence of minute bubbles of gas, as if these had been given out at the moment of fracture. In the main the fractured ends present the appearance to be expected from an extremely viscous and fairly homogeneous solid.

The gold wires were practically free from gases, and their fracture was almost perfectly viscous. Fig. 96 is a

photograph of the fractured ends of a gold wire, one of which was slightly etched to show the stream-lines marked out by granules.

Gold—Purity, 9997 parts in 10,000. Diameter of Wires tested, 0 55 and 0·54 mm.	Tenacity, Tons per Square Inch at	
	15°.	−182°.
Annealed at 320°, then drawn to 13½ times its original length without further annealing.	14·6	22·4
Annealed at 320°, and then drawn to 3½ times its original length without further annealing.	15·6	—

In the first test at 15° the wire broke without any general stretching. In the test at −182° there was a general stretch of 11½ per cent, and the diameter was reduced accordingly.

The tenacity is therefore calculated on this reduced diameter. The second test shows that the first wire had been weakened by overdrawing.

Silver—Purity, 10,000 parts in 10,000. Diameter of Wires tested, 0 55 and 0·46 mm.	Tenacity, Tons per Square Inch at	
	15°.	−182°.
Annealed at 300°, and then drawn to 13½ times its original length without further annealing.	25·7	34·4
A piece of the same wire further drawn to 1·4 times its length.	22·5	—

In the first test at 15° the wire broke without any general stretching. In the test at −182° there was a general stretch of 11 per cent. The tenacity was therefore calculated on the reduced diameter. The result of the second test of the further drawn wire makes it probable that the first wire had been overdrawn.

Copper—100 per cent Conductivity. Diameter of Wires tested, 0·54, 0·46, 0·425, and 0·38 mm.	Tenacity, Tons per Square Inch at	
	15°.	−182°.
Annealed at 300°, and drawn to $5\frac{1}{2}$ times its original length without further annealing. This wire is referred to as (*a*).	28·4	36
A piece of (*a*) further drawn to 1·4 times its length.	27·1	—
A piece of (*a*) further drawn to 1·7 times its length.	27·4	—
A piece of (*a*) annealed at 300°, and drawn to 1·4 times its length.	22·0	—
The same further drawn to 1·7 times its original length.	23·7	—
The same further drawn to 2 1 times its original length.	25·9	—

In all the tests at 15° C. the wire broke without any general stretching; in the test at −182° there was a general stretch of 12 per cent. The tenacity was therefore calculated on the reduced diameter. The further tests show that the full tenacity is not reached by drawing to $2\frac{1}{2}$ times the original length after annealing. Taken in conjunction with the gold test, however, it would appear that a stretching of three or four times is sufficient to develop the maximum tenacity.

A series of observations which show that, in hard-drawn wires, the transition from the hard to the soft state occurs over the same comparatively short temperature range in which recrystallisation takes place.[1]

Four indications of change of state were used:

1. "Mechanical stability," being the load required to produce an extension of 1 per cent.

2. Micro-structure, showing the initiation and completion of crystallisation.

3. Electro-motive force of couples consisting of hard and soft wires.

[1] *Proc. Roy. Soc.* A, 79, 1907.

4. Acoustical measurement of the elasticity of reed vibrators.

1. *The Mechanical Stability Test*

The experiments just quoted show that wire-drawing can be carried to a point at which a certain condition of mechanical stability is reached, so that the wire will break practically without further extension if a sufficient stress is applied. The ductile metals show their highest tenacity when they are in this condition, and, owing to the relatively small amount of molecular slipping or displacement which occurs before fracture, it may be accepted that the rigidity and the tenacity break down practically at the same point. This state of stability, therefore, supplies a definite and convenient starting-point from which to measure any reduction in stability which may result from heating the hardened metal to various temperatures. For the purpose of this research it was decided to measure the alterations in stability not by the yield-point as usually understood, but by the stress required to produce a permanent extension of 1 per cent. The standard extension was fixed at this amount only after considerable experience on the behaviour of hard-drawn and annealed wires had been accumulated in this and previous researches. The results obtained by its use show that while considerable irregularity is found in the earliest beginnings of yielding, yet after a 1 per cent extension is reached the strain responds fairly promptly and regularly to changes of stress.

The Heating of the Wires

The oven in which the hard-drawn wires were heated consisted of a thin steel tube about 5 mm. in diameter and

1 metre long, through which a current up to 125 amperes could be passed. The current was regulated by a water-cooled resistance, while the temperature was watched by means of a thermo-electric pyrometer. The uniformity of the heating along the tube was tested once for all by moving the thermo-couple from end to end and noting the temperature. In this way it was found that with the exception of a short distance at either end the temperature was practically uniform throughout. The wires annealed were 500 to 600 mm. long; they were slipped into a thin glass tube, which in turn was slipped into the heated steel tube, so as to occupy its middle portion. As the available supply of silver wire of uniform quality was all required for the E.M.F. tests, the principal series of stability tests was made with gold and copper, but after the conclusion of these a few stability tests were made with silver wire.

The hard-drawn gold wire had a tenacity of 14·6 tons per square inch; this corresponded with an actual load of rather over 13 lbs. on the wire. Under this load the wire stretched less than 0·3 and then yielded no further. The load of 13 lbs. was then applied to wires which had been heated at 30°, 100°, and 200°, and in no case did the extension exceed 0·3 per cent. The stability, therefore, was still unimpaired. A wire which had been heated at 225° was loaded with $12\frac{3}{4}$ lbs., and stretched 0·7 per cent. From the behaviour of the next wire after heating at 235°, it was judged that the 225° wire would have stood the full load of 13 lbs. without stretching more than 1 per cent. The 235° wire was gradually loaded with 12 lbs., and only stretched 0·3 per cent, but on increasing the load to 13 lbs. it broke without any general stretching. The measurement of the broken pieces showed an extension of rather

less than 1 per cent. While the last two wires fully conformed to the arbitrary standard of stability, their behaviour indicated that a slight impairment of stability had set in. The 250° wire was gradually loaded to 13 lbs. and stretched exactly 1 per cent. The 260° wire showed the first failure to reach the full standard ; it was gradually loaded to 12 lbs. and stretched 1 per cent. The 270° wire broke at 11·6 lbs., and the measurement of the pieces showed that it had stretched 1 per cent. The 280° wire, gradually loaded to 11 lbs., stretched rather less than 1 per cent, but when the load was increased to $11\frac{1}{2}$ lbs. it stretched rapidly and broke. The measurement of the pieces showed an extension of 5 per cent, of which 4 per cent had occurred under the last $\frac{1}{2}$ lb. of load. It is to be noted that this serious reduction of stability occurred at 280°, which, as will be shown later, is the temperature at which well-developed crystalline grains were first visible, Fig. 103. The 300° wire stretched 1 per cent with a load of $5\frac{1}{2}$ lbs., and the 335° wire gave a similar extension at 4 lbs. The latter is equal to a stress of 4·55 tons per square inch ; the stability has thus fallen to less than one-third of its original value, the chief part of the reduction having occurred under an increase of 100° in the annealing temperature.

The tests with copper wires showed the unexpected result that hardened copper begins to lose its stability at a lower temperature than gold, and that the loss proceeds much more rapidly thereafter. The full load of 21 lbs., which was still carried by the wire at 200°, had to be reduced to 19 lbs. for the 210° wire, though at this point the extension was rather less than 1 per cent. With the 230° wire a load of 11 lbs., or little more than half the

original load, produced an extension of 1·1 per cent. A minimum load of 6 lbs. was reached by the 305° wire; thus the stability had fallen to 0·28 of its original value

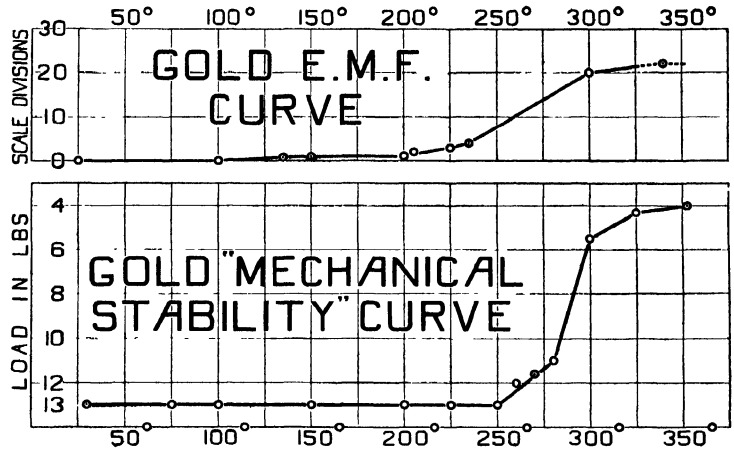

FIG. A.

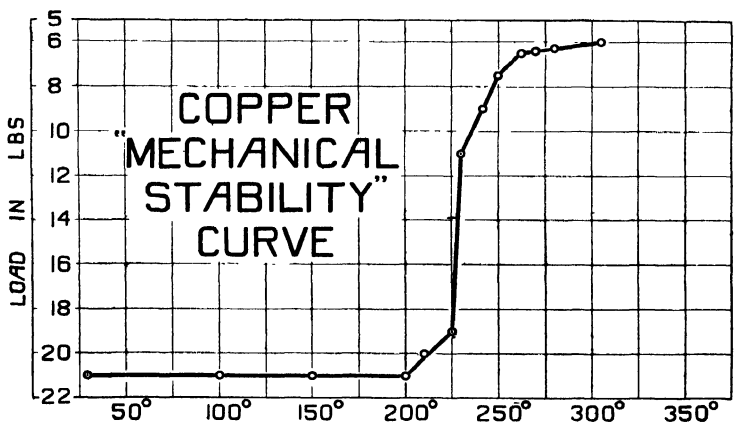

FIG. B.

under an increase of less than 100° in the annealing temperature. The stability curves of gold and copper are given, Figs. A and B. These curves are shown in

an inverted position for more convenient comparison with the E.M.F. curves.

Mechanical stability in the foregoing observations refers to that property as it exists in the mass of metal as an aggregate. Up to a certain point the stability diminishes as the crystallisation becomes more complete; but even in the wires annealed at the higher temperatures the size of the crystalline grains is small when compared with the whole cross-section of the wire. It is probable, therefore, that the stability of even the softest aggregate is much higher than that of the individual crystals. In gold the aggregate stability fell to 4·5 tons per square inch, but it may safely be assumed that this does not represent the minimum stability of the individual crystalline units. This has an important bearing on the behaviour of metals under alternating stresses. When the theory of hardening by flow was first put forward by me in 1904, it was then pointed out that the theory might be applied to the elucidation of the disintegration of metals under alternating stresses. This application of the theory will be considered later.

Micro-Structure of Hard-drawn Gold Wires

On etching the surface of hard drawn gold wires, the structure disclosed appeared to be finely granular, no traces of crystalline grains or of patches of uniform orientation being visible. Specimens were ground so as to expose longitudinal sections at various depths, and these were etched until the true understructure was disclosed. At low magnifications the structure appeared to consist of parallel strands or fibres which became thinner, and either

pinched out or drew closer together at the point of fracture.

For the proper resolution of the intimate structure of these strands or fibres, a lens of fairly high N.A. is necessary, and in the photo-micrographs, Figs. 100 and 101, a 4 mm. objective of 0·95 N.A. was found most suitable. On Fig. 100 the etching has not penetrated very deeply, and portions of the surface are still covered by the remains of the disturbed layer which had been produced by the grinding and polishing, but on the lighter parts of the photograph the internal structure is plainly disclosed, and it is seen that the strands or fibres are composed of grains which have been drawn out and pinched into long torpedo-like forms.

Fig. 101 above shows the effect of etching away still more of the matrix of vitreous metal and with it the smaller fragments of crystalline grains. In photographing this specimen, as the irregularity of the surface made it impossible to get more than a small part in perfect focus at one time, that adjustment of focus was chosen which gave the best general idea of the arrangement of the comparatively large masses which have survived the severe treatment of wire-drawing. The material which had been removed from between these ridges is the more soluble, but also the more mechanically stable vitreous metal, which has acted as a rigid matrix to the deformed grains which are enclosed within it. During the successive stages of stretching it seems probable that, within any given portion of the wire, the rôles of protector and protected may be taken in turn by the substance of adjoining grains. A break-down of structure occurring in certain grains or lamellae will result in the momentary production of a relatively large quantity of the mobile phase at the rubbing

surfaces, so that for this moment the line of least resistance will be through these grains, which will therefore take the chief part in the adjustment of strain. But the momentary mobility having given place to the rigidity of the hardened state, this will become the line of greatest resistance, and the stress will now fall on the adjoining grains or lamellae. These will in their turn break down and flow, and in so doing will play their part in the adjustment of strains. Under an augmenting stress these alternations will naturally continue till the rigidity of the matrix as a whole becomes so great that it will break rather than yield. The present observations show that this stage is reached while there are still comparatively large masses of crystalline substance concreted into rigidity by the flow which has occurred at surfaces within the mass. These masses do not consist of uniformly oriented lamellae, but are a conglomerate made up of deformed lamellae cemented together by flowed metal, Fig. 101. These results are confirmed by the researches on the micro-structure of the thinnest gold films. The drastic operations of gold-beating and wire-drawing fail to convert the whole of the metal into the vitreous state, and this suggests that the complete conversion cannot be effected by any purely mechanical process.

2. *Micro-Structure showing the Initiation and Completion of Crystallisation*

The crystallisation of various ductile metals has been studied, but the most complete series of observations has been made on gold, partly because it does not oxidise or tarnish on heating, and partly because it is rather less

difficult to develop the crystalline structure by etching in gold than in silver or copper.

Specimens from hard drawn gold wires, having the micro-structure shown in Figs. 100 and 101, were ground and polished, and were then heated in an air bath for one hour at temperatures ranging from 195° to 335°. They were afterwards etched in warm *aqua regia*, in which a good deal of gold had been dissolved. The microscopic examination of the etched specimen was made by normally reflected light with lenses of 0·65 and 0·95 N.A. These lenses were preferred to the immersion lens of 1·4 N.A., on account of their greater depth of focus. Depth of focus was specially important, as the etching was conducted so as to bring out the crystalline grains in relief, and not merely as the traces of geometrical figures on a perfectly flat field. This relief was brought more clearly into view by giving to the illuminating beam a slight obliquity, so that there was a considerable play of light and shadow among the different crystalline facets. In tracing the changes of structure brought about by heat, attention was directed firstly to the disappearance of the strained type of structure, Figs. 100 and 101, and secondly to the appearance of a new crystalline structure, Figs. 102 and 103. Microscopic appearance of the etched specimens :

1.	Heat for 1 hour at 195°.	Distorted grains unchanged, Figs. 100 and 101.
2.	,, ,, ,, ,, 215°-219°.	Distorted grains still unchanged.
3.	,, ,, ,, ,, 225°-230°.	Distorted grains disappearing, Fig. 102.
4.	,, ,, ,, ,, 258°-267°.	New crystalline masses, but no grains.
5.	,, ,, ,, ,, 278°-284°.	Well-formed crystalline grains, Fig. 103.
6.	,, ,, ,, ,, 220°-330°.	Well-formed crystalline grains, Fig 103.

Fig. 102 shows the structure of No. 3, and is the first stage in the recrystallisation due to annealing.

Fig. 103 shows the structure of No. 5 at a magnification of 700 diameters. The differently oriented grains and lamellae can be distinctly traced on the photograph, but were of course much more plainly seen in the microscope, as the natural advantage of the accommodation of the eye as well as the power of rapidly focussing the microscope from one plane to another have to be sacrificed when the image is received directly on the photographic film.

This great change of structure has been brought about in the solid metal at a temperature 800° below the liquefying-point and by a temperature rise of only 50°.

The disappearance of the distorted structure which set in about 225° was clear and unmistakable, as was also the appearance of the definitely oriented crystals at 280°, Fig. 103. The intermediate changes of structure were more difficult to follow, but the impression gained from frequent re-examination of the specimens was that regular orientation sets in from many centres simultaneously, the oriented units being small but numerous. Fig. 102 taken by the lens of N.A. 1·4 shows these minute crystal aggregates. As the kinetic energy of the molecules rises with the temperature, the larger of these units impress their orientation on their smaller neighbours, and thus absorb them. This process of growth is only arrested when the smaller units have all been absorbed and the surfaces of the larger crystal grains are in contact with each other. With each rise of temperature a new state of equilibrium among the grains is quickly established, and no readjustment of their various spheres of influence takes place thereafter till the kinetic energy of the molecules is again increased by a further rise

in temperature. The exact conditions of crystalline growth at higher temperatures have not been studied, but there are definite indications that growth and readjustment of equilibrium continue at temperatures considerably above 300°.

3. *Electro-motive Force of Couples consisting of Hard and Soft Wires*

In the earliest experiments the thermal E.M.F. between silver in the hard and soft states was determined by gradually heating the couple till the maximum deflection of the galvanometer was reached. This occurred before the full crystallisation temperature was reached, as at that point crystallisation of the hard wire took place, and the E.M.F. dropped back nearly to zero.

Preliminary experiments having shown that by heating to 100° the hardness of the hard drawn wires was only slightly reduced, while they were at the same time brought into a permanently stabilised condition from the electrical point of view, it was arranged that all the standard hard wires should be stabilised in this way. It was also arranged that, in making the E.M.F. tests with the experimental couples, 100° should be adopted as the standard maximum temperature to which they were to be heated. Under these conditions the couples could be depended on to give identical readings from day to day for an indefinite time, for secular changes in the hard wires were completely eliminated by the preliminary heating at 100°. The soft wires of the couples were prepared by heating hard wires to the predetermined temperatures in the electrical oven. After heating, it was necessary to handle the soft wires with great care, so as to avoid straining them by bending or twisting. The

two wires of the couple were slipped through separate glass tubes, and the junction was made by binding the projecting ends together with very fine silver wire. The junctions with the galvanometer leads were kept at 17°. The couples were heated to 100° by plunging them into a glass tube through which steam was freely blowing at atmospheric pressure ; they were cooled by dipping them in water at 17°.

A number of hard drawn silver wires were brought into the stable state by hanging them in a glass tube through which steam was blowing freely. Some of these were reserved as standard hard wires, and the others were heated at various temperatures in the electrical oven. In the principal series of observations, wires which had been heated in the annealing oven at 200°, 220°, 240° were used. Each of these wires was tested in a couple with the standard hard wire, and in addition the heated wires were tested in pairs among themselves. These latter tests were a useful check on the former. An example will show the extent to which the two sets of observations were in agreement, and will at the same time indicate the order of accuracy of the observations as a whole. Let the letters *a*, *b*, *c*, etc., stand for the different couples, then

(*a*)	100°-200°	heated	and	cooled	between			
	17°	and	100°	gave	a deflection	of	65	scale divisions.
(*b*)	200°-220°	,,		,,	,,		86	,, ,,
(*c*)	100°-220°	,,		,,	,,		156	,, ,,
(*d*)	200°-240°	,,		,,	,,		215	,, ,,
(*e*)	220°-240°	,,		,,	,,		125	,, ,,
(*f*)	100°-240°	,,		,,	,,		280	,, ,,

Therefore—

(*f*)	measured in one step	= 280	scale divisions.	
(*f*)	,, ,, three steps	= 276	,,	,,
(*f*)	,, ,, two steps	= 280	,,	,,
(*f*)	,, ,, two steps	= 281	,,	,,

Observations were made on the effects of heating hardened wires at temperatures below 100° C.; in these the couples were heated and cooled by plunging them alternately in water at 17° and in melting ice.

With a couple consisting of silver wires in the hardest and softest states respectively, the maximum deflection obtained for the temperature difference of 83° was 500 scale divisions, equal to 27 micro-volts. This corresponds with an average of 0·09 micro-volt per 1° over the whole range. For the different sections of the annealing range the electro-motive force per 1° was as follows:

From 100° to 200°,	65 scale divisions	= 0·035	micro-volt	per	1°.
„ 200° to 220°,	86 „	= 0·232	„	„	
„ 220° to 240°,	125 „	= 0·337	„	„	
„ 240° to 260°,	45 „	= 0·121	„	„	

The deflections have been plotted exactly as they were observed, and no attempt has been made to smooth the

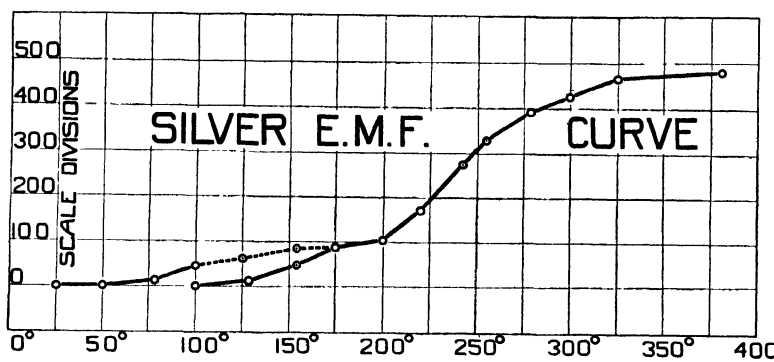

FIG. C.

curve (Fig. C, above). The rapid increase of the electro-motive force over the crystallising range is sufficiently obvious. The branch curve, which starts at 0° and runs up to 200°, is the result of electro-motive force measurements

with hard wires which had not been brought into the stable condition by a preliminary heating in steam. Considerable irregularity at the lower part of the curve was found among wires which had been drawn at different times. These were traced to secular changes of the same nature as those observed by Muir in his experiments on glass-hard steel. Taken in connexion with other observations, the lower part of the curve suggests that the changes which occur up to 200° are largely due to the relief of strains of this nature, but that above this point a fundamentally different change sets in.

The gold curve of electro-motive force (Fig. A, p. 161) confirms generally the conclusions drawn from the other observations. It will be noted that the steepest part of the curve corresponds with the temperature range within which complete crystallisation occurs.

4. *Acoustical Measurement of the Elasticity of Reed Vibrators in the Hard and Soft States*

My first experiments on this subject were made in 1904, though the results were not completed and published till 1907. My attention was called to the subject by a statement by Roberts-Austin to the effect that it had been found that, while a bell made of cast lead had some quality of resonance when struck, a bell made of hammered lead was dead and non-resonant.

The experiments made in 1904 were the following: A reed vibrator was made, the tongue of which was formed by beating a piece of pure iron wire into a thin elastic strip. Gently blown the reed gave a note between D and D♯. By further hammering the pitch was lowered to D. The

tongue was then annealed by heating it to 300° and allowing it to cool slowly to the temperature of the room. The pitch of the note was now between E.E. and F.F. Taking the rate of vibration as 67 per second and of E–F as 75, the increased rate was 8 vibrations per second.

Another reed was made, the tongue of which was formed by beating a piece of pure silver wire into a thin elastic strip.

Pitch after hammering approximately		G = 97·5	per second.
,, ,, heating to 100°	,,	G = 97·5	,, ,,
,, ,, ,, ,, 150°	,,	G = 97·5	,, ,,
,, ,, ,, ,, 200°	,,	G♯ = 108·5	,, ,,
,, ,, ,, ,, 235°	,,	G♯ = 108·5	,, ,,
Gain in rate of vibration		5·5	,, ,,

A steel tuning fork, blue temper	. .	Note C = 522	per second.
Heated to bright redness and cooled slowly, slightly sharper than	. . .	Note C = 522	,, ,,
Heated to bright redness and instantly quenched in cold water	. . .	Note B = 500	,, ,,
Restored to blue temper	. . .	Note C = 522	,, ,,

These experiments show that the elasticity is impaired either by hammering or by chilling, and that in both cases the elasticity is restored by heat-annealing.

During the following years this method of measuring minute changes in the true elasticity of solids was developed so that it could be applied with ease and accuracy. It should be observed that it is a measure of the molecular elasticity, not of the resilience of the tongue. The tongue in the hardened or vitreous state is very much more resilient than it is in the softened or crystalline.

Reed vibrators were prepared in which the vibrating tongues were made of gold, silver, copper, and iron. These reeds could be fitted on a wind chest and sounded in the usual way by compressed air. The pitch of the notes pro-

duced was compared with that of the corresponding notes on an organ pipe provided with a sliding piece, by which its length could be altered and its pitch adjusted to that of the reed vibrator. With the metals experimented on, it was found that the pitch of the hardened tongue was raised from one to two semitones by annealing at the crystallising temperature. The pitch of the vibrators used was in the neighbourhood of G = 195 vibrations per second, so that an interval of a semitone was equivalent to about 10 beats per second or 600 per minute.

Fig. D is a complete vibration curve for silver. The two stages in the relief of strain which are indicated on the

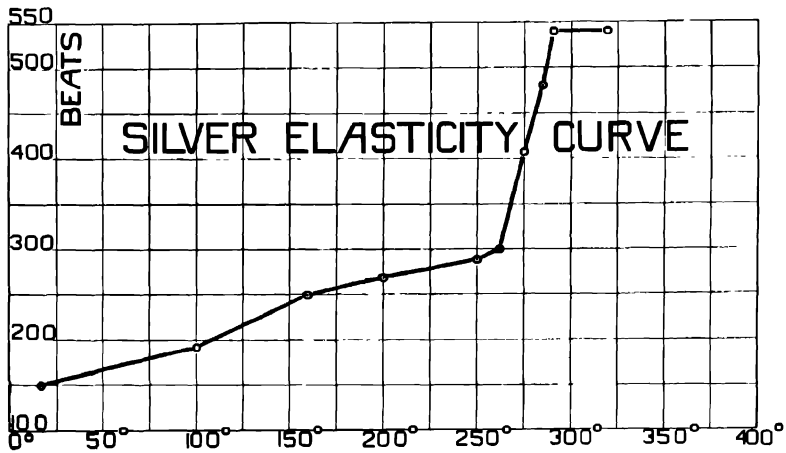

FIG. D.

electro-motive force curve are here shown much more distinctly. After rising at the rate of about 1 vibration per 1° from 100° to 150°, the rate of increase falls to about 0·4 vibration, and remains at this rate until 250° is reached. A fresh increase begins at 250°, which develops at 260° into the final very rapid rise of eight vibrations per minute per 1° over the next 30°. At 290° the maximum elasticity is

reached, and further heating to 320° produces no increase in the rate of vibration. This method of measurement lends itself particularly well to the study of secular changes of elasticity in newly strained metals; for example, in one instance the rate of vibration of a freshly beaten silver tongue, which was kept at the room temperature of 16°, rose 30 beats in three hours.

The amplitude of the vibrations of tongues of gold and silver in the crystalline state is very small, owing to the extreme softness of the metal; indeed, unless a small and very thin tongue is used, the stresses caused by the vibrations are sufficient to cause permanent strain. This was first discovered with a gold vibrator. As the annealing temperature was raised, the rate of vibration increased quite normally up to 250°, but at this point the rate suddenly fell back to what it had been at 100° C. The annealed tongue was so soft that at first it could only be sounded by a very gentle stream of air; after continued blowing a portion of its former spring was restored, but with it a lower degree of elasticity. In the case of the silver vibrator, the first tongue used showed the same effect; it was therefore rehardened by beating it to one half of its thickness, after which it showed no signs of reverting to the less elastic condition, even after annealing at 320°.

The Production of Amorphous Vitreous Gold of Exceptional Rigidity

The experiments on wire-drawing having shown the limits to which the increased tenacity and rigidity of the hard state can be developed in gold by this method, experiments have been made on the building up of an entirely

vitreous mass of gold. Gold was precipitated from a solution of the chloride as a spongy brown powder. The washed and dried powder was compressed in a die after the gases it had contained had been pumped off at a temperature of about 150°. The pressure was applied by a small hydraulic press. This pressure was so great that the gold plug made a depression in the bottom plate of the die, which was of tool steel. The pressure must have been 60 to 80 tons per square inch. The gold squirted very slightly through a hole in the bottom plate, and also between the plunger and the sides of the die. The squirted gold was very hard and rather brittle, quite unlike pure gold prepared in any other way. The specific gravity of the compressed plug was 19·05, or rather lower than the specific gravity of crystalline gold. Its micro-structure was granular and slightly spongy, Fig. 95. This amorphous gold was certainly very much more rigid than even the hardest of cold-worked gold; it was also almost devoid of plasticity. Another plug of compressed gold was made from the same powder, but a tiny spiral of very fine soft wire was dropped into the die before it was packed with powder. When a very moderate pressure was reached, the soft gold squirted quite freely past the plunger, leaving the plug of hard gold behind.

The first compressed plug was heated to 350°, and showed no development of crystallisation. In the absence of crystalline nuclei the amorphous vitreous form is stable even at this temperature. The squirted metal from the second plug which did contain nuclei crystallised freely at 350°.

These experiments do not by any means exhaust the subject, but they certainly confirm the view that plasticity depends to a very large extent on the presence of crystal-

line substance, and conversely, that aggregation in the amorphous vitreous form, while it greatly increases the rigidity, reduces the plasticity to an almost negligible quantity.

Hardness due to Alloying

These conclusions have a bearing on the question of hardness and softness in alloys. The two ductile metals, gold and silver, form mixtures which are more rigid than either of the constituent metals. These mixtures may in part consist of non-crystalline portions in which the molecules of the two metals are so distributed as to prevent the formation of crystals, either pure or mixed. The molecules of the two components are thus uniformly distributed, as they would be in a solution which has been obtained in the vitreous amorphous state by chilling. Sometimes a very minute addition of a second substance to a pure metal is sufficient to prevent crystallisation in the regular way, or even to prevent it altogether. The product is then more rigid and less plastic than the pure metal.

Hardness produced by the Evolution of Gases

The evolution of a dissolved gas when a critical point is reached, *e.g.* hydrogen in iron, may so effectually prevent or modify crystallisation that the metal is hardened. The gas molecules, as they find their way among the metal molecules of the solid, are quite capable of producing sufficient movement to arrest crystallisation, or even to flow the crystals which are already formed into the amorphous vitreous variety.

On one occasion I was, through a fortunate chance, able to watch actual liquid-like movement taking place in a

metal surface. A piece of copper which contained from 5 to 7 per cent of nitrogen had been drawn over the surface of a fine Turkey stone. On examining the streak left by the copper by normally reflected light with a 4-mm. objective of 0·95 N.A. and a high-power eye-piece, it was noticed that movement of some kind was going on on the surface. By careful watching it was seen that the surface was being broken up by the issue from the metal of minute gas-bubbles. The bubbles were detected by the holes which they left on bursting. The holes were from 500 to 1000 $\mu\mu$ in diameter. The process lasted for fully an hour, during which time the appearance of the metal completely changed, the original smooth surface having given place to a spongy structure. Fortunately a careful record of the observation was made at the time, for I have not yet been able to reproduce the particular combination of conditions to which it was due. The liquid-like mobility of the metal was evidently caused by the passage of the gas from among its molecules and its issue as minute bubbles. The thickness of the mobile films produced by the issuing bubbles was of the same order as those which were actually measured on polished calc-spar, namely 500 to 1000 $\mu\mu$.

Hardness produced by Electro Deposition

Under certain conditions electro-deposited metals may be produced in a highly strained state. Professor Huntingdon found that the strip copper which is deposited in a remarkably hard condition on a spinning mandril, by the process of Mr. Cowper-Coles, if annealed developed a new type of crystallisation. I repeated this experiment, and obtained a similar result. The annealed structure was of the same type as that which results from the annealing of

cold-worked metal. This fact, as well as the great hardness and tenacity of the electro-copper, led me to the conclusion that the deposition of the metal under conditions of strain had caused the molecular aggregation to be of the vitreous amorphous type.

Hardness due to Flow and Vitrification resulting from Shrinkage Strains

Flow may occur in a cooling mass as a result of shrinkage strains. When a rod of pure iron is case-hardened by heating it at 850° to 900° in sodium cyanide, a thin but very hard case is formed. If the rod is quickly chilled the shrinkage of the case profoundly alters the micro-structure of the ferrite grains in a way which distinctly suggests that the lamellae have slipped and that considerable internal flow has occurred. If the case is ground away and the bar reheated and chilled, the ferrite grains resume their normal structure.

A half-inch bar of mild steel, the analysis of which is given below, was heated at 900° C. and quickly chilled in cold water. It is generally recognised that only a very slight increase of hardening results from chilling a low-carbon steel of this type. It was therefore not anticipated that the chilled bar would show any change of structure as a result of chilling from 900°, and this anticipation was confirmed by the examination of a cross-section of the bar after polishing and etching, Fig. 91. The structure consists essentially of undeformed ferrite grains embedded in eutectic.

A similar bar was heated for two hours in molten sodium cyanide at 900° C. It was chilled by plunging in cold water and was tempered at 250° to 300°. The polished cross-

section showed that a hardened case about $1\frac{1}{2}$ millimetres in thickness now surrounded the bar, and etching developed the micro-structure of the case and of the portion within it. The thickness of the hardened case is determined by the depth to which the action of the sodium cyanide penetrates. The effect of this action is to add carbon and nitrogen to the iron, and to convert it into an alloy which can be made glass-hard by heating to 900° and chilling. Fig. 94 shows the structure of the hardened case which had been converted into high carbon steel. Fig. 92 shows the general structure of the metal enclosed by the hardened case, and Fig. 93 shows under high resolution of the oil immersion lens the structure of individual ferrite grains near the centre of the section that is as far as possible from the hardened case. The ferrite grains are still visible, but slipping and turning of the lamellae have occurred under the powerful stresses brought about by the shrinkage of the case, and vitreous films of pure iron have been formed at all these surfaces, general hardening of the highly ductile ferrite having resulted. That this change in the internal structure was due to mechanical movement and flow, and not to chemical change, was proved by removing the hardened case from the bar by grinding, heating the bar to 900°, and again chilling it in water. An etched cross-section now showed the same ferrite structure as in Fig. 91.

The micro-structure of the hardened ferrite grains in Figs. 92 and 93 may be compared with the analogous structure produced in the crystal grains in gold hardened by beating a plate, Fig. 90, and in gold globules which had been flattened by the blows of a drop hammer, Figs. 82 and 86. In all ductile metals a new structure or " texture " of greater rigidity is produced without chemical change, and

purely as a result of mechanical disturbance and flow. Though in the case of alloys chilling may produce hardening by stereotyping a particular form of crystalline structure which is in equilibrium at the high temperature, it also acts by producing and stereotyping the results of mechanical flow and the formation of the vitreous state.

The development of the maximum intrinsic hardness of the metals can thus be brought about in many different ways, but in every case it appears to depend on the special development of the cohesive forces which is associated with the vitreous state.

General Conclusions on the Properties of the Crystalline and Vitreous States in Metals

1. It has not as yet been found possible to produce a homogeneous specimen of metal entirely in the vitreous or hard state, for mechanical working, however severe, of even the purest specimens always produced a mixed structure consisting of the hard and soft states. The rigidity and tenacity of the hardened metal appear to depend quite as much on the "texture" or type of structure developed as on the actual proportions in which the two states are present.

2. As regards the heat treatment of metals in the hardened state, the temperature ranges over which (1) recrystallisation, (2) loss of mechanical stability, (3) development of thermal E.M.F. between wires in the hard and soft states, and (4) the complete restoration of elasticity in hardened metal occur are so well marked, and they coincide with each other so closely, that there can be no doubt that they point to the occurrence of a true change of state in the hardened metal when a certain temperature is reached. The nature of this change of state is shown by

the microscope to be a development of the crystalline from the non-crystalline or vitreous condition.

3. In annealing by heat, no important softening of the metal or reduction of mechanical stability occurs till the recrystallisation range of temperature is reached, but at that point there is a sharp drop in the stability curve, which drop continues as the temperature of annealing is raised over a range of about 50°. Over this range there is a corresponding growth of the crystalline grains. Above this range the curve flattens rapidly, but there is evidence that the crystals may continue to grow further as the temperature is raised. The mechanical stability diminishes as the crystals grow larger, and it is probable that the true stability of the crystalline state, as it occurs in single crystals, is considerably lower than that of any aggregate of crystalline grains.

4. The thermo-electric observations, especially those on silver, show that the thermal E.M.F. is an exceedingly delicate indicator of a state of strain in hardened wires. The observed E.M.F. is therefore in part due to strains of a temporary character and in part to a physical change of state of a fundamental nature. By using as the hard wire of the thermo-junction a wire which had already been annealed at 100°, these temporary strains were partly eliminated, but the curve obtained still indicated that strains of this type persisted till a temperature of 180° to 200° was reached.

5. The secular changes in hardened metal appear to be limited to the gradual relief of strains similar in kind to the contraction strains observed by Muir in the case of glass-hard steel.

This relief of strain differs not only in degree, but also in kind, from the molecular change which occurs when

the crystallisation temperature is reached and complete orientation of the molecules takes place. The first state is unstable, even at ordinary temperatures, while the second is stable up to the lower limit of the crystallisation range. The first stage in the relief of strain is not accompanied by any change of micro-structure, while in the second a very obvious change occurs.

With reference to these two kinds of molecular constraint in hardened metal, it is suggested that in the first state the molecules themselves are strained, while in the second state they are merely restrained by their mutual cohesion from turning into a uniformly oriented condition.

6. By using an acoustical test for the detection of minute changes of elasticity in the metal tongue of a reed vibrator, elasticity curves have been obtained which show even more clearly than the E.M.F. curves that the relief of strain by heat occurs in two distinct stages, and that the rate of change per degree of temperature is much greater in the second than in the first stage.

7. It is believed that the hardening of metals by chilling from a high temperature is, in certain cases, due to the development of contraction strains. These strains, if of sufficient magnitude, will lead to the displacement of the molecules from their crystalline orientation at the internal surfaces of grains and lamellae, thus forming a rigid structure of the mixed states in the same way as mechanically applied stress would do.

From this point of view *the hardening produced by hammering and that produced by chilling are both due to the same kind of molecular change of structure.* The present observations explain why ductile metals like gold and copper are not hardened when they are chilled from a high

temperature. In the case of gold, for example, recrystallisation can occur over the whole range from the solidifying-point at 1080° down to the minimum crystallising temperature at 220°. It is clear, therefore, that the contraction strains which occur at any point over this range will immediately be relieved by recrystallisation. In cooling below 220° the contraction is probably too small to give rise to strains of sufficient magnitude to deform the crystals and to produce a hardened condition. From this point of view, a substance with a high crystallising temperature and a high coefficient of expansion is more likely to harden by chilling than one in which these constants are lower.

Substances like the silicate and borates, owing no doubt to their high viscosity, have a comparatively high crystallising temperature; it is therefore easy to cool them quickly through the crystallisation range, hence they most naturally pass into the vitreous state on cooling.

8. In considering the effects of repeated alternations of stress in metals, it is evident that the endurance of the specimen will be determined not only by the mechanical stability of the aggregate as a whole, but also by the stability of its separate units of structure.

In ductile metals the stability of the crystalline state is greatly inferior to that of the vitreous state; this inferiority may at first be completely disguised in a mixed structure composed of the two states, though it may ultimately make itself apparent under repeated alternations of stress. The observations indicate why the superior plasticity of the crystalline state, instead of being in all cases a source of strength in the mixed structures produced by hardening, may actually be an element of weakness.

Of the three metals used in these particular observa-

tions, copper is the only one which is of any industrial importance in the pure state, but as copper of this degree of purity is regularly used on a very large scale, the observation that hard drawn copper begins to lose its mechanical stability at so low a temperature as 210° may have an important bearing on its use for purposes in which it might be subjected, even for short periods, to a temperature above 180°. *Pure hard worked copper is clearly a treacherous material to use in the construction of steam-pipes which are to be used for high pressure or superheated steam.* If used at all for this purpose the pipes ought to be finally brought into a uniformly crystallised condition by annealing at 300° to 350° after all work upon them has been done. Between the hard and soft states there is a mechanically unstable condition in which the loss of stability is not compensated for by the development of plasticity, which only occurs when the whole mass consists of properly developed crystals.

Application of the Theory of the Crystalline and Vitreous States to the Break-down of Metals under Alternating Stresses

Wherever the effects of alternating stresses on the micro-structure have been carefully observed, as in the researches on iron and steel of Ewing and Humphrey and of Stanton, it has been found that the cracks which led to the ultimate destruction of the specimens generally passed through ferrite grains or areas. Ferrite grains consist of pure iron in its crystalline or softest state. From the analogy of other ductile metals it may be concluded that the stability of the ferrite grains is much less than that of the aggregates in which they occur, so that a stress which

would be insufficient to produce permanent strain in the aggregate would, if it could gain access to them, be more than sufficient to break down these crystalline units.

It is necessary, therefore, to consider in what way disintegrating stresses can gain access to these elements in the mixed structure. It will be shown that, while the crystalline state is more perfectly elastic than the vitreous state, yet that the amplitude of the vibrations is greater in the latter state. In a reed vibrator the vibrations of the tongue when it is in the hard state are slower but more ample than when it is in the soft state ; the hard tongue is less elastic but more resilient.

In an aggregate composed of the two states which is subjected to rapidly alternating stresses the hard elements may for this reason be able with safety to themselves to transmit stresses which will unduly strain the soft elements.

Consider, now, the part played by the mobile phase through which the crystalline passes into the vitreous or hardened state. A study of the hardened structure produced by wire-drawing showed that this structure owes its hardness and stability to the cementing or concreting effect of the flowed metal. It has been shown that it is possible to overdraw a wire and thus to reduce its hardness and tenacity. *The latter result may be taken to mean that, during the final drawings, the mobile phase was not produced in sufficient quantity to cement together again the surfaces at which slipping had occurred.*

Something of the same nature must occur at the surfaces of slip caused by alternating stresses. When the stress is reversed, slip will occur in the opposite direction, but not on the identical plane on which it occurred before, for the cementing action of the hard state will prevent this.

Suppose the second slip to occur at a thickness of one lamella from the first, a new layer of hard material will be formed at the other face of the intervening lamella, and a sheet of crystalline material will thus be sandwiched between two hard sheets. The next reversal of stress may find the sandwiched lamella so strengthened that it can resist further slipping. But suppose that one result of the sandwich has been to leave the crystalline lamella under a slight tension normal to the surface, then with each reversal of stress there will be further slips, and the thickness of the hard sheets will increase at the expense of the crystalline substance. Eventually, if the process continued, and assuming that the tension also continued, the whole of the crystalline material would be used up in thickening the hard sheets and an incipient crack would develop between them, which, in the absence of further supplies of the mobile phase, every additional slip would rub into greater distinctness. These steps are shown diagrammatically in Fig. E.

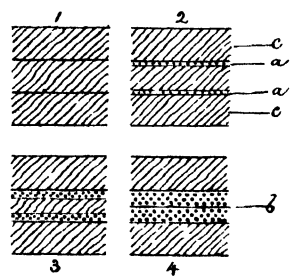

FIG. E.

1. Unstrained lamellae in *c* phase.
2. Layers of hard phase *a* formed by slipping.
3. Layers thickened by further slipping.
4. *c* phase all used up and a crack, *b*, developing.

SECTION VIII

INFLUENCE OF THE CRYSTALLINE, MOBILE, AND VITREOUS STATES ON THE FLOW OF ROCKS AND ICE

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SECTION VIII

INFLUENCE OF THE CRYSTALLINE, MOBILE, AND VITREOUS STATES ON THE FLOW OF ROCKS AND ICE

"*Mass Flow*" and "*Surface Flow*"

In Section VII. it has been shown that molecular flow, which in polishing is a purely surface effect, also takes place throughout a mass of metal at all the internal surfaces at which deformation and slip occur.

Prior to the discovery of the true nature of surface flow, flow in metals had always been regarded as necessarily involving the employment of great pressures, as in die-stamping and in the production of rods and tubes by extrusion.

In the classical experiments of Tresca and of Spring, high differential pressures were employed, and at first sight it might appear as if there could be little in common between the flow with which they were dealing and the flow which is now being considered. In reality, however, "mass flow" and "surface flow" equally depend on the passage of the solid through a truly liquid state, the transient existence of which is, in both cases, permanently recorded in the micro-structure of the solid.

In "mass flow," high differential pressures are necessary in order to overcome at the same instant the

resistance due to the cohesion of myriads of molecules throughout the mass. In " surface flow " the resistance of the individual molecules to disturbance is at least as great as that of the molecules in a massive aggregate, but as the polishing agent only seizes a layer of molecules which is from 10 to 500 $\mu\mu$ in thickness, the energy which has to be expended is only a minute fraction of that necessary to produce " mass flow."

To produce " mass flow " in the hardened steel of which a razor is made, a differential pressure of hundreds of tons per square inch would be required, yet the " surface flow " necessary to keep the edge of the razor in perfect cutting condition can be effected by lightly stropping the blade on the bare hand a few times daily, before and after use !

Differential Pressure and Elastic Compression

In the earlier discussions on mass flow it was not always recognised that the function of the high pressures employed was to produce movement of the molecules among themselves, and that this could only result from the establishment of differential pressure throughout the mass.

In solids which expand on fusion, the effect of hydrostatic compression is to raise the melting-point and to increase the rigidity of the aggregate, which is thus removed further and further from the liquid state.

The effect of hydrostatic pressure is to reduce the volume by elastic compression, and thus to store energy which will become kinetic if the mass is allowed to expand through a small opening.

A mass of metal subjected to a pressure of 100 tons per

square inch in a cylinder which it completely fills is much further from the liquid state than it was before compression, but energy of a high order has been stored in the mass by elastic compression. If now a small hole is drilled through the wall of the cylinder, the highly energised metal within begins to flow round the inner edges of the hole, and the molecular movement thus started leads to continuous liquid-like flow into the hole. The fluidity lasts long enough to enable the metal to flow through the hole, from which it issues in the solid state as a wire or rod.

Flow in Marble and Other Rocks

In Section V. it has been shown that, in the case of calcite, a very moderate pressure with the finger is sufficient to produce free flow in a surface layer of 100 to 500$\mu\mu$ in depth. It has also been shown that the vitreous layer which results from the solidification of this layer is harder and more resistant than the original crystalline surface and tends to protect the crystalline layers underneath from further flow.

These new facts, the free liquefaction and flow of calcite in the crystalline state, and the increased rigidity of the vitreous state which results from flow, throw an interesting light on the *Experimental Investigation of the Flow of Marble*, which was published by Adams and Nicholson in 1900.[1]

The results of this investigation are summarised by the authors in the following " Conclusions."

[1] *Phil. Trans. Roy. Soc.*, No. A. 195, p. 363.

Summary of Results

1. By submitting limestone or marble to differential pressure exceeding the elastic limit of the rock, and under the conditions described in this paper, permanent deformation can be produced.

2. This deformation, when carried out at ordinary temperatures, is due in part to a cataclastic structure, and in part to twinning and gliding movements in the individual crystals composing the rock.

3. Both of these structures are seen in contorted limestones and marbles in nature.

4. When the deformation is carried out at 300°, or better, at 400° C., the cataclastic structure is not developed, and the whole movement is due to changes in the shape of the composing calcite crystals by twinning and gliding.

5. The latter movement is identical with that produced in metals by squeezing or hammering, a movement which in metals as a general rule, as in marble, is facilitated by increase of temperature.

6. There is, therefore, a flow of marble just as there is a flow of metals under suitable conditions.

7. The movement is also identical with that seen in glacial ice, although in the latter case the movement may not be entirely of this character.

8. In these experiments the presence of water was not observed to exert any influence.

9. It is believed from the results of other experiments now being carried out, but not yet completed, that similar movements can, to a certain extent at least, be induced in granite and other harder crystalline rocks, and that several structures developed by these rocks in nature, in highly contorted regions, can thus be introduced.

In Conclusions 1 and 2, the authors clearly distinguish the respective parts taken in the general deformation by (*a*) cataclastic and (*b*) true bending. Under (*a*) the rock is broken up into more or less detached layers and fragments ; under (*b*) the continuity of the mass is maintained in spite of the internal movements which have given rise to a modified micro-structure.

The internal rearrangements involved in (*b*) are ascribed

by the authors to " twinning and gliding movements in the individual crystals composing the rock."

The photo-micrographs which illustrate the paper fully justify the statement that twinning and deformation of the crystalline grains do occur; and in Conclusion 5 a parallel is drawn between these phenomena in calcite and the similar phenomena which had been demonstrated by Ewing and Rosenhain in the case of ductile metals.[1] The crystalline theory of plasticity of these authors is accepted by Adams and Nicholson in its entirety. According to this theory, the plasticity of crystals is not due to flow, but to the slipping of the internal elements of which the crystals are built up on a number of definite geometrical planes.

Slipping and twinning are definite steps in the deformation of crystals under stress, but behind and beyond these movements are the deeper and more fundamental phenomena of " flow " in its newer and more intimate sense.

The liquid-like flow which occurs at all the surfaces of slip, provides the lubricant which makes this slipping possible, while the immediate resolidification of the liquid films provides the cement which binds the deformed crystals into a structure of greatly increased rigidity.

The fact that higher temperatures favour true bending means that the more highly energised molecules flow more freely.

The remarkable extent to which the mobile liquid phase is produced in calcite, even at ordinary temperatures, renders this mineral peculiarly suitable for the study of the changes in rocks and minerals which result from " flow "; but, as Adams and Nicholson have pointed out,

[1] *Phil. Trans. Roy. Soc.*, No. A. 195, p. 279.

there are evidences that these phenomena are not confined to marble, but may also be traced in the harder rocks, like granite and others of a crystalline structure. The observations on the flow of quartz, which are described in Section V., confirm this view.

I believe that the phenomena of crystalline flow are of universal application, and that their effects will yet be traced in new and unexpected directions.

The Flow of Ice

The examples of flow in solids, which are described in Sections V. and VII., all, with the possible exception of lead, refer to substances in which the vitreous state is stable at ordinary temperatures. Recrystallisation in many metals occurs between 200 and 300°.

A number of salts have been experimented with, and in these also it was found that the vitreous state is stable at ordinary temperatures, and that recrystallisation only takes place over a short range of temperature below the melting-point.

As ice is in some respects unique as a solid, it seemed desirable that its behaviour under surface flow should be studied, and that the recrystallisation temperature of the vitreous form should if possible be ascertained. Arrangements were accordingly made to carry out some experiments at Adelboden in the winter of 1906.

Experimental Observations in Switzerland

Though the winter was not a severe one, the temperature before sunrise was generally from −12° to −10° C., and on one occasion touched −17°.

The working bench was placed out of doors, in a sheltered situation, surrounded on all sides by snow-covered slopes. The sun did not appear over the edge of the snow-covered mountains till about 10 A.M., so that two hours of good daylight were available, during which the temperature was practically constant. Throughout the experiments, a thermometer on the stage of the microscope indicated temperatures of $-10°$ to $-12°$.

The illumination of the microscope was by reflected skylight from the substage mirror, the beam from which passed through a polarising prism and a selenite plate, and then through the ice film to the objective and the second prism.

When a small drop of water was placed on a glass slip which had previously been cooled to $-12°$, it instantly froze and became like a hemispherical lens, perfectly transparent and structureless. Under the microscope it showed no signs of crystalline structure, but on lightly pressing it with the polished face of a steel burnisher, it recrystallised throughout. This experiment was frequently repeated with drops of various sizes. The smaller drops invariably assumed the vitreous form, while the larger drops generally crystallised as they froze. The arrest of crystallisation in the smaller drops was probably due to the more rapid cooling of these as compared with the larger drops.

A drop of water was allowed to spread on a glass slip till it formed a thin, uniform film. The slip was then exposed in the open air till it was cooled to $-11°$. The ice film which was formed was then flowed by the steel burnisher, the maximum pressure used being of the order of 30 to 40 lbs. per square inch. The slip was at once

placed under the microscope, and the film was seen to be of different thicknesses, due to the flow which had taken place. It was composed of distinct polygonal grains, each of which was uniformly coloured, showing that it was built up of similarly oriented units. The film was again flowed by the burnisher, but though the surface had obviously been again flowed, the micro-structure was still the same. This experiment was repeated on many occasions, and always with the same result.

On one occasion the microscope, with the crystallised film in its place on the stage, was taken indoors, where the temperature was about 5°, and the behaviour of the film was watched as the temperature gradually rose. The crystalline grains did not alter their boundaries, and there was no growth of some grains by the absorption of others. The first sign of fusion was visible in the inter-granular boundaries, and as the fusion progressed, the grains became circular under the influence of surface tension, and finally appeared as a collection of separate drops.

Though the temperatures available were not sufficiently low to enable the recrystallising temperature of vitreous ice to be determined, the observations show conclusively that true flow occurs at $-12°$ under a moderate differential pressure far short of the hydrostatic pressure which would be required to lower the melting-point to that temperature. They also show that, down to this temperature, the flowed material resolidifies at once in the fully crystallised state. The general impression left by these experiments was that the recrystallisation temperature of vitreous ice is considerably lower than $-12°$, and may be in the region of $-22°$, at which temperature Tamman discovered a new type of crystallisation of ice.

Fusion under Pressure and Regelation of Ice

In 1849 Professor James Thomson from theoretical considerations predicted that, as ice contracts in volume on fusing, its melting-point would be lowered by hydrostatic pressure. This prediction was experimentally confirmed by his brother, Lord Kelvin, in 1850, and in 1880 Sir James Dewar obtained further confirmation and established the fact that, for each additional atmosphere of pressure, the melting-point is lowered by 0·0072° C.

A theory of the formation and flow of glaciers based on the fusion of ice under pressure, and its regelation on the removal of pressure, has been widely accepted, though many students of the subject have recognised that this theory could only be made to cover all the known facts by straining both the facts and the theory.

It is now suggested that, while the phenomena on which the theory is based do exercise an influence on glacial formation and flow, under the appropriate conditions of temperature and pressure, these conditions do not cover a sufficiently wide range to justify the universal application of the theory.

The Adelboden observations show that true molecular flow can be brought about at −12° by the application of deforming stresses of a very different order from the hydrostatic pressures required to cause fusion at temperatures below 0°, for, applying Dewar's figure to the Adelboden temperature of −12°, it would appear that, to produce flow by fusion at this temperature, a pressure of 1666 atmospheres would be necessary, or about 20 tons per square inch.

It is interesting and informative to work out the significance of the pressures required to lower the melting-point of ice by various amounts.

On the base of a vertical column of ice about 36 feet high, the pressure would be 1 atmosphere per square inch, and the lowering of melting-point which would result from this pressure would be 0·0072°. To lower the melting-point by 1° would require a pressure of 138 atmospheres, and the vertical column of ice necessary to develop this pressure would be about 5000 feet high, while, for the lowering of the melting-point to the Adelboden temperature of −12°, an ice column of nearly 60,000 feet would be necessary!

It is obvious that the pressures actually available in glacier formation and flow must be of a much lower order even than that necessary for the lowering of the melting-point by 1°. It follows, therefore, that with the much lower order of pressures available in glaciers, fusion under pressure, and regelation when the pressure is relieved, can only take effect when the mass of ice is at, or only very slightly below, its normal freezing-point of 0°.

Fusion under Pressure can only play a Limited Part in the Formation and Flow of Glaciers

These facts appear to justify the conclusion that this theory cannot have more than a limited application to the phenomena of the formation and flow of glaciers. True molecular flow, which occurs alike at the external and internal surfaces of crystalline aggregates, has, therefore, a wider and more fundamental relation to the phenomena

of ice flow than fusion and regelation. The reasons for this conclusion will now be dealt with more fully.

The Special Features of Molecular Flow in Ice

The temperature of ice even at high altitudes is not far removed from its melting-point. As the melting-point of any substance is approached, molecular flow takes place under increasingly favourable conditions, for two reasons.

The first of these is that the molecules are so highly energised by heat that the cohesive force by which they are retained in fixed positions relatively to each other, and on which the rigidity of the solid state depends, is almost neutralised.

The second reason is that the flowed substance on solidification does not remain in the vitreous state, but passes at once into the crystalline, so that flow can be indefinitely continued without the arrests which occur when, after each movement of the internal structure, solidification of the flowed films takes place in the vitreous or hardened state.

At temperatures *below* the recrystallisation range, flow in ice—as in the ductile metals—would be subject to these arrests, each of which would add to the rigidity of the mass, and would call for the application of higher and higher differential pressures, if the flow were to be recommenced.

We now know, however, that the crystallisation temperature of ice is lower than $-12°$, so that at and above this point the crystalline state is preserved or restored during flow. So long, therefore, as the same differential pressure is maintained in the mass, flow will continue

unchecked. On the other hand, in ice at temperatures *below* the crystallisation range, arrests due to the formation of vitreous layers will occur, and flow will only continue if greater and greater differential pressures are applied. This condition will probably only prevail in glaciers at very high altitudes.

SECTION IX

MOLECULAR PULSATION CELLS

A Tentative Hypothesis

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SECTION IX

MOLECULAR PULSATION CELLS: A TENTATIVE HYPOTHESIS

Introductory: Molecular Strain in the Vitreous State

ONE of the central facts which emerges from the foregoing studies is that the molecules of a pure substance can be assembled in aggregates which possess widely different degrees of mobility in response to heat or to mechanical disturbance. The contrasted qualities of hardness and softness, of rigidity and mobility, must therefore be intimately associated with the ultimate molecular structure of the aggregate. These studies have also disclosed certain facts in connexion with the more rigid form of aggregation, the vitreous, which indicate that in this state the molecules are in a state of elastic strain. This is shown by the loss of electrical conductivity and by the impairment of the elasticity under the acoustical test. That the strain is probably elastic is suggested by the complete restoration of elasticity which occurs when the aggregate is raised to a certain critical temperature. The full restoration of elasticity is coincident with the restoration of the regular orientation of the crystalline state. A further proof that the strain is elastic may be found in the fact that the heat of solution of the strained aggregate is greater than that

of the unstrained or crystalline aggregate. In the vitreous state energy is stored in the molecules as in a collection of coiled springs, and this energy becomes kinetic when the molecules are set free from constraint by the action of a solvent upon the aggregate and supplies the heat of solution which would have had to be drawn from an outside source.

It appears, then, that the elastic strain is maintained by some kind of constraint which the molecules exercise upon each other in the vitreous aggregate. The contrasted states in the aggregate, therefore, correspond with the contrasted states of the molecules; rigidity in a solid aggregate is associated with molecular constraint, while mobility is associated with molecular freedom. Constraint is due to the mutual cohesion of the molecules; freedom is due to the vibration induced by heat.

In the Absence of Heat the Sway of Cohesion would be undisputed

In an address to Section B of the British Association in 1905 certain deductions were made: (*a*) from the phenomena of the vitreous crystalline transformations; and (*b*) from the increase of tenacity or rigidity which occurs in solids when heat energy is diminished by the lowering of temperature. It was suggested that matter at the absolute zero of temperature must be in a completely inert condition so far as our senses enable us to judge, the potentialities of its atoms being latent and undeveloped: that these potentialities only begin to develop with the advent of heat waves from the surrounding ether: that one of the earliest of these potentialities to manifest itself

is the crystalline arrangement of the atoms or molecules: that the later phenomena of liquefaction and gasification are in a certain sense less rather than more significant than the earlier steps of crystalline development.

In seeking to develop these views it became necessary to consider more closely the part played by heat in thus unfolding the potentialities of the atom.

All the experimental researches on the properties of matter at low temperatures go to show that while the qualities of extension and mass which are common to matter in all its forms are unaltered by the removal of heat, the outstanding characteristic of the solid state, rigidity, becomes more and more pronounced as the absolute zero of temperature is approached. In other words, the physical properties which depend on cohesion show by their steady development as the absolute zero is approached that in a heatless universe cohesion would hold undisputed sway. In this universe the diverse properties of the majority of the elements as we know them would be entirely latent; the radio-active elements alone would continue by their disintegration to pass the product of their inter-atomic energy into a universe in which it would be dissipated and disappear.

With the advent of heat the all-powerful grip of cohesion is relaxed and the latent potentialities of matter begin to unfold. The waves of ether-borne energy, as they stir the responsive vibrations of the molecules, are to dead matter as the first breath of approaching spring is to the sleeping buds. As among the trees of the forest the response is more ready in some than in others, so among the elements, the lighter and more easily energised, like hydrogen and helium, are already far on in their develop-

ment towards the ideal freedom of the gaseous state before the less responsive like platinum and carbon show any signs of stirring from their lethargy. In the more slowly energised elements we can study the earlier steps in this development, and I think we are now entitled to say that one of the first of these is the acquirement by the molecules of the power of automatic crystalline arrangement.

Molecular "Pulsation Cells": a Tentative Hypothesis

The following is a brief outline of a tentative hypothesis which has been found helpful in visualising the changes of state which occur as the temperature of matter is raised from the absolute zero. The molecule, which for simplicity we shall take to be monatomic and spherical, is elastic and is capable of responding to ether-borne vibrations by vibrations of a period proper to itself and of an amplitude proper to the temperature attained. Its elasticity may be either of form or of volume; again, for simplicity's sake, let us assume the elasticity to be that of volume. The vibrations of the spherical molecule will be spherical pulses. The effect of these pulses, the period of which is necessarily enormously rapid, will be to surround the sphere with a "pulsation cell," the thickness of which will depend on the amplitude of the pulsations. The amplitude of the pulsations will in its turn depend on the temperature, so that for each temperature the cell will be of definite thickness.

When an aggregate of spheres at the absolute zero is energised by heat, each molecule as it becomes energised will surround itself with a pulsation cell proper to the temperature which it has reached, and the molecules will

be pushed apart to a corresponding distance. The outer surface of the cell, though it is purely kinetic in its origin, forms in certain respects a perfectly real bounding surface. The recognition of this is fundamental to the present hypothesis. An elastic molecule pulsating in response to heat waves from the ether does not merely surround itself with a vague " sphere of influence," as it is sometimes supposed to do, but with a well-defined outer surface, which for most purposes marks off the space occupied by the molecule just as effectually as a rigid static boundary would do.

According to this hypothesis the mutual cohesion of the molecules is weakened by heat, because the molecular bounding surfaces are so enlarged by their pulsation cells that they are gradually pushed further and further out in the sphere of influence till the cohesive force per unit of surface is reduced to a negligible quantity. When this stage is reached the molecules are no longer held together by their mutual attraction: they are free to fly apart in the gaseous state. But even in this state of freedom there does not appear to be any reason to suppose that the bounding surface of the pulsating cell is any less real and effective than it is in the molecules in the solid state of aggregation. If this is the case, then the molecular encounters in the gaseous state will take place at the bounding surfaces of the pulsation cells, not at the original surface of the molecules. It appears from this that we may regard the energy of pulsation of the gas molecules as the original source of the kinetic energy, from which the translational and rotational forms are naturally derived during the encounters of the pulsating molecules.

Consider now the bearing of this hypothesis on the

subject in which we are immediately interested. The development of pulsating cells in an assemblage of molecules must increase the mobility of the aggregate for two reasons. In the first place, the extension of the molecular boundaries will correspondingly reduce the cohesive force per unit of surface, and in the second place the new boundaries are kinetic, they are in rapid to-and-fro movement normally to the tangent planes at their points of contact.

In a collection of molecules under the influence of cohesion alone, the packing tends to be entirely haphazard, for the spheres stick to each other at the points at which they first touch, and can only be moved into new positions by externally applied force. The packing is not the closest possible; on the contrary, it can be extremely open; neither is it homogeneous. While the molecules in an assemblage of spheres of this description have no powers of self-arrangement, it is fairly evident that the development of pulsation cells introduces a new set of conditions, all of which make generally for an increase of mobility, or a reduction of rigidity in the assemblage.

Certain of these conditions will also tend to develop the power of self-arrangement among the molecules. While this latter power would probably be at a minimum in spherical molecules vibrating with spherical pulses, it would become a very powerful influence if the pulses were equatorial or polar, for then the spherical molecules would develop around themselves oblate or prolate spheroidal cells. Kinetic cells of these forms would probably tend to arrange themselves in some simple and homogeneous mode of assemblage. This kind of assemblage is, we know, the really essential feature of the crystalline state; the pulsation cell hypothesis has therefore enabled us to

visualise to some extent the advent of the automatic power of crystallisation in the molecules as they are energised by heat.

It is evident from these illustrations that the hypothesis is capable of considerable development, not only in this, but in other directions. When it is applied to the case of complex molecules consisting of two or more atoms of the same kind, or to compound molecules containing atoms of different kinds, it becomes possible to picture a great variety of forms which the compound pulsation cells might assume, and the changes in these forms which would result at different temperatures. The latter point is of special importance, because it may supply the physical explanation of the different crystalline phases of the same substance which are only stable over a certain temperature range, *e.g.* the rhombic and prismatic forms of sulphur.

If it is accepted that crystallisation results from the efforts of the pulsating molecular cells to reach certain positions of equilibrium, it follows that their displacement from these positions by mechanical disturbance and flow will leave the assemblage in the non-crystalline or vitreous state unless the substance is at, or above, the temperature at which the cells are sufficiently developed to ensure their automatic return to the crystalline formation.

Rigidity in Relation to the Availability of the Collective Cohesive Force of Different Molecular Groupings

The study of the phenomena of the hardening of the pure ductile metals by any form of cold working as a means of throwing light on the molecular structure of solids, possesses certain great advantages. Chief among these is

the fact that in a pure metal we have only one kind of chemical or ultimate atom, and that in certain ductile metals the chemical molecule is monatomic. It follows that in dealing with a given mass of metal, either "hard or soft," we are dealing with the same number and kind of atoms or molecules occupying practically the same volume in whichever state the aggregate is found. In a problem which is essentially a physical one, it is no small advantage to know with certainty that chemical questions have been completely excluded. The ease and certainty with which the pure ductile metals, in particular gold, silver, and copper, can be passed from one state to the other, soft to hard, or hard to soft, is an important practical advantage in experimental work. Further, these metals recrystallise from the hardened or vitreous state at temperatures which are so much above the ordinary atmospheric temperature that their permanence in the hardened state is assured, while the fact that their recrystallising temperatures are more than 800° below the liquefying point at once removes any suspicion that the mobility of the atoms or molecules, which is a necessary feature of recrystallisation, is of the same degree as the mobility of the liquid molecules.

The problem of the two states in the pure ductile metals may be stated thus:

A centimetre cube of metal in the hard state containing x ultimate atoms or molecules has certain well-marked physical qualities. This cube, when heated to about 300°, loses these characteristic qualities, so that from the physical point of view it might be a different metal. It still contains x ultimate atoms or molecules, and the volume they occupy is still practically a centimetre cube. As the

number of molecules and the space they occupy are both constant, the *intrinsic cohesive force* of the aggregate is also constant, though the *effective cohesive force*, on which the greater or less rigidity of the aggregate depends, will vary (1) with changing energy conditions, and (2) with the relative positions of the atoms or molecules to each other *if they possess polarity*. With respect to energy changes in passing from one state to the other, it has been conclusively proved that there is a considerable storage of potential energy in the hardened state, and that this storage is associated with a marked reduction in the vibrational freedom of the atoms or molecules. We may picture this as due to the molecules being so pressed together that they curtail each other's vibrational freedom.

From the first it has appeared most probable that the atoms or molecules do possess polarity, either as an intrinsic property or more probably as a property developed by heat vibration, and that the metal in the hard condition is truly vitreous, inasmuch as its atoms or molecules are crowded together heterogeneously as regards their polarities. The mechanical stability curves, the acoustical vibration curves, and the curves of thermo-electric potential all show the existence of distinct stages in the recovery from strain as the annealing temperature is raised. There is a comparatively quick relief when the metal is heated to 100°, followed by a slower rate, till the crystallising range is reached. Over the comparatively short crystallising range the relief is so rapid that it definitely suggests that a new type of structural change has set in. The micro-structure shows that this corresponds with (1) the disappearance of the characteristic hardened structure, (2) the appearance of minute detached crystalline aggregates,

and (3) the apportionment of the whole mass among well-developed crystalline grains.

It seems natural to picture the earlier steps in the relief of strain as due to the energising effect of rising temperature on the amplitude of the molecular vibrations. A slight general expansion of the mass will occur, and the potential energy released by this expansion will augment the kinetic energy of the vibrating molecules, but not to the point at which they can free themselves sufficiently to enable them to take their true orientation under the influence of the crystalline nuclei in the mass which always persist in spite of the most drastic deformation. When the temperature is raised to the beginning of the crystallising range, we may suppose that the pulsation cells of some of the molecules have attained the necessary amplitude of vibration to set them free to orient, and with rising temperature further progress towards complete orientation and re-orientation takes place over the remainder of the crystalline range till the whole mass is apportioned into crystalline grains, each with its own orientation. *Re-orientation* of the freely vibrating molecules must certainly occur when the larger grains impress their orientation on their smaller neighbours or on other partially oriented aggregates.

In this type of recrystallisation at a temperature which may be as much as 800° or 1000° below the liquefying-point, it is not necessary to suppose that there is any transport of molecules from crystal to crystal. Orientation of the molecules only requires that they shall turn *in situ* in response to the cumulative vibration of a more powerful crystal.

The experimental evidence has all shown that the

crystalline state is the state of minimum mechanical stability and of maximum thermal stability; the opposing forces which are in equilibrium in this state are cohesion and heat vibration. The tentative hypothesis here advanced may be of service in enabling a mental picture to be formed of the molecular mechanism by which this equilibrium is attained.

Conclusions

Whether or not pulsation cells as they are here pictured are a physical reality is at present only a matter of conjecture; but the presentation of this hypothesis may be of value by bringing together in a collected form the ascertained facts, new and old, which bear directly on the aggregation of solids in the crystalline and other states, and the passage of aggregates from one state to another. The new facts are:

(1) The breakdown and liquid flow of crystals with the production of a vitreous aggregate and the reversal of this transformation by heat.

(2) The effect of the crystalline vitreous change on the elastic freedom of the molecules.

(3) The influence of surface tension in the aggregation of solids.

(4) The influence of the cohesive force of the individual molecules on aggregation under different conditions.

SECTION X

EXTENSION OF FARADAY'S WORK ON THE OPTICAL AND OTHER CHARACTERISTICS OF THIN METAL LEAVES

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See PLATE XXXIV.

SECTION X

EXTENSION OF FARADAY'S WORK ON THE OPTICAL AND OTHER CHARACTERISTICS OF THIN METAL FILMS

Faraday's Experimental Work and Conclusions

THIS subject was studied by Faraday with that wonderful care and resourcefulness which marks all his experimental work, and the results of that study were published in the Bakerian Lecture of 1857 (*Phil. Trans. Roy. Soc.*, 1857, p. 145). The lecture was entitled, "The Experimental Relations of Gold and other Metals to Light," and he states that the researches described were undertaken in the hope that some insight might be obtained into the influence of extremely small solid particles on a ray of light.

While this was the main object of the research, a number of new and interesting observations on the chemical and physical behaviour of the noble metals in their most attenuated forms were made and recorded. In view of the particular object of the research, Faraday did not allow himself to diverge far into the side paths which opened off the main road on which he was travelling.

This is much to be regretted from the point of view of the study of the physical behaviour of metals. A close study of his experiments and his reflections on them indicate that,

had he allowed himself to wander a little further along the side paths, he would quickly have met and grasped the true explanation of the puzzling phenomena which he had encountered.

The Thinning of Gold Leaf by Floating it on Potassium Cyanide Solution

Faraday began by dealing with gold leaf and silver leaf. He found that the average thickness of a gold leaf was $\frac{1}{280,000}$ of an inch, or "$\frac{1}{5}$ to $\frac{1}{8}$ part of a single undulation of light." By floating the leaf on a dilute solution of cyanide of potassium he reduced its thickness to such a degree that he estimated "that 50 or even 100 might be included in a single progressive undulation of light." According to this estimate the thickness of the reduced leaf would be $\frac{1}{10}$ to $\frac{1}{12}$ that of the original leaf, or about $\frac{1}{3,000,000}$ of an inch or less than 10 $\mu\mu$. He states that the transmitted light was still green.

In his Estimates of the Thickness of Leaves, Faraday ignores the Effect of "Open Formation" on the Density of the Metal

In the earlier observations on thin films, Faraday's conclusions were adopted that, when a gold leaf is floated on a solution of potassium cyanide, the metal is uniformly reduced in thickness by the action of the solvent. Subsequent observations have shown that this is not the case. The cyanide does not proceed by dissolving away the surface uniformly, but it first attacks the vitreous metal, removing it and penetrating right through the substance of the leaf, so that the attenuated film which remains is a skeleton built up of the minute units of the crystalline

phase which have survived the severe ordeal of beating. These units are, of course, much too minute to exhibit any crystalline micro-structure, so that but for their difference in solubility they would have escaped detection. A gold leaf may be compared to a light gauzy fabric which has been stiffened by a coating of gum or starch. As the removal of the gum by solution will restore the fabric to its original openness and pliability, so the removal of the flowed vitreous metal by solution leaves the gold leaf with an open spongy texture. A leaf which has been treated in this way absorbs water like a sponge, and in the wet condition appears to have a thickness much greater than that of the original leaf. When spread on a glass plate and dried, it becomes less transparent owing to the replacement of the water by air, and at the same time the appearance of thickness vanishes.

The Optical Continuity of Gold and Silver Leaves

For the object Faraday had in view, it was of the utmost importance to determine whether the transparence and colour of gold leaf were genuine and intrinsic, or whether they were due to the effect of a discontinuous and granular texture. His conclusions as to the first point were " that in spite of great irregularity in thickness caused by the ribs and foldings," yet " in the best microscope and with the highest power, the leaf seemed to be continuous, the occurrence of the smallest hole making the continuity of the other parts apparent," and every part " possessing its proper green colour." Using modern lenses of the highest resolving power, together with intense and critical illumination, I have confirmed this conclusion as to the optical continuity of gold leaf.

Gold Leaf becomes Transparent when heated at a Temperature not exceeding 500°

Faraday's next experiments were on the effects of heat on gold leaves spread on glass or quartz plates. At a temperature much below the softening point of glass the appearance of the metal is completely changed. The metallic lustre and reflecting power seem to disappear, and white light is freely transmitted. He discusses this phenomenon from various points of view. The suggestion is made that there has been retraction of the gold into minute globular portions, leaving the glass uncovered between, but by further experiments he shows this is not the case when a moderate temperature is employed for the annealing. The microscopic appearance still shows the same irregularities and folds as the original leaf and the same continuity, though the colour of the light transmitted is now white. In this case also, my observations made under the more critical conditions, confirm those of Faraday. Fig. 104 is a photo-micrograph of an annealed gold leaf by transmitted light.

Restoration of Comparative Opacity and Metallic Lustre by Burnishing

When the gold leaf which has been altered by heat is gently pressed by the smooth rounded end of an agate pestle, the parts of the film which have been reached by the pressure are restored to the original green colour, and the metallic reflecting power of the leaf reappears.

Faraday discusses the phenomena of the alternate appearance and disappearance of transparence and reflecting

power without arriving at any satisfactory conclusion. This discussion is again resumed by him after the corresponding experiments with silver leaf have been detailed.

Experiments repeated with Silver Leaf

He found that silver leaf also is continuous. It is much more opaque than gold leaf, being also much thicker (nearly four times as thick).

When laid on plates of glass or rock-crystal and heated, it became very translucent and lost its metallic reflecting power, looking more like the film of chloride of silver, which is produced when a silver leaf is exposed to chlorine gas. Fig. 105 is a photograph of a piece of silver leaf which has been annealed at 350°. Before annealing, the leaf would have so completely stopped all light that its photographic image would have been simply silhouetted in black. When the silver leaf altered by heat is pressed by the agate burnisher, the metal becomes opaque and recovers its metallic reflecting power.

Faraday found that, when a number of silver leaves were rolled together and heated in a glass tube to a temperature below the softening point of the glass, " it was changed so that the light of a candle could be seen through forty thicknesses ; it had not run together, though it adhered where one part touched another. It did not look like metal, unless one thought of it as divided dead metal, and it even appeared too unsubstantial and translucent for that ; but when pressed together, it clung and adhered like clean silver and resumed all its metallic characters."

" When the leaf is much heated, there is no doubt that it runs up into particles more or less separate. But

the question still remains as to the first effect of heat, whether it merely causes a retraction of the particles, or really changes the optical and physical nature of the metal from the beaten or pressed state to another form which pressure can return back again to its more splendid conditions. It seems just possible that the leaf may consist of an infinity of parts resulting from replications, foldings, and scales, all laid parallel by the heating which has produced them, and that the first action of heat is to cause these to open out from each other; but that supposition leaves many of the facts either imperfectly explained or untouched. The arts do not seem to furnish any process which can instruct us as to this condition, for all the operations of polishing, burnishing, etc., applied to gold, silver, and other metals are just as much fitted to produce the required state under one view as under the other."

Faraday's Alternative Explanations of the Transparence of Annealed Leaves

In this paragraph Faraday leaves us with two alternative suggestions, the one being that the metal may exist in two forms — the transparent, dead form, and the metallic reflecting form, the other being that the changes produced by heating or by pressure are purely due to a certain mechanical subdivision into films of the metal, the beaten leaf being like a Venetian blind with its louvres closed, the effect of heating being to open the louvres so that light can pass through freely.

This last suggestion at first seemed to me to supply an explanation, not only of Faraday's observations, but also of a number of independent observations of my own on

the flake-like texture of beaten plates and leaves. But a more extended investigation of the whole question of surface structure has convinced me that its application is very much more limited than I had at first supposed. In the operations of beating, rolling, and planishing, flakes and layers are produced between which air films may be entangled. One of the first effects of heat is to expand this air and to drive it to the surface. As the mobility of the metal molecules has been developed by heat, the escaping air opens up the structure and produces a foam-like structure as in Figs. 26 to 31, or the still more open structure of the annealed leaves of silver and gold, Figs. 17, 18, 104, 105.

The present observations support the view that the transparence in the annealed leaves and films results from "open formation" in the molecular, not in the cruder mechanical sense. This conclusion was confirmed by the mathematical investigations of the subject by Mr. J. Maxwell Garnett in 1904–1905,[1] which are referred to later.

For the investigation of this subject leaves of gold and silver are in many respects not the most suitable forms of film. The folds and ribs, and the general irregularity of surface and thickness, complicate the problem unnecessarily.

By various chemical methods smooth continuous films of any thickness can be obtained. With these films the difficulties of examination are much reduced and many troublesome features can be safely eliminated.

Films of gold and silver and platinum have been made which ranged from 10 $\mu\mu$ to 200 $\mu\mu$ in thickness; and on annealing by heat these films have become highly trans-

[1] *Phil. Trans. R.S.*, Series A, vol. 203, pp. 385-420, and vol. 205, pp. 237-288.

parent or translucent, while their smoothness and continuity have been greatly superior to that of gold and silver leaf. With such films before us it is possible to feel quite sure that the transparence is an intrinsic property of the metal, and that it does not result from a merely mechanical alteration of its particles.

Faraday described how he prepared gold films of varying thickness and of great smoothness and continuity by placing specks of phosphorus on the surface of a dilute solution of gold chloride.

Annealing of Gold Films prepared by this Method

Films made in this way were annealed by heating on glass. Figs. 13, 14, 15, 16 show the effects of annealing four films of various degrees of thickness. Before annealing, the thicker films Figs. 13 and 14 were olive-green by transmitted light, having a full yellow colour and metallic reflection by reflected light. The thickest film Fig. 13 required a very intense light to show its green translucence. Fig. 14 had the same depth of colour by transmitted light as gold leaf, and Fig. 15 was thinner and paler. Fig. 16 was much thinner than any of the others, showed hardly any metallic reflection, and its colour was blue-purple by transmitted light. The thickness of these films was estimated to range from 10 $\mu\mu$ to 150 $\mu\mu$.

After annealing, the colour of the thinnest film Fig. 16 was rose pink by transmitted light. The photograph shows that it was quite continuous, but with thickenings or aggregations distributed regularly over the surface. The photograph has been made somewhat dark in order that the structure may be shown more distinctly; but, as seen

under the microscope, the surface was entirely free from dark or opaque patches. In the next thicker film, Fig. 15, the retraction into globular or rounded forms of greater opacity is very pronounced, but the continuous transparent film covering the whole surface is distinctly seen. Under the microscope this film was of a very pale pink colour, the thicker parts being of a slightly deeper shade. The opaque-looking granules in this film were actually of a dark brown-green colour.

In the two thicker films, Figs. 14 and 13, the thickest patches are of larger size and of greater opacity. The transparent parts show an optically continuous pink or rose-coloured film, which has been gathered into regular thickenings by surface tension. The surface tension forms developed in these four films have already been referred to in Section II.

Annealing of Films made from Colloidal Gold and Platinum Paints

The bright gold and platinum paints made for ceramic gilding by the Gold and Silver Scheide Anstalt of Frankfurt supply an excellent means of obtaining continuous films of almost any thickness. In these paints the metal has been brought into colloidal suspension in an essential oil.

A plate of glass or of mica is smoothly coated with the paint, which is allowed to dry naturally. It is then heated in an air bath to about 400°, when the solvent oil and other volatile constituents are driven off, and a smooth bright metallic film is found firmly adhering to the glass. At this stage the film is translucent and green by transmitted light. If the film is kept at a higher temperature for some

time it becomes more transparent, and the colour by transmitted light changes to blue or purple. By long-continued heating the film assumes a frosted appearance by reflected light, and the colour becomes paler by transmitted light.

These films are sometimes blistered by air bubbles, and an excellent idea of their continuity and transparence is obtained by carefully examining the spot where a bubble has been formed. So horn-like and translucent are these films that it was at first assumed that the paint contained a binding flux or frit, but, on careful inquiry, I was assured by Dr. Fritz Roessler, the Scientific Director of the Frankfurt works, that the films left on the glass are pure gold and platinum and free from any flux or frit. Fig. 24 is a gold film of this kind which has been annealed to the purple stage.

The thickness of a similar film was estimated by weighing the gold from a given area. Assuming that the density of the gold in this form is the same as that of gold leaf, the thickness of the film works out as 166 $\mu\mu$ or about twice the thickness of a gold leaf. Under the microscope, however, the thickness as seen at bubbles and broken edges, and measured by focussing, appeared to be much greater than this.

These metallic paints are prepared for the production on porcelain of films with bright metallic lustre. For this purpose the layer must be of sufficient thickness to be opaque, and its density must not be too much reduced by molecular open formation. The colloidal solution of the metal is therefore fairly concentrated, so as to secure the necessary opacity of the final film, and the time of heating and the temperature used are limited to a minimum, so as to avoid the frosting of the surface and consequent loss of lustre which would result from prolonged annealing.

The paints can, however, be diluted by a suitable solvent to any extent, and metal films of any desired thinness can be prepared. In this way films from 2 or 3 $\mu\mu$ up to 200 $\mu\mu$ in thickness were prepared and used in the study of the colour changes produced by annealing.

In connexion with the colour changes in these films, the following quotations from Mr. J. Maxwell Garnett's paper[1] are of interest.

Beilby has prepared gold films by using paints in which "the metal had been brought into solution in an essential oil." Having smoothly coated a plate of glass or mica with the paint, he heated it to a temperature of about 400°, thereby driving off the oil and other volatile constituents. A film of pure gold with full metallic reflection, and transmitting green light, is left adhering to the glass.

When these films are kept at a high temperature for some time, they change colour. By transmitted light, the original olive-green colour becomes at first bluer, then changes to purple, in which, as the annealing process is still continued, the red predominates more and more over the blue, until finally the purple has given place to pink. The reflecting power of the film has, meanwhile, diminished. But the colour of the light reflected from the blue films remains yellow, while the pink films reflect a green colour. I have before me a gold film prepared in this way and subjected to lengthy annealing. By transmitted light it appears striated with pink and blue bands. By reflected light the blue striae become golden, but the pink striae green. Under the microscope the film appears continuous and is quite thick.

These colour changes, both with transmitted and with reflected light, are just those which have been shown above to be consequent upon a continuous diminution in the density of a gold film, which throughout remains either amorphous or granular (*i.e.* possessing a micro-structure of small spheres). The view that the film is initially amorphous or granular, and that heating diminishes its density is supported, as has already been pointed out, by the fact that the curves show that the absorption of light increases rapidly as μ begins to diminish from unity, while Beilby's films exhibited just

[1] *Phil. Trans. Roy. Soc.*, A. 205, p. 279.

such an increase of absorptive power when first heated. This view is also in accordance with the loosening of structure which is suggested by the great decrease in electric conductivity which accompanies heating. But direct evidence of the correctness of the view that heating produces decrease in density is not wanting, for Beilby has estimated the thickness of a film which had been annealed to the purple stage. He found, by weighing the gold from a given area that, had the density of the gold been then normal ($\mu = 1$), the film would have been 160 $\mu\mu$ thick, whereas, under the microscope, the thickness seemed to be much greater than this. The density of the gold in the purple film thus appeared to be less than in the normal green films.

We conclude therefore that:

(*a*) The films, as first prepared, are amorphous or granular in structure; and

(*b*) Heating diminishes the density of the film, while pressure is able to increase the density again.

Further, Beilby found that, when the heating of a film was continued after it had reached the purple stage, "the film assumes a frosted appearance by reflected light and becomes paler by transmitted light." The frosted surface appeared, under the microscope, to consist of granules at least 100 $\mu\mu$ in diameter. This phenomenon suggests that, in the earlier stages of annealing, smaller granules were formed, which, as annealing proceeded, ran together to form larger granules; and the formation of such minute granules, while, according to our analysis, it does not affect the optical continuity of the film, will explain the diminution in density which occurs on heating. It is, therefore, most probable that

(*c*) The diminution in density produced by heating is effected by the passage of metal from the amorphous to the granular phase, and the growth of the larger granules at the expense of the smaller; and the increase in density produced by pressure may be accompanied by the passage of metal from the granular to the amorphous phase.

The optical properties of the films of gold which Faraday produced by reducing that metal from its solution by means of phosphorus tend to show that these films are composed of amorphous or granular gold of density less than the normal. The films appeared to consist of pure gold; when first prepared the films appeared of a grey colour, which was frequently resolvable into a mixture of green and amethystine striae. These colours would be shown by an

amorphous or granular film for which the density was in parts as low as $\mu = \cdot 7$. Moreover, such a structure agrees with the fact that the films did not sensibly conduct electricity, "and that the films cannot be regarded as continuous." Faraday further states that, though they are certainly porous to gas and to water vapour, the films have evident optical continuity.

Heating diminished the conducting power and changed the colour to amethyst or ruby, just as with Beilby's films pressure, which we should expect to increase the density of the film, changed the transmitted colour to green and increased the reflecting power; and these are precisely the changes which would, according to calculation, accompany an increase in μ to the neighbourhood of unity in the case of an amorphous or granular film.

Ruby Gold Glass

By means of refined and ingenious optical methods Szigmondy and Siedentopf have succeeded in making the ultra-microscopic gold particles visible in the microscope as diffraction discs; they have, further, counted the number of particles per unit area, and have from the intensity of their reflection calculated their size. In ruby glass the size of the particles in different specimens was found to vary from 4 to 791 millionths of a millimetre. No relation was found to hold between the colour of the particles and their absolute size. This conclusion is in direct contradiction of Faraday's belief already referred to. Mr. Garnett's researches had shown that the colour of metallic glasses and films is determined, not only by the absolute size of the metal particles, but also by the proportion of the total volume they occupy in the medium in which they are diffused. The results of Mr. Garnett's calculations are in close agreement with a number of the observations on the colour and micro-structure of thin metal films which I had already recorded, and they appear to me to supply the

explanation of much that had appeared puzzling before. My own observations lead me to think that the actual microscopic particles which are to be seen, and the larger of which can also be measured, in films and solutions or suspensions, do not in any way represent the ultimate units of structure which are required by Mr. Garnett's theory, but that these particles are aggregates of smaller units built up in more or less open formation.

Films of Magnesium Oxide in Open Formation

That a relatively opaque substance like gold may be so attenuated that when disseminated in open formation it becomes transparent, is contrary to all our associations with the same operation when performed on transparent substances like glass or crystalline salts. The familiar experiment of crushing a transparent crystal into a perfectly opaque powder would not prepare us for the effect of minute subdivision on the transparence of metals. At first it might be supposed that this difference is due to the very rough and incomplete subdivision of the crystal by crushing; but this is not the case, for the perfectly transparent oxide of magnesium may be obtained in a state of attenuation comparable with that of the transparent gold, by allowing the smoke from burning magnesium to deposit on a glass plate. The film of oxide obtained in this way is found to be built up of particles quite as minute as those of which the gold films are composed, yet the opacity of the oxide film is relatively much greater. The minute particles of the dielectric, magnesium oxide, scatter and dissipate the light waves by repeated reflection and refraction, while the similar particles of the metallic conductor, gold, act as electrical resonators which pass on some of the

light waves while reflecting others. When the metallic particles are in this state of open formation and relative transparence, it was found that the electrical conductivity of the films had completely disappeared. Films of this description were found to have a resistance of over 1,000,000 megohms as compared with only six ohms in the metallic reflecting condition.

Conclusions

The first step in the interpretation of these phenomena was only possible after recognition of the part played by surface tension in the aggregation of metallic films. The surface tension form of structure had been identified in a great variety of substances and over a wide range of magnitudes, and it had gradually become evident that it could not, by itself, be taken to indicate the existence of definite units of structure in the solid aggregate.

This aspect of the subject has already been developed in Sections II. and III., and need only be referred to here in connexion with the annealed gold films of various thicknesses shown in Figs. 13, 14, 15, and 16. In these films the surface tension structure is as evident in the most transparent portions as in the most opaque, the relative magnitude of the structure in the different portions being evidently determined by the thickness of the films. The ultimate explanation of the transparence of the thinner films was not therefore to be found in the structure developed by surface tension. Though surface tension played an important part in the outward forms assumed by the annealed films, the change in the optical properties had to be assigned to a deeper and more intimate cause, namely *the opening up of the molecular structure.*

The proofs of this opening up were :

1. The increased volume of the metal in the transparent form, as shown by the increased thickness of the films after annealing.

2. The enormously reduced electrical conductivity of the annealed films.

3. The micro-structure, which varied from the horn-like character of the colloidal films made from the bright gold and platinum paints to the more lace-like structures made from gold and silver leaves.

4. The sponginess of the lace-like structures as shown by their absorption of water and other liquids.

The horn-like structure of the films produced from the paints was believed to be due to the colloidal state of the metal in the paints. This state appeared to persist in the films produced by driving off the solvent by heat, and was developed into a more open and transparent structure by continued heating.

In the case of other films the opening up of the structure was traced to the action of gases or of liquid solvents.

The " frosted " state on the surface of metals in their more massive form was also traced to the molecular or chemical activity of gases or solvents.

The very intimate opening out of the molecular groupings having been definitely associated with the transparent state, the last link in the evidential chain was supplied by the interpretation of these observations on physical and mathematical lines by Mr. Garnett.

It appears justifiable, therefore, to conclude that the problem set by Faraday in 1857 was finally solved about half a century later.

SECTION XI

PHOSPHORESCENCE OF CRYSTALS AFFECTED BY THE CHANGE FROM THE CRYSTALLINE TO THE VITREOUS STATE

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SECTION XI

PHOSPHORESCENCE OF CRYSTALS AFFECTED BY THE CHANGE FROM THE CRYSTALLINE TO THE VITREOUS STATE

Introductory

THE experiments which are described below show that certain forms of phosphorescence or luminescence are due to change of physical state, *e.g.* to the passage from the crystalline to the vitreous state, or from one vitreous state to another, and that the molecular movement required to bring about these changes may be caused (1) by disintegration produced by mechanical means, as in the crushing or flowing of crystals; (2) by the expulsion of a volatile constituent, as in the dehydration of crystals, the molecular movement which necessarily occurs at the moment of expulsion being taken advantage of by the forces of cohesion to establish new arrangements of the molecules either crystalline or vitreous; and (3) by a condition of excessive vibration and ultimate overstrain set up by a stream of electrons, as in the radium or the cathode rays.

In the latter case various observers had noticed that barium platino-cyanide, after continued exposure to the rays from radium, becomes brown or red, while the phosphorescence excited by the rays falls off considerably.

The following observations were made with the object of ascertaining the conditions under which the change occurs.

Action of the Beta and Gamma Rays of Radium on Barium Platino-Cyanide

A specimen of Merck's barium platino-cyanide was recrystallised and obtained in prisms from 3 to 5 mm. long. The crystals were bright canary yellow and showed a pale blue fluorescence by obliquely reflected light. The radium used was the pure bromide contained in a cell with a thin mica cover, and as all the experiments were made without removing the cover, the effects produced were due entirely to the β and γ rays.

When yellow crystals of platino-cyanide are left on the mica cover of the radium cell for half an hour, the beginnings of the colour change from yellow to red are distinctly visible. In one hour those surfaces most directly in the path of the rays become strongly reddened. In eight hours the phosphorescence has fallen to a minimum of $\frac{8}{100}$ of its original amount, at which it remains, however long the exposure may be continued. Some of the crystals were exposed to the rays for eight days, but the phosphorescent value did not further diminish, though the colour became rather deeper. When the reddened crystals are removed from the action of the rays they at once cease to phosphoresce. At the outset, therefore, there are two well-marked characteristics in the behaviour of the platino-cyanide. (1) The phosphorescence starts at a maximum value which rapidly falls to about $\frac{1}{12}$; and (2) there is no after phosphorescence.

Other observers have stated that platino-cyanide

screens which have been reddened by over-exposure to radium rays may be restored to the sensitive state by exposure to sunlight.[1] Reddened crystals were exposed on a glass plate to a condensed beam of sunlight for several hours, but no restoration of colour or phosphorescent quality could be observed. These observations seem to suggest that the restorative effect of sunlight, where it has been observed, must have been due to some condition supplied by the other materials of which the screen was composed. The present observations show that the red crystals retain their new character over a period of many weeks either in the dark or in diffused daylight, and none of these observations have given any indications that the change is other than permanent.

The only way *completely* to restore the red crystals to the yellow state is by solution in water and recrystallisation. The properties of the crystals obtained in this way appear to be in all respects the same as they were before exposure to the rays. It would appear, therefore, that the reduction of the phosphorescent value is not primarily due to chemical change in the salt. The fully developed crystalline condition of the yellow salt is evidently necessary if the highest phosphorescence is to be obtained. Anything, therefore, which interferes with this condition impairs the phosphorescence. When the water of crystallisation is wholly or partially expelled, the crystals, either yellow or red, are left in the form of a vitreous powder of a brick-red colour. In this vitreous state the value of the phosphorescence has fallen to $\frac{3}{100}$, and the colour of the glow is no longer green, but red. As crystals reddened by exposure to the β rays lose water and become opaque on

[1] Rutherford, *Radio-Activity*, p. 168.

heating to 130°, just as the yellow crystals do, it may be concluded that the change from yellow to red under the influence of the β rays is not due to the loss of the water of crystallisation.

Reduction of Phosphorescence due to the Change from the Crystalline to the Amorphous Vitreous State

As the reduction of the phosphorescent value in the change from the yellow to the red form is neither due to chemical decomposition nor to loss of water of crystallisation, it was thought that it might be akin to the change from the crystalline to the amorphous vitreous state which takes place in metals and other solids when they are flowed by mechanical movement. The falling-off of the phosphorescence under the long-continued action of the rays suggested a failure in elasticity or elastic response analogous to that described in Section VII., p. 170, while the colour changes appear to be of the same nature as those observed in the crystalline and amorphous vitreous states of the metals.

Change of Colour from Pale Greenish Yellow to Brownish Red

When a small fragment of a yellow crystal is bruised on a glass plate by the rounded end of an agate pestle, the bright yellow colour is changed to a deep red-brown wherever the pressure has acted so as to cause flow, Fig. 106. This colour change is remarkably sharp and distinct. By rolling the pestle firmly over the smaller crystalline specks these are completely flowed into transparent patches with smooth rounded outlines. The colour of the thinnest patches is obviously more intense, as well as much redder

than that of the original crystal, while the thicker patches are of a very intense red-brown by transmitted light. The colour of the flowed patches by reflected light is complementary to that by transmitted light, which is greenish yellow. The crystalline structure of the yellow salt is to all appearance completely replaced by the granular structure of the vitreous state.

A small quantity of the vitreous platino-cyanide was prepared by bruising and flowing the yellow crystals on a glass plate. With each portion the operation was repeated several times, that is to say, the flowed patches on the plate were scraped off, broken up, and again rolled with the pestle. In this way a fairly complete conversion into the vitreous form was obtained. The final product consisted partly of brown powder and partly of deep brown scales, with a greenish sheen. The phosphorescence in the β rays was reduced to $\frac{3}{100}$ of its value, and it appeared as a dull red glow, in which an occasional speck of bright green indicated the presence of minute portions of the untransformed crystalline state.

It has already been shown that the change of state from the crystalline to the amorphous vitreous takes place by mechanical movement of the molecules over each other, as in a liquid, and that the reverse change from the amorphous vitreous to the crystalline takes place only when a definite transition temperature or stability point is reached. The low temperature at which platino-cyanide loses its water of crystallisation presented a difficulty in attempting to bring about the change from the amorphous vitreous to the crystalline by heat, but an encouraging result was obtained on quickly raising a small portion of the vitreous salt to 85°, for the dark-brown scales immediately assumed

the bright greenish yellow of the crystalline state. The reality of this change was further confirmed by finding that the phosphorescent quality, which had fallen to $\frac{2}{100}$ in the amorphous vitreous state, had been restored by the heating to $\frac{33}{100}$. The analogy between the changes in colour and phosphorescent quality brought about by the change from crystalline to amorphous vitreous and the corresponding changes which result from the action of the β rays is thus shown to be very close; it remains to be seen if the analogy also holds good in the reverse transformation by heat.

Restoration of Phosphorescence and Colour by Heating the Reddened Salt to 120°

Crystals which had been reddened by the β rays were lightly crushed and quickly heated to 110° in a capillary tube with an open end. The colour of the salt became much paler and its phosphorescent quality was considerably increased. As the temperature necessary to bring about the change was also high enough to drive off some of the water of crystallisation, a fresh portion of lightly crushed red crystals was packed tightly into a capillary tube, which was sealed off as close to the surface of the salt as possible. The tube was heated to 120°, when the transformation into the yellow salt took place quite sharply, beginning simultaneously at the middle and at one end of the tube and quickly spreading all over, the brown colour giving place to bright yellow. The change was carried out at 120°, so that no water in the liquid state can have taken part in it. After cooling, some minute drops of condensed water were visible on the inner surface of the

tube. Necessarily, a corresponding portion of the salt must have parted with some of its water of crystallisation, but this did not affect the transformation of the remaining part. The phosphorescent quality was raised from the $\frac{8}{100}$ of the red crystals to $\frac{33}{100}$.

Even in the sealed tube, however, the conditions for the change from the vitreous to the crystalline are distinctly unfavourable to anything like a perfect conversion or the production of a uniformly crystalline material, therefore the very definite results obtained, namely, the partial restoration both of colour and phosphorescence, are strongly confirmatory of the view of the change brought about by the β rays.

The retention by the reddened crystals of their crystalline form and transparence points to a persistence of a proportion of the crystalline material side by side with the vitreous. This persistence of the crystalline state is quite in keeping with the earlier observations on metals, when in the case of gold it was shown that even after severe and repeated beating of the metal in the form of the thinnest foil the crystalline structure could not be obliterated. In the case of the platino-cyanide, the over-stimulation to which the vibrating molecules are subjected by the β rays during the preliminary stage of the bright phosphorescence, results in a state analogous to that of elastic fatigue in vibrating metal wires or glass fibres. Up to a certain point this fatigue may be recovered from, that is to say, if the relative displacements of the molecules from their proper crystalline relations have not passed beyond a certain stage; but beyond this stage there is no power of self-recovery, and heat is required to endow the molecules with freedom of movement sufficient to enable them to return to their

crystalline positions. This final stage of permanent fatigue or overstrain in the salt corresponds with the vitreous condition which results from mechanically produced flow.

Sir Herbert Jackson, F.R.S., on the Phosphorescent Response of Various Glasses

The relation between phosphorescence and the crystal line and vitreous states in glass has been extensively studied by Sir Herbert Jackson,[1] who states that:

Certain facts, from which it appears reasonable to conclude that many glasses have something of a crystalline nature in them, have been obtained from a study of the phosphorescence of various glasses and other vitreous compounds exhibiting different degrees of readiness to pass into the crystalline state on heating. Much of the work was done about twenty years ago, but more recent experiments have not modified the conclusion then formed that a truly vitreous body exhibits no phosphorescence in ultra-violet light or X-rays, or under cathodic discharge. Nearly every glass shows some phosphorescence and some show it very strongly, as, for example, the glass from which X-ray bulbs are largely made, and which gives the well-known green glow when the tube is in use. If some of this glass be fused and very rapidly chilled, as, for example, by making a Rupert's drop from it, the glass is practically non-phosphorescent so far as its surface is concerned. A very little distance below the surface the chilling was not sudden enough to prevent some change of the truly vitreous to an attempt at crystalline structure, so that just below the surface, as shown by broken pieces of the drop, the glass exhibits phosphorescence. The tail of such a Rupert's drop, if heated below the temperature at which the thin thread of glass bends, is found to be strongly phosphorescent, and the glow under cathode discharge can be seen to fade slowly away towards the part which was not heated. Many observations

[1] Trueman Wood Lecture, *Journ. Roy. Soc. Arts*, vol. 68, No. 3504, January 1920.

with vitreous borates and silicates have shown similar phosphorescence, appearing more and more strongly as the vitreous bodies are made to approach the crystallising stage. There does seem, therefore, reason to state that, given a body which in its crystalline state exhibits phosphorescence, it will not do so when in a truly vitreous state, and to infer that if a glass be phosphorescent there is something of a crystalline nature in it. It would not be right to come to the conclusion that a glass showing no phosphorescence is free from anything crystalline, since there may be crystalline structure in it which is not in the sensitive state to be revealed by phosphorescence. A number of experiments on glasses, borates, etc., go to show that in some non-phosphorescent glasses there is most likely some crystalline formation, since the introduction of minute amounts of certain bodies not usually present in these glasses, as manufactured, will render them quite markedly phosphorescent; and again, the surfaces of Rupert's drops made from these sensitive glasses show no phosphorescence. It may be pointed out that boric anhydride, which has a marked effect in preventing crystallisation in glasses and in enhancing the stability of the vitreous form, is a fatal ingredient to add to a uranium glass if strong fluorescence in ultra-violet light be aimed at.

After due allowance has been made for the element of physical change, there remains a large class of phosphorescent phenomena which cannot be thus explained; but the clear recognition of the part played by physical change at once makes the consideration of the latter class much simpler. Even in the case of platino-cyanide, where it is seen that physical changes play so large a part in the phosphorescent phenomena, there remains a certain residuum of phosphorescent effect which appears to be independent of the physical condition of the substance. Platino-cyanide itself, therefore, opens the way to a further study of the phenomena of phosphorescence, but other substances in which the physical state plays a less important part are better suited for this study.

Phosphorescence: Primary, Secondary, and Revived

In speaking of luminescence in the following experiments the different phases will be referred to as *primary phosphorescence*, or the luminescence produced under the direct influence of a stimulus, *e.g.* the β rays or the cathode rays; *secondary phosphorescence*, or the luminescence which continues after the direct stimulation has ceased; *revived phosphorescence*, or the luminescence revived by heat after the secondary phosphorescence has diminished or ceased altogether.

It has been shown that primary phosphorescence is exhibited under various forms of stimulation, and under conditions in which the elastic vibration of molecules or molecular aggregates might alone account for the generation of light waves. But when the secondary and the revived forms of phosphorescence appear, it becomes necessary to suppose that these effects are due to some more intimate changes among the atoms themselves; in other words, to the play of chemical affinity. The association of phosphorescence with certain forms of slow oxidation was early recognised, and possibly for this reason there has sometimes been a tendency to limit the chemical view to this type of action. But, from the observations which follow, it will be seen that with many substances the chemical actions which occur must necessarily be self-contained and independent of atmospheric or other surroundings.

The chemical action of the rays from radio-active substances has been recognised from the first. Among the most prominent examples of this action are the reduction of sensitive silver salts in photographic films, which led to

the original discovery of the rays by M. Becquerel; the coloration of glass, first observed by M. and Madame Curie, and afterwards attributed by Elster and Geitel and other observers to the reduction and separation of the alkali metals in a state of solid solution; the electrolysis of water; and the separation of iodine from iodoform, observed by W. B. Hardy and Miss Willcox in the liquid state, and more recently by van Aubel in the solid state. Some of these actions have been recognised by direct chemical tests, while others have been inferred from the colour changes occurring in the substances exposed to the rays.

The observations which follow were made to try and trace the connexion between the chemical, the coloration, and the luminescent effect of the β rays, and are to some extent a repetition of the experiments of previous workers on the subject, but they have been extended in particular directions with the express object of throwing light on the problems of secondary and revived phosphorescence. As already recorded in the previous observations, the substances here used were also exposed to the β and γ rays only.

A polished lens of rock-crystal, after exposure to the rays for four days, showed a patch of dark-brown coloration at the spot where the rays had entered. On removal from the radium the coloured patch phosphoresced faintly. This could only be seen in complete darkness. After an interval of six weeks the lens showed no trace of phosphorescence at the ordinary temperature, but on heating it on a hot plate to rather over 100° the coloured patch glowed so brightly that it lighted up the rough edges of the lens and showed its complete outline quite distinctly.

On raising the lens to a considerably higher temperature, probably over 250°, it glowed more brightly, and then the glow ceased altogether. The brown coloration had now completely disappeared.

A colourless crystal of calcspar was exposed to the rays for six days. A faint yellow coloration marked the spot where the rays had entered. The coloration had penetrated about 2 mm. below the surface. When the crystal was first placed on the radium cell it phosphoresced with a pale greenish light; but after a few minutes the spot at which the rays entered glowed with an orange-red phosphorescence. This glow rose to a certain pitch, and then continued fairly uniformly throughout the exposure to the rays. On removal from the radium at the end of six days the crystal continued to phosphoresce as brightly as it had done in the path of the rays. Twenty-four hours later the crystal still phosphoresced, though less brightly. On warming it to 80° the glow became brighter than it had originally been. On cooling again to the ordinary temperature the glow was feebler than it had been before heating. The reserves of phosphorescent power had evidently been more quickly expended at the higher temperature. The gradual disappearance of the phosphorescence was watched day by day for a week. Four days after removal from the radium the crystal could still be seen in complete darkness. Heated to over 100°, the phosphorescence was much augmented, but the glow was distinctly whiter than it had originally been. Five days after removal from the radium the crystal had become quite invisible in complete darkness, but on heating it to over 100° it again phosphoresced. On the sixth day it still phosphoresced feebly when heated to 100°, but on raising it to 150° it glowed so brightly that

it could be seen distinctly in a dimly lighted room. The phosphorescence was now even whiter and more diffused than it had been before. On the fifth day the patch of yellow coloration had completely disappeared. This disappearance coincided with the loss of phosphorescence at the ordinary temperature, and also with the development of the whiter and more diffuse glow when the crystal was heated. On the seventh day the crystal heated to 150° gave a feeble white phosphorescence. On this occasion a crystal of calcspar, which had not been exposed to the radium, was heated side by side with the other which had. This fresh crystal gave absolutely no phosphorescence at 150°.

A piece of potash glass exposed to the rays showed a feeble phosphorescence. After sixty hours it was removed from the radium. Where the rays had entered the surface a strong brown coloration had taken place. This coloured patch phosphoresced feebly. Six weeks later the glass was examined and showed no phosphorescence at the ordinary temperature, but on heating to 100° it gave a faint greenish glow. The depth of colour of the brown patch in the glass showed no diminution of intensity at the ordinary temperature with the lapse of time, but on heating to about 200° the coloration completely disappeared.

A lens of colourless flint glass was placed on the radium cell and at once phosphoresced feebly. After twelve hours' exposure to the β rays, it showed no secondary phosphorescence when it was heated to about 200°. A brown coloration which had resulted from the action of the rays had completely disappeared after the heating to 200°. After a further exposure of forty-eight hours to the β rays, the

brown coloration was much stronger, but it showed neither secondary nor revived phosphorescence.

Similar experiments were carried out with potassium chloride, potassium bromide, and potassium iodide, and these were observed to show the same association of colour with luminescence as calcspar, quartz, and glass, but all effects were of a more evanescent character. A crystal of potassium chloride was crushed and then flowed into vitreous scales. The scales placed on the radium cell phosphoresced faintly and in thirty minutes were tinted with a red violet. In six hours the colour had deepened. On removal from the rays there was secondary phosphorescence, but both this and the colour disappeared more quickly than had been the case with the more massive crystal. A small crystal of calcspar was crushed and flowed in a similar way and the vitreous scales were placed on the radium cell. They phosphoresced very faintly, and there was no obvious increase over a period of three hours' exposure. Removed from the rays there was faint secondary phosphorescence, and when heated to rather below 100° they glowed with a bright orange phosphorescence and continued to do so for some minutes.

In the last two observations, after making due allowance for the small quantities employed and their fine state of division, it appears that the fact of a substance being in the vitreous instead of the crystalline condition does not necessarily interfere with the generation and storage of energy which can afterwards be set free by heat and give rise to revived phosphorescence.

In the foregoing observations the coloration effects have, with one exception [that of flint glass], been directly associated with the luminescence appearances. The one

exception is valuable, however, because it draws attention to the fact that the intensity of the affinities of the dissociated ions, as well as their suitable insulation, is a necessary factor in the production of phosphorescence. The lead silicate is easily electrolysed, and its ions are duly insulated, as shown by the coloration; but in their recombination the energy developed in this particular case was insufficient to develop visible light waves. In the haloid salts of potassium the conditions are entirely different, for the affinity of the haloid and the metallic ions is so intense that the insulating power of the molecules is only sufficient at ordinary temperatures to keep them apart for a very short time. It appeared probable that in these salts so much energy might be stored by the action of the rays at a low temperature as would result in a more brilliant luminescence on a return to the ordinary temperature. To test this the following experiments have been made at a temperature of about $-100°$.

Calcspar crushed to powder, and exposed to the radium rays for an hour at this temperature, showed the usual primary and secondary phosphorescence. On emptying the salt from the cold tube upon a metal plate at the ordinary temperature, the glow increased considerably as the temperature of the salt rose; but this revived phosphorescence was not so vivid as that observed between $15°$ and $100°$. Potassium chloride exposed to the rays for an hour at $-100°$ showed well-marked violet coloration. The primary and secondary phosphorescences were brighter than the ordinary temperature. When the cooled salt was emptied on the metal plate it glowed with a brilliant pink phosphorescence, which died down in less than a minute. On returning the salt to the cold tube the

phosphorescence completely ceased. Potassium bromide treated in the same way was coloured greenish blue in one and a half hours. It showed distinct primary but no secondary phosphorescence. Emptied on the metal plate, it glowed with a brilliant greenish phosphorescence, which quickly died down, and entirely ceased when the salt was returned to the cold tube. Barium platino-cyanide in yellow crystals exposed to the rays at $-100°$ turned red more slowly than at the ordinary temperature. After five hours' exposure the primary phosphorescence had fallen to 33 per cent of its former value. There was no secondary phosphorescence, but, when emptied on the metal plate, the salt glowed brilliantly for a few seconds. To make sure that this revived phosphorescence was not due to the purely physical effect of cooling and heating, another portion of yellow crystals was cooled under identical conditions, except that the radium was absent. The crystals showed no phosphorescence of any kind even on the metal plate.

These observations at $-100°$ confirm the view that the effect of low temperature is to increase the insulating power of molecules, and thereby to enable some substances to store chemical energy which are unable to do so at all at higher temperatures, *e.g.* barium platino-cyanide ; and to increase the storage capacity of other substances in which the secondary phosphorescence is very short-lived at higher temperatures, *e.g.* potassium chloride and bromide. In the case of calcspar the insulating capacity at ordinary temperatures is already so excellent, as shown by the persistence of secondary phosphorescence, that there is comparatively little gain at the lower temperature.

If, as seems most probable, the coloration of solids by

the β rays is due to the presence of ions, it is interesting to note that the different salts of potassium give perfectly distinct colours, the chloride being a red violet and the bromide and iodide a greenish blue. This difference is most likely due to the modification of the colour of the potassium ions by the presence of the haloid ions: chlorine, bromine, and iodine.

Another feature brought out by the foregoing observations is the remarkable persistence of latent phosphorescence, as shown by the indefinitely long time for which this storage of energy continues under favourable conditions, as in rock-crystal and potash glass.

Colour and Luminescence Effects may be explained by the Ionisation Hypothesis

In tracing the various steps in the action of the rays as disclosed by the intensity and colour of the phosphorescence, and by the appearance and disappearance of coloration, the chemical or electrolytic hypothesis seems to explain each step in a satisfactory way and without any straining of the facts. When the rays are first applied there may be a preliminary stage during which the luminescence is mainly of physical origin. This is borne out by the undoubted influence of crystalline structure on primary phosphorescence, and its relatively small influence on the later stages of luminescence. But as electrolytic dissociation proceeds, a point is reached when the neutral molecules are no longer able to keep the increasing number of ions apart. Recombination then sets in, and with it the production of a new kind of luminescence. When once the insulating power of any given layer of the substance is

saturated, the number of ions dissociated at each moment will be balanced by the recombination of a like number. This is the probable explanation of the fact that the phosphorescence reaches a steady value after a certain time. When this steady state has been reached for the whole depth to which the electrons can penetrate, the limit of storage of energy for the production of secondary and revived phosphorescence has been reached.

When the stimulus of the rays is removed, electrolytic dissociation will cease, but a certain number of ions continue to find their way to each other and to combine, producing secondary phosphorescence. This state may last only for a moment or it may continue for days. The insulating power of the molecules depends on their mobility, and this in turn depends on the temperature. For every rise in temperature a new equilibrium point must be established, and a further combination of ions with a fresh outburst of luminescence will occur. At whatever stage a rise of temperature takes place, the effect must be the same, whether it be at the first stage while dissociation is active, at the second stage while recombination is taking place, or at the third stage when equilibrium at the lower temperature has been reached and luminescence has entirely ceased.

From this point of view it becomes possible to explain the comparatively conflicting observations on the behaviour of the same substance in the cathode rays or in the radium rays. To take only one example of this: in 1881 [1] Sir W. Crookes stated that calcite showed the residual glow longer than any substance he had experimented with. "After the current has been turned off the crystals shine

[1] *Chem. News*, 1881, p. 237.

in the dark with a yellow light for more than a minute." This short period of secondary phosphorescence as compared with the four days in the experiment here recorded becomes perfectly intelligible when the temperature is taken into account. No mention of the actual temperature is made in Crookes' observation, but it may fairly be assumed that the temperature of a substance exposed to a powerful cathode discharge would be very much raised. Even a temperature of 100° would break down the insulation of the calcite molecules to such an extent that only a very brief secondary phosphorescence could occur.

The effects of low temperature in developing and increasing secondary phosphorescence, as shown by Crookes and Dewar, fall naturally in line with the dissociation hypothesis. By the increased insulating power of the molecules at the lower temperature the capacity of a substance to store dissociated ions may be increased to an enormous extent, so that the break-down of insulation by a rapid return to the ordinary temperature will set free a great store of energy and produce an outburst of phosphorescence. It is evident that substances which have too little insulating power at ordinary temperatures to enable them to produce secondary phosphorescence, may at the lower temperatures develop this power to a very high degree. Even the much feebler stimulus of light waves may thus be enabled to record dissociation effects which have altogether escaped notice at ordinary temperatures.

The conclusions drawn from the foregoing experiments may be briefly summarised under the following divisions:

1. Certain types of phosphorescence are due to the molecular movement or displacement which is produced

by heat, by mechanically applied stresses, or by radiant energy.

2. Certain other types of phosphorescence are distinguished by their appearance in three stages, called here primary, secondary, and revived phosphorescence. These can be explained as due to atomic changes in which chemical affinity is the controlling factor.

3. The phenomena of this type appear to support the view that a species of electrolysis occurs in solids exposed to the β or cathode rays; that the products of electrolytic dissociation are insulated or partly insulated from each other by the neutral molecules as in a viscous electrolyte; and that it is the breaking down of this insulation and the recombination of the ions which cause revived phosphorescence.

THE END

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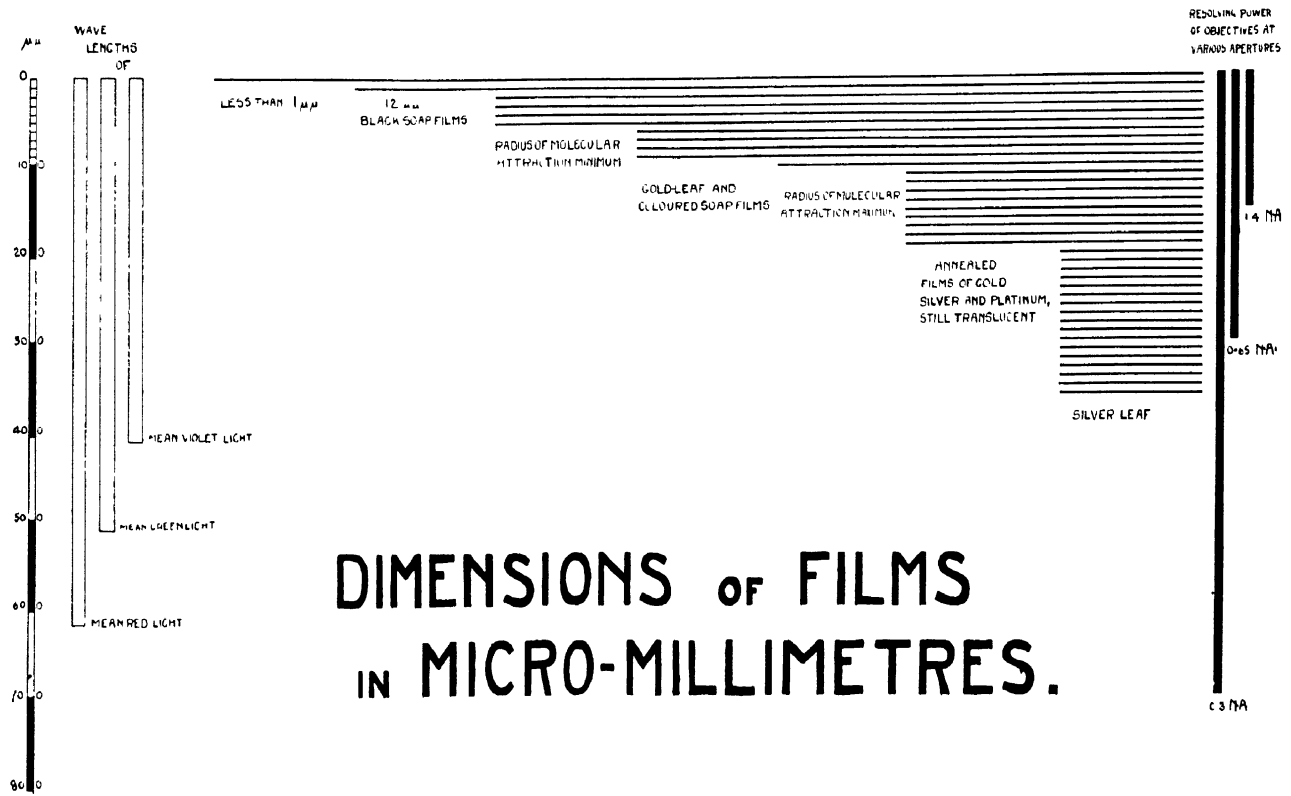
PLATE I

Plate I

	SEE PAGE
Diagram showing on a scale of 100,000 : 1	13
The wave-lengths of mean red, mean green, and mean violet light.	
Sections of thin films ranging from 1 to 360 $\mu\mu$	
The resolving power of lenses of various numerical apertures.	
The following examples will show the importance of dealing with the subject "to scale," so that the molecular dimensions and the range of the cohesive force may always be present in our minds when considering the phenomena dealt with.	
The films removed from gold and glass, Figs. 9-10 and 33, were probably of the order of 1 to 20 $\mu\mu$, or only a small fraction of the thickness of a coloured soap-bubble film, or of a gold or silver leaf . .	28
The transparent films of gold, silver, and platinum, Figs. 13-19, 21-25, ranged from 20 to 200 $\mu\mu$ . . .	24
The thickness of the upper portion of the film of gas black, Fig. 35, was about 2000 $\mu\mu$, and of the lower or shrunken portion, 200 $\mu\mu$.	65
The zinc globules in Plate XIII. ranged from 5000 to 33,000 $\mu\mu$.	72
In the step-by-step etching of polished calcite, layers were explored at eleven different depths, ranging from ·62 to 1000 $\mu\mu$ . . .	99



DIMENSIONS OF FILMS IN MICRO-MILLIMETRES.

PLATE I

PLATE II

FIGS. 1, 2.

Plate II

DIAGRAMS ILLUSTRATING SURFACE TENSION FORMS

SEE PAGE

Fig. 1.—An oil film spreading on water is at first continuous but soon becomes perforated by small round holes 20

Fig. 2.—The holes increase in size until they are only separated from each other by ridges 20

PLATE II

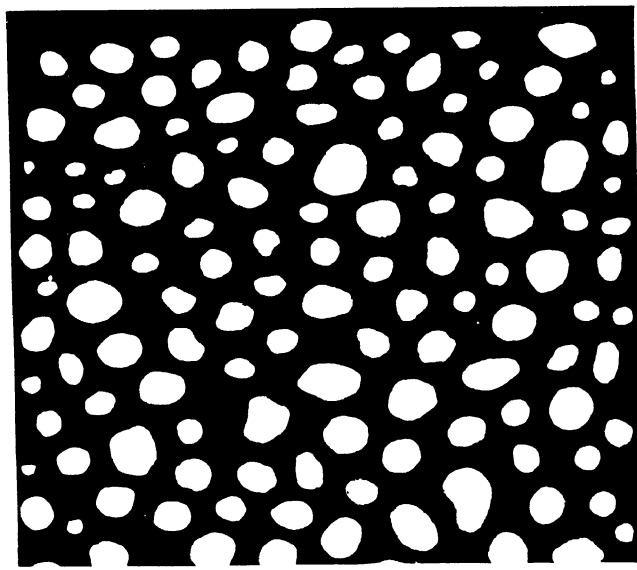


FIG. 1.

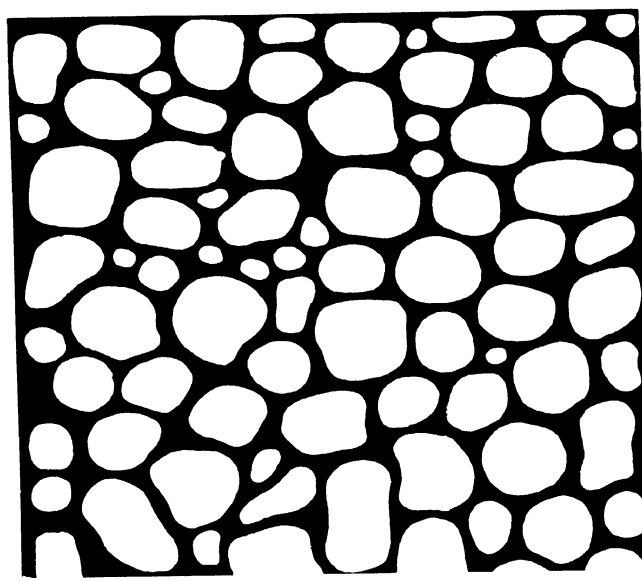


FIG. 2.

PLATE III

FIGS. 3, 4.

Plate III

DIAGRAMS ILLUSTRATING SURFACE TENSION FORMS

SEE PAGE

Fig. 3.—The ridges break across and tend to draw up into rounded forms . 20

Fig. 4.—The film is completely resolved into separate discs . . 20

PLATE III

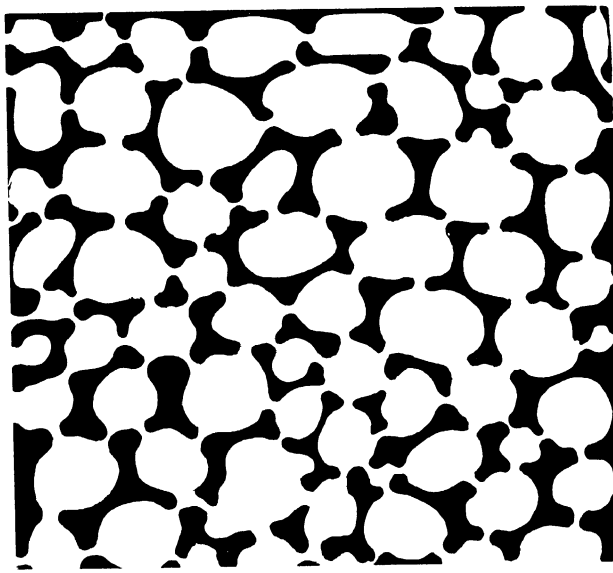


FIG. 3.

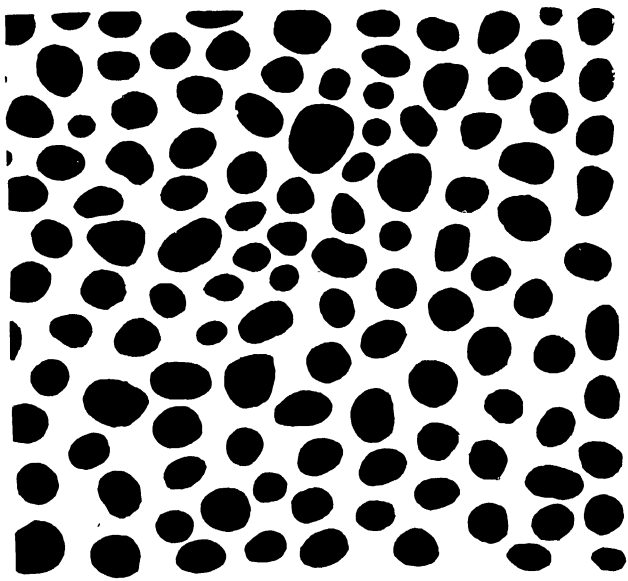


FIG 4,

PLATE IV

FIGS. 5, 6, 7, 8, 9, 10.

Plate IV

See page

Fig. 5.—Burnisher mark on frosted silver, oblique light. 16 mm. objective. N.A. 0·3. ×250 8

Fig. 6.—The same, by normally reflected light . . 8

These two photographs show the reversal of lights and shadows by the two methods of lighting.

A thin film of eosin solution allowed to dry on glass shows all the stages observed in a thin oil film.

Fig. 7.—Shows all the forms from perforations to discs . . 21

Fig. 8.—The same, showing the intermediate forms more distinctly . 21

Fig. 9.—Polished surface of a plate of pure gold lightly etched with chlorine water. ×1000 28

Fig. 10.—Fire-glazed surface of a glass slip lightly etched with hydrofluoric acid gas mixed with air. Transmitted light. ×1000 . . . 28

FIG. 5.

FIG. 6.

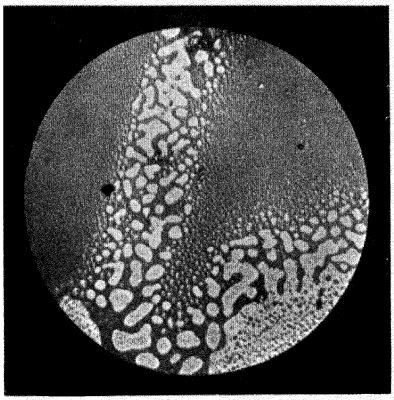


FIG. 7.

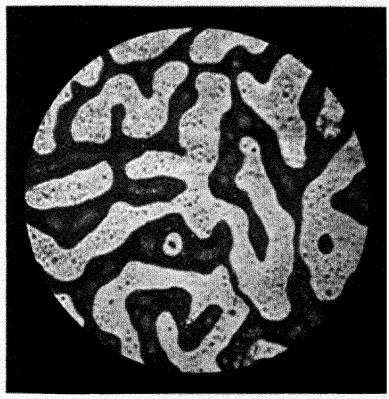
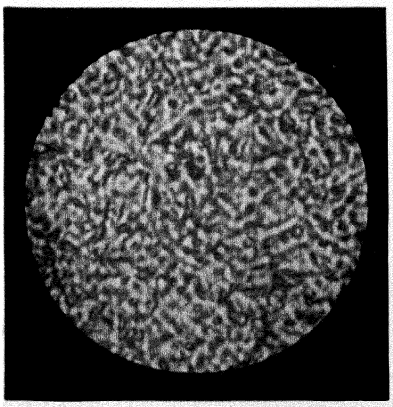


FIG. 8.



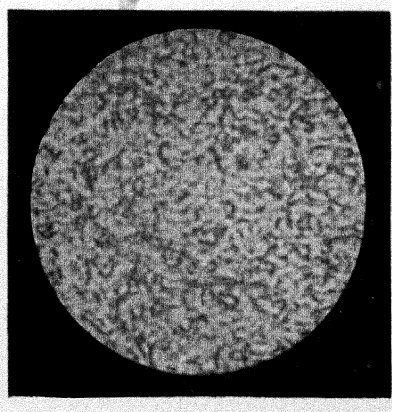


PLATE V

Figs. 11, 12.

Plate V

SEE PAGE

Fig. 11.—Fire-glazed surface of glass slip lightly etched with hydrofluoric acid gas mixed with air. Transmitted light. Magnification = 250 . 28

Fig. 12. The same, more deeply etched. Magnification = 250 . 29

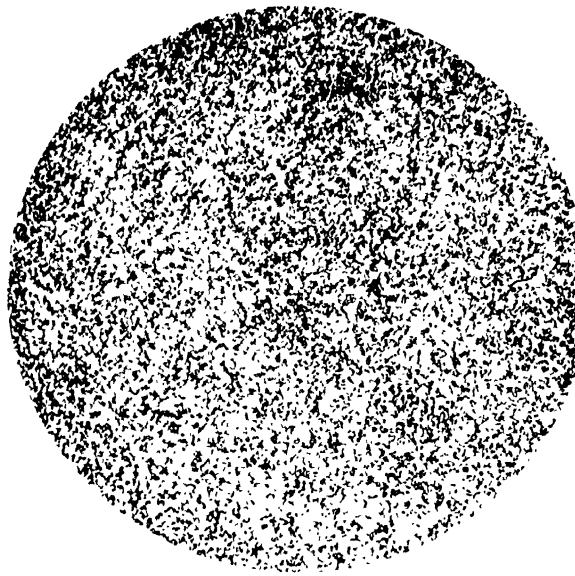


FIG. 11.

FIG. 12.

PLATE VI

Figs. 13, 14, 15, 16, 17, 18.

Plate VI

GOLD FILM PHOSPHORUS REDUCED, ANNEALED BY HEATING ON GLASS

Transmitted light with green screen. Objective 12 *mm Apo. N. A.* 0·65.

SEE PAGE

Fig. 13.—The thickest part of the film. × 440 . . . 24, 221

Fig. 14.—A thinner part. The dark patches were deep green and the light patches pale pink by transmitted light. × 440. Compare with Fig. 101 24, 221

Fig. 15.—A still thinner part. × 440 . 25, 224

Fig. 16. The thinnest part. × 440. Compare with Fig. 101 25, 221

Fig. 17.—Thin film of silver annealed. Transmitted light. × 1000 25, 40

Fig. 18.—Silver film. Oblique light. The film has been partly scraped off, so as to show the bare glass. × 580. Compare with Fig. 105 . . 25, 51

PLATE VI

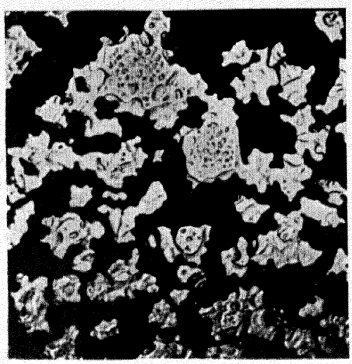


FIG. 13.

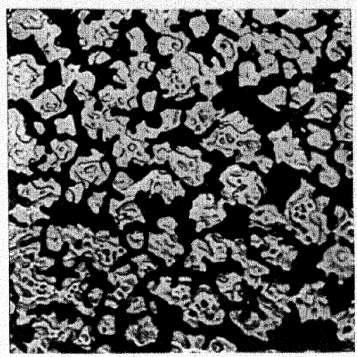


FIG. 14.

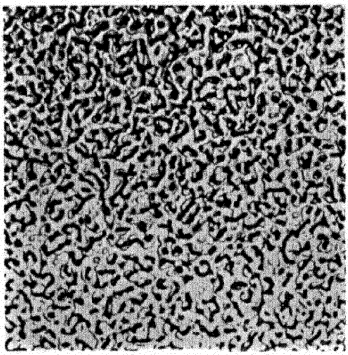


FIG. 15.

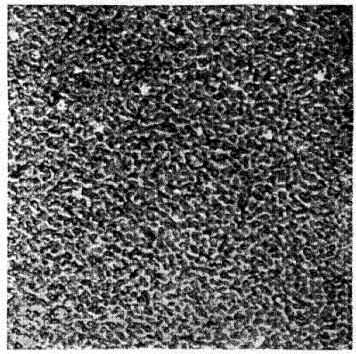


FIG. 16.

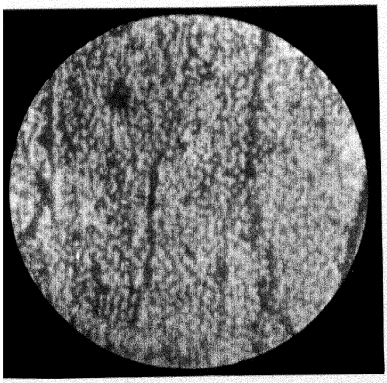


FIG. 17.

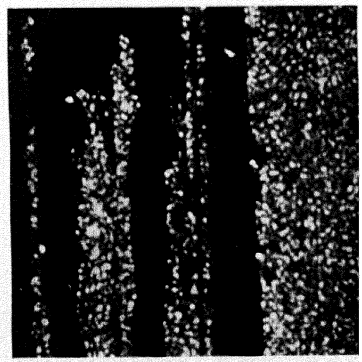


FIG. 18.

PLATE VII

FIG. 19

Plate VII

SEE PAGE

Fig. 19.—Annealed gold film shown in Fig. 11, enlarged to 1760 . . 24

PLATE VII

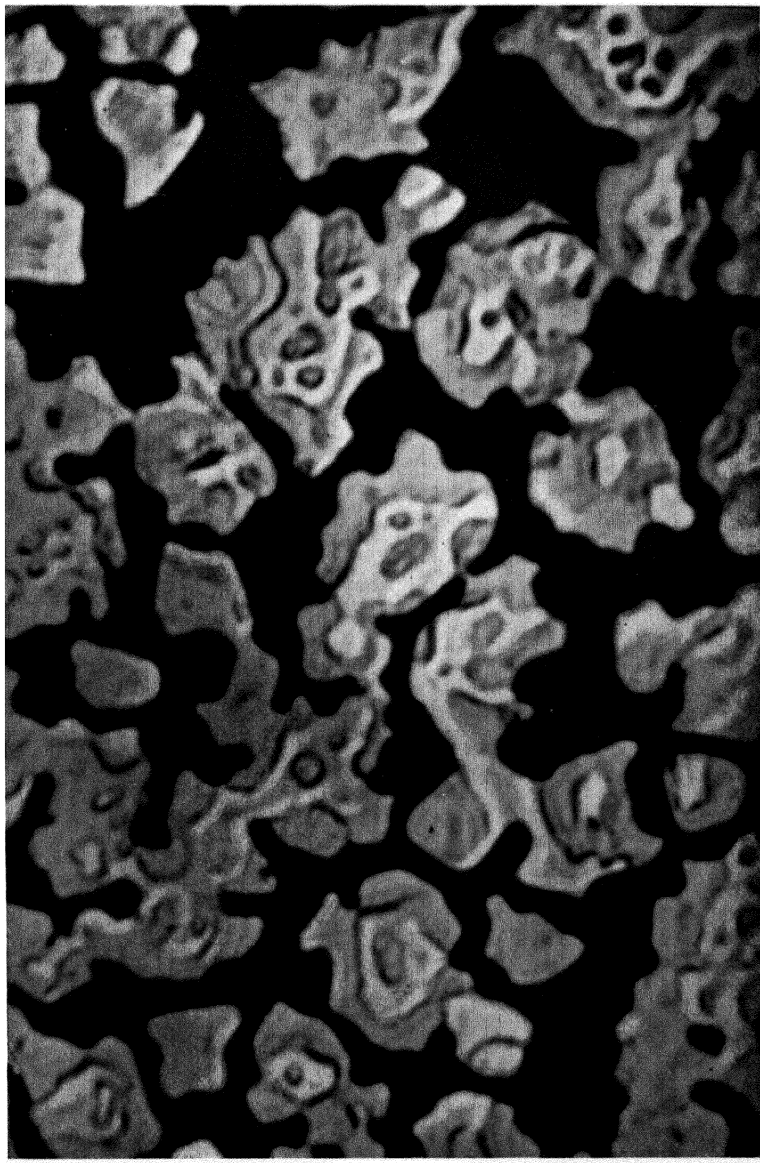


FIG. 19.

PLATE VIII

FIGS. 20, 21, 22, 23, 24, 25.

Plate VIII

Fig. 20.—Gold plate. A spot amalgamated with mercury, which was then driven off by gentle heat. The dark part was most affected by the treatment, and the light part least. Normally reflected light, green screen. Objective 12 mm. Apo. N.A. 0·65. ×250 . 27, 51

Fig. 21.—The light part of this plate more highly magnified. Objective 3 mm. Oil immersion. Apo. N.A. 1·4. ×775 . . . 27, 51

Fig. 22.—Dark part more highly magnified. Objective as in Fig. 20. ×775 . 27, 51

Fig. 23.—Gold leaf on glass, exposed to mercury vapour, and then heated sufficiently to drive off the mercury. Transmitted light, green screen. Objective 12 mm. N.A. 0·65. ×440. The dark patches were deep green, and the clear parts between them were colourless . . 27, 52

Fig. 24.—Gold paint on glass, annealed by heating. Transmitted light. ×500 226

Fig. 25.—Thin film of platinum on glass fully annealed. Transmitted light. ×450 25

PLATE VIII

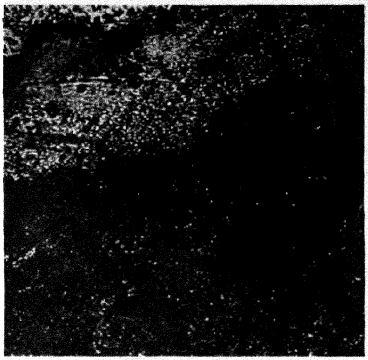


FIG. 20.

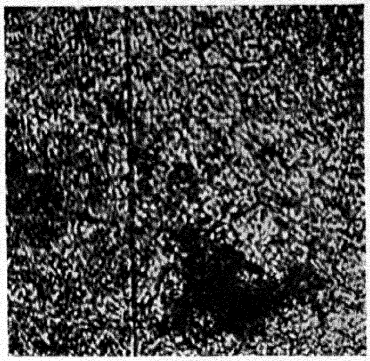


FIG. 21.

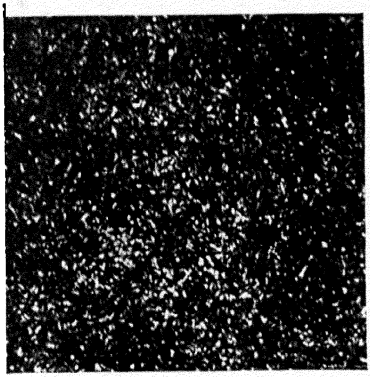


FIG. 22.

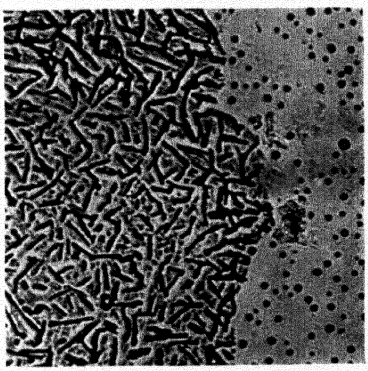


FIG. 23.

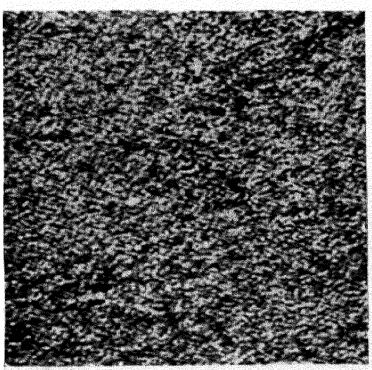


FIG. 24.

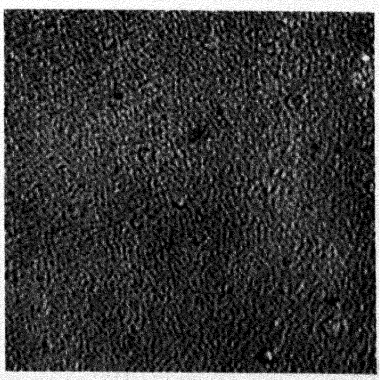


FIG. 25.

PLATE IX

FIGS. 26, 27, 28, 29, 30, 31.

Plate IX

SEE PAGE

Fig. 26.—Gold plate planished and polished. Normally reflected light, green screen. Objective 3 mm. Oil immersion. Apo. N.A. 1·4. Magnification × 1500 46

Fig. 27.—The same, after heating for 10 minutes to 700°-800°. Surface broken up into films by escaping gas 46

Fig. 28.—The same, after further heating for 1 hour. Surface subsiding after escape of gas 46

Fig. 29.—The same, after further heating for 2 hours. Surface further subsided 46

Fig. 30.—Gold plate, another specimen, heated for 1 hour. Surface subsiding after escape of gas. Lighting and objective as in Fig. 26. Magnification × 1500 (enlarged from 775) 47

Fig. 31.—The same after further heating for 1 hour. The surface has subsided and has assumed an appearance of viscous flow 47

PLATE IX

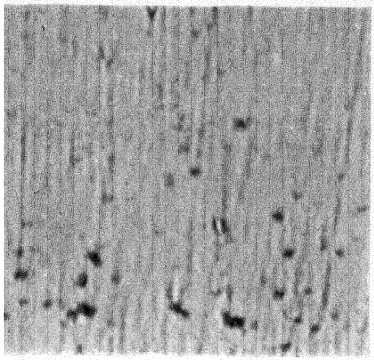


FIG. 26.

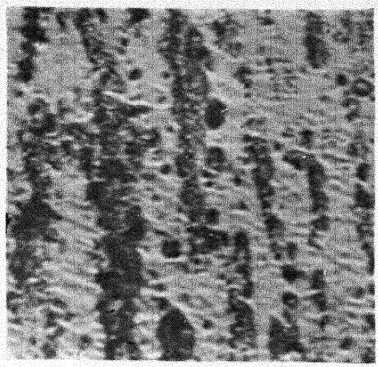


FIG. 27.

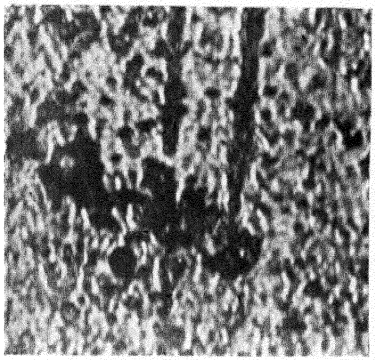


FIG. 28.

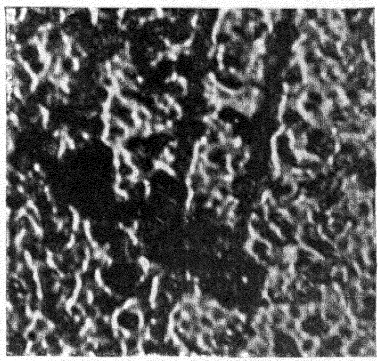


FIG. 29.

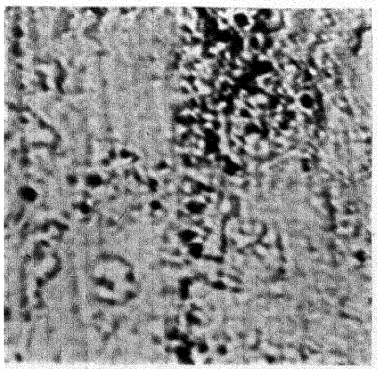


FIG 30.

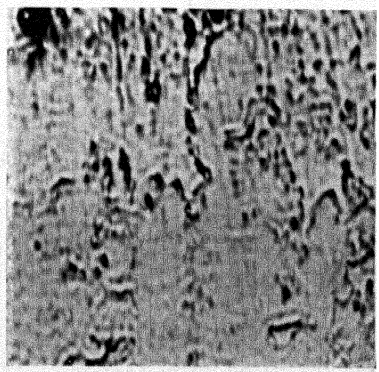


FIG. 31.

PLATE X

FIGS. 32, 33.

Plate X

SEE PA

Fig. 32.—Lead cut surface showing ridges partly broken up into surface tension forms. Oblique light. × 580 . . . . .

Fig. 33.—Gold plate polished on the finest emery-paper and lightly etched with chlorine water, showing ridges breaking up into surface tension forms. Oblique light. × 250 . . . . . .

PLATE X

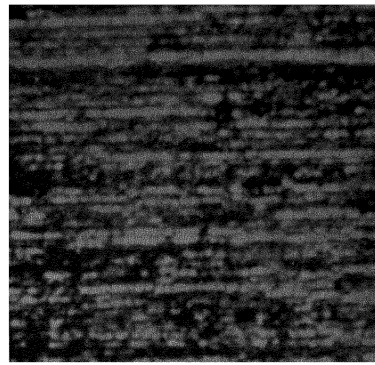


FIG. 32.

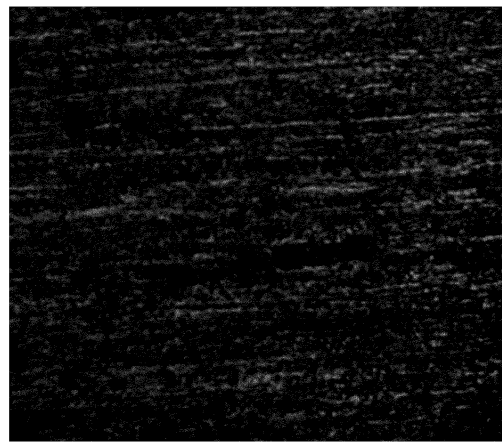


FIG. 33.

PLATE XI

FIGS. 34, 35.

Plate XI

SEE PAGE

Fig. 34.—End of a quarter-inch hard drawn silver rod very carefully polished and etched by quickly dipping in warm nitric acid in which a good deal of silver had been dissolved. The appearance of crystallisation was entirely confined to the thin polished film. When this was removed the general structure was of the broken-up type which is always seen in hard drawn metals. Magnification × 10 19

Fig. 35.—Film of gas black deposited on glass surface. The upper portion is in open formation as it was deposited; the lower portion has been shrunk by a drop of absolute alcohol. Transmitted light. Magnification × 700 65

PLATE XI

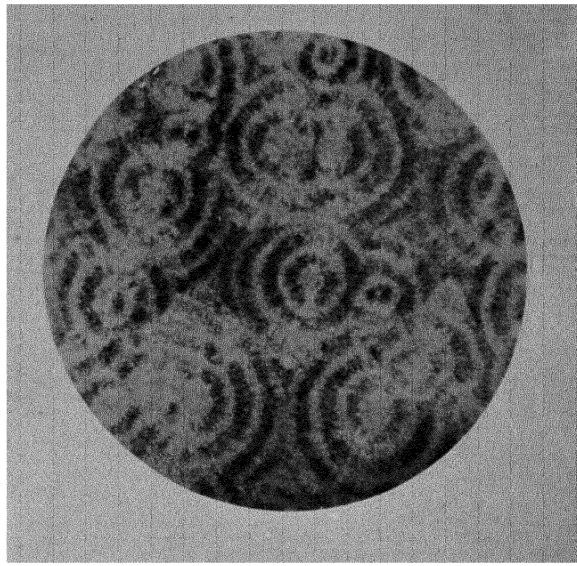


FIG. 34

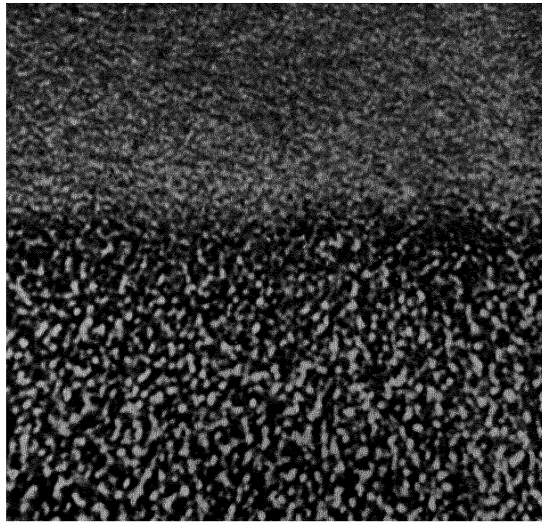


FIG. 35.

PLATE XII

FIGS. 36, 37.

Plate XII

SEE PAGE

Fig. 36.—A polished silver plate on which silver filings had been sprinkled. The plate was then turned upside down, so that the filings here shown had been left adhering to and suspended from the polished surface. Magnification × 10 71

Fig. 37.—Gold filings adhering near the point of a steel needle. Magnification × 10 71

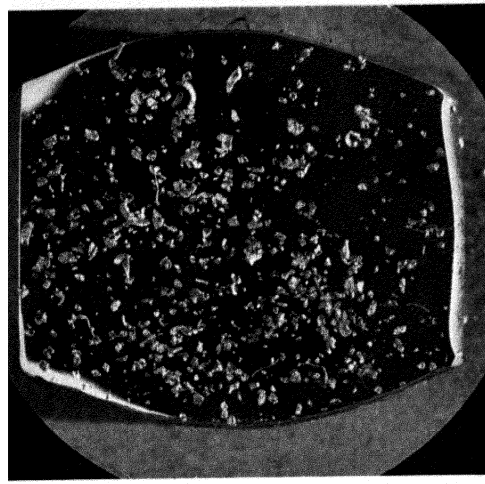


FIG. 36.

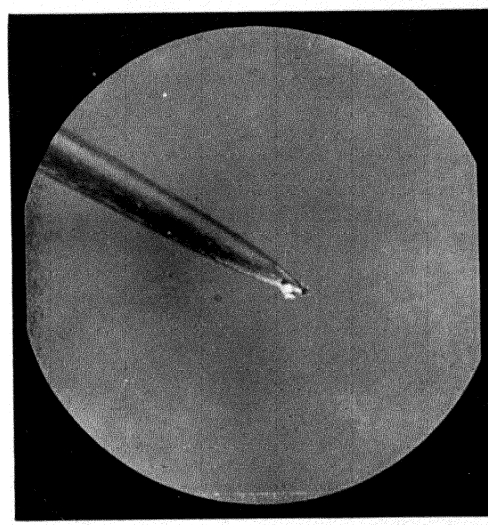


FIG. 37.

PLATE XIII

Figs. 38, 39, 40.

PLATE XIII

SEE PAGE

FIG. 38.—Zinc globules left on a glass micro-slip, on which the levigated dust had been sprinkled, the slip being then turned upside down. The illumination was from above by obliquely reflected light and from below by reflection from the substage mirror. Magnification × 120 . . 72

FIG. 39.—The zinc globules were picked up on the edges of a thin steel blade. Magnification × 60 72

FIG. 40.—The same, at higher magnification × 120 . 72

PLATE XIII

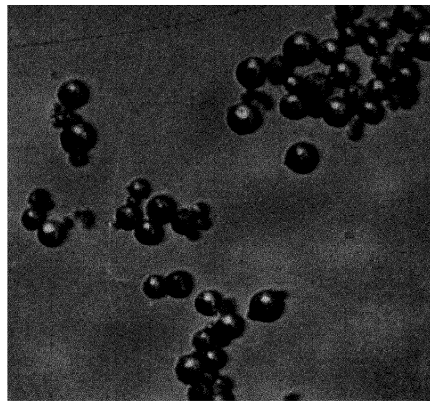


FIG 38

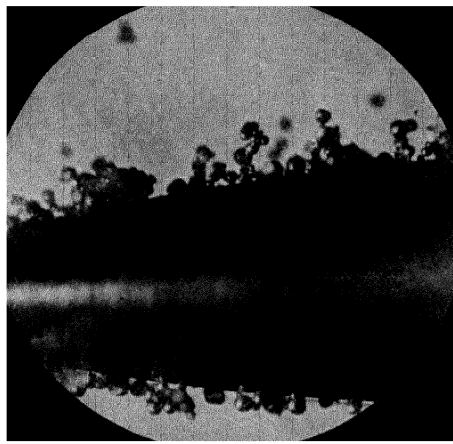


FIG 39.

FIG. 40.

PLATE XIV

FIGS. 41, 42, 43, 44, 45.

Plate XIV

SEE PAGE

Fig. 41.—Speculum metal. The broad horizontal band is a very fine needle scratch, in which the particles of metal from the emery scratches have been intercepted. Light normal reflected, green screen. Objective 3 mm. Oil immersion. Apochromat, N.A. 1·4. ×1500 . . . 84

Fig. 42.—Speculum metal polished on rouged leather across the furrows left by fine emery, showing flow of metal across the furrows. Light and objective as in Fig. 41. ×775 84

Fig. 43.—The same, further polished. The outline of the crystalline grains shows under the surface. Light and objective as in Fig. 41. ×775 . 84

Fig. 44.—The same, with the surface film removed with KCy., showing the grains surrounded by the eutectic. Light and objective as in Fig. 41. ×775 84

Fig. 45.—The same, again polished on rouged leather, showing the formation of a fresh film on the surface. Light and objective as in Fig. 41. ×775 85

All the above are from direct photographs, without enlargement or reduction.

PLATE XIV

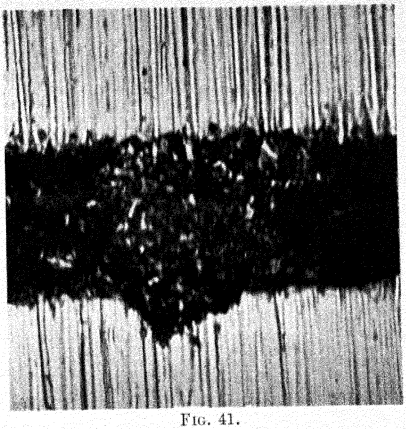


FIG. 41.

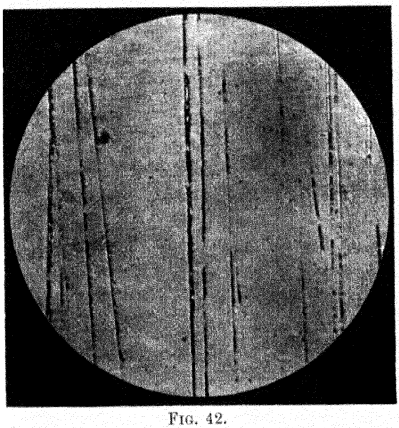


FIG. 42.

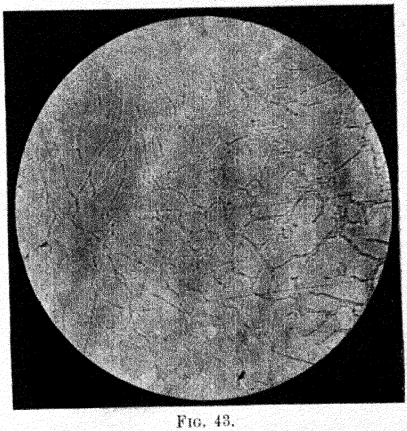


FIG. 43.

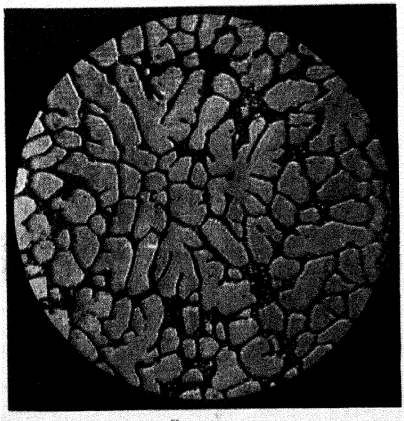


FIG. 44.

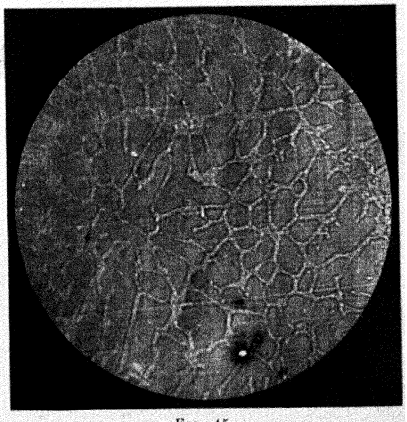


FIG. 45.

PLATE XV

FIGS. 46, 47, 48, 49, 50, 51.

Plate XV

SEE PAGE

Fig. 46.—Crystalline antimony, after rubbing on fine emery-paper. Light normal reflected, green screen. Objective 3 mm. Oil immersion. Apochromat, N.A. 1·4. ×775 85

Fig. 47.—The same, after polishing on rouged leather. Light and objective as in Fig. 46. ×775 86

Fig. 48.—The same, after partial etching with KCy. Light and objective as in Fig. 46. ×775 86

Fig. 49.—The same, showing pits covered with a film of flowed metal. Light and objective as in Fig. 46. ×775 87

Fig. 50.—The same, showing another pit over which a film is being built up by the flowing metal. Light and objective as in Fig. 46. ×775 . 87

All the above are from direct photographs without enlargement or reduction.

Fig. 51.—Etched pits on cleavage face of calcite crystal . . 92

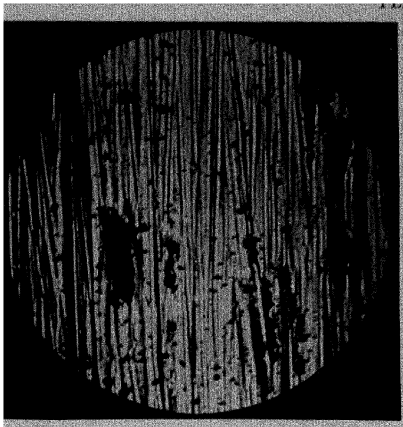


FIG. 46.

FIG. 47.

FIG. 48.

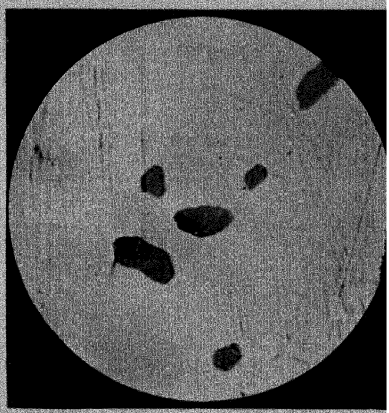


FIG. 49.

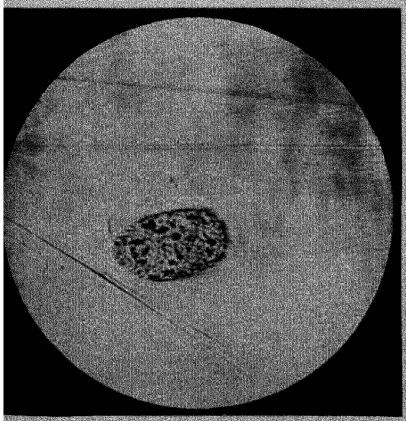


FIG. 50.

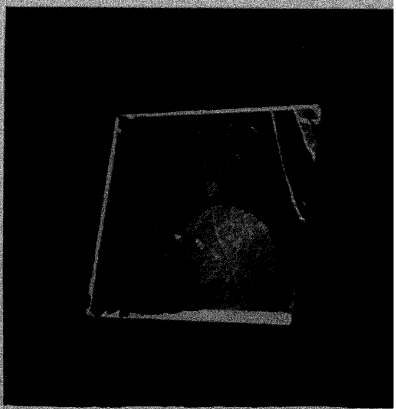


FIG. 51.

PLATE XVI

FIGS. 52, 53.

Plate XVI

SEE PAGE

Fig. 52.—Enlargement of Fig. 49, to show film of flowed metal covering pits 87

Fig. 53.—Enlargement of portion of Fig. 50, showing a large pit in process of being covered over by the flowing metal 87

PLATE XVI

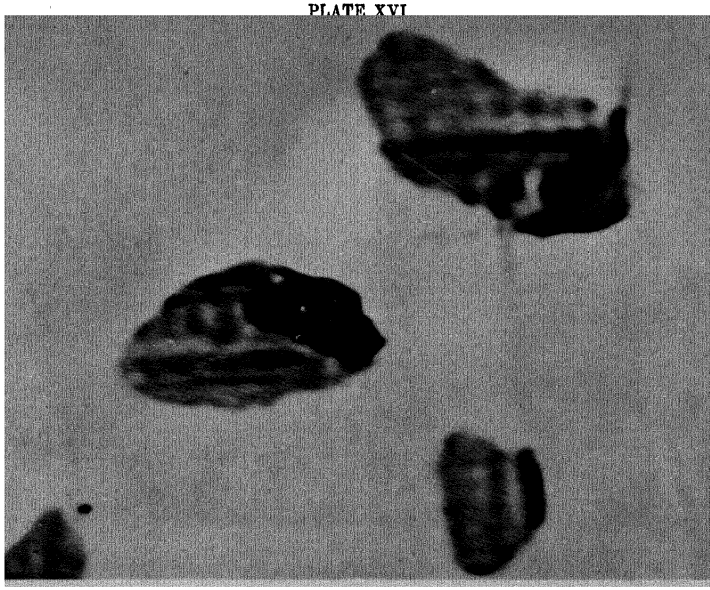


FIG. 52.

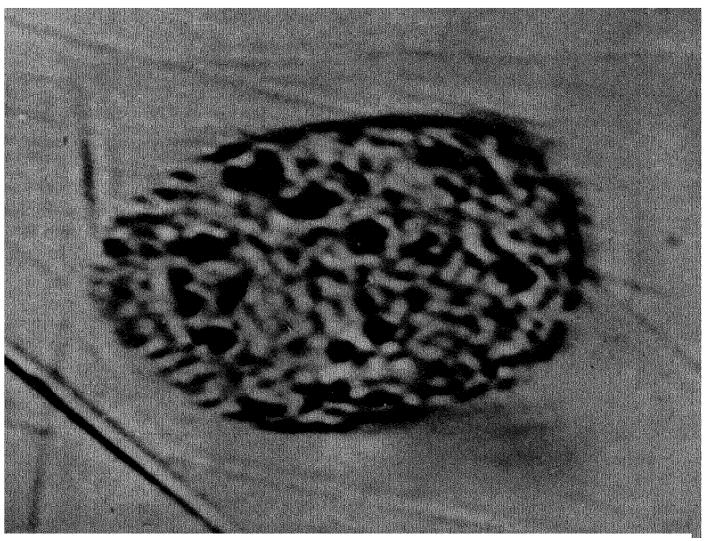


FIG. 53.

PLATE XVII

FIGS. 54, 55, 56, 57.

PLATE XVII

SEE PAGE

Pits on a polished copper surface, showing the transparence or translucence of the surface film produced in polishing.

FIG. 54.—Film covering pits. × 800 90

FIG. 55.—Film removed by etching. × 800 90

At a higher magnification :

FIG. 56.—Film covering pits. × 1800 90

FIG. 57.—Film removed by etching. × 1800 90

The red patches in the covering films in Figs. 54 and 56 correspond with spots of light reflected from the convex surfaces of the pits in Figs. 55 and 57.

PLATE XVII

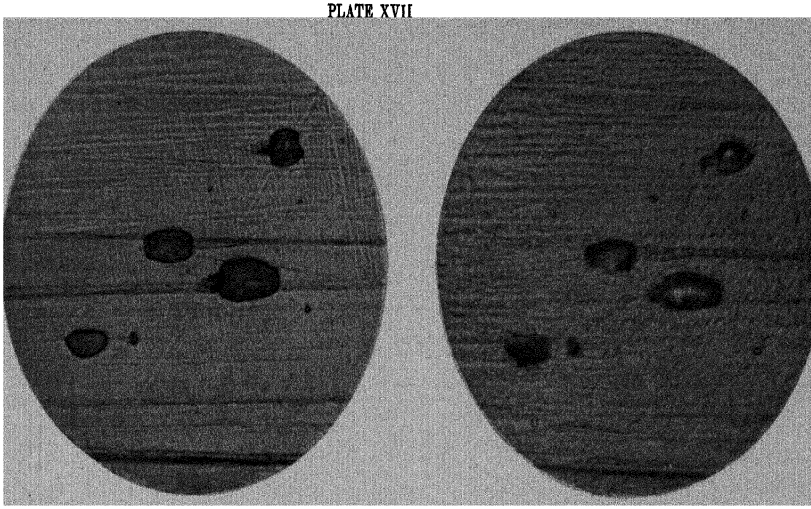


FIG. 54.

FIG. 55.

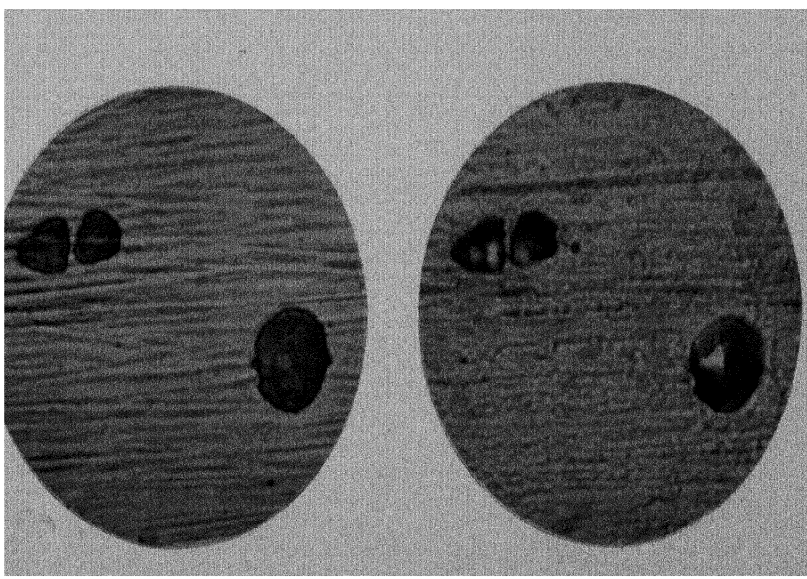


FIG. 56.

FIG. 57.

PLATE XVIII

FIGS, 58, 59.

Plate XVIII

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Fig. 58.—Calcite, showing etched and unetched surface. Light oblique. Objective 16 mm. Apochromat N.A. 0 3. ×215. Compare with Figs. 76 and 77 93

Fig. 59.—Portion of calcite surface enlarged, showing etched and unetched surface. Light transmitted, slightly oblique, green screen. × 860 . 93

PLATE XVIII

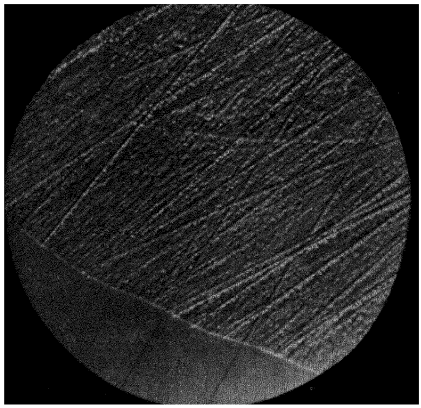

FIG. 58.

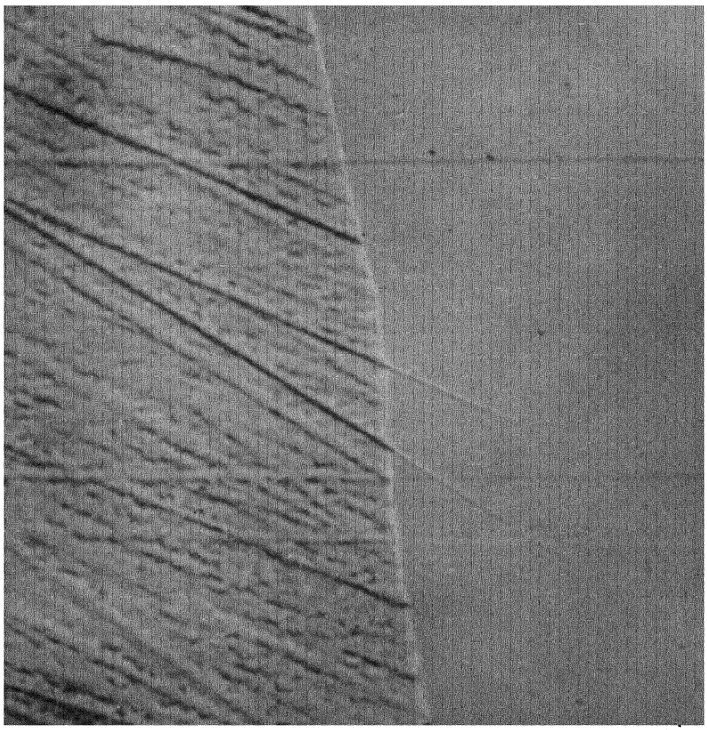

FIG. 59.

PLATE XIX

FIGS. 60, 61, 62.

Plate XIX

SEE PAGE

Fig. 60.—Etched calcite surface, showing the untouched skin and the under surface at 500 and 1000 $\mu\mu$ 99

Fig. 61.—The deeper scratches at a higher magnification . . . 100

Fig. 62.—Flow-lines at 100 to 150 $\mu\mu$ below the surface. In this figure the flow-lines are about 1500 $\mu\mu$ apart. 100

PLATE XIX

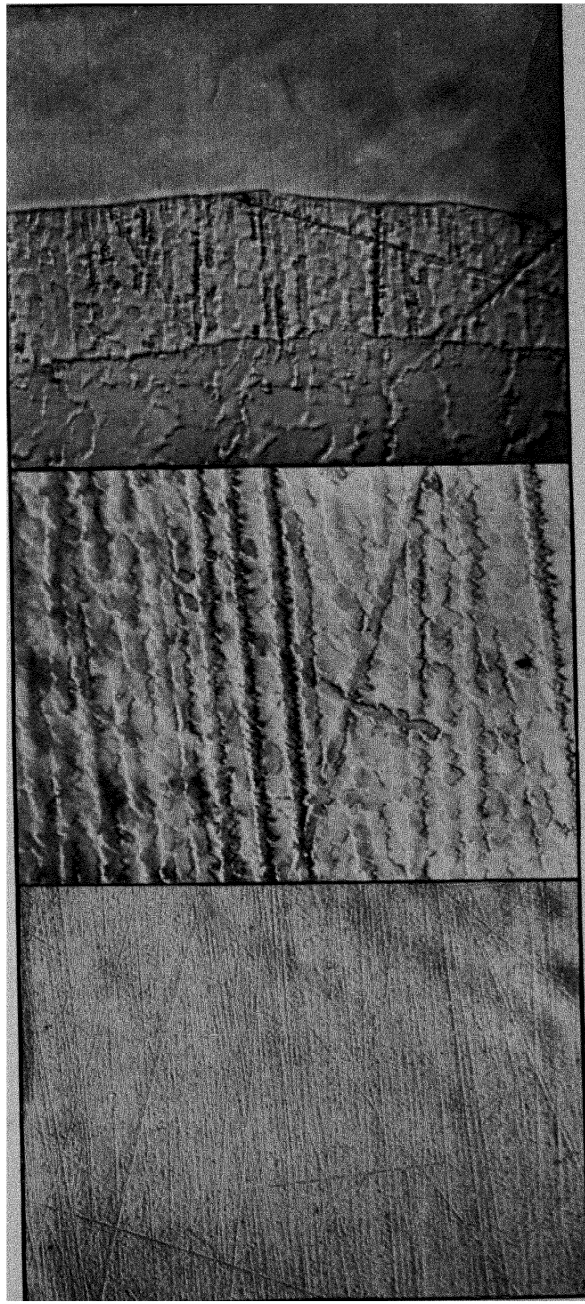

FIG. 60.

FIG. 61.

FIG. 62.

PLATE XX

FIGS. 63, 64, 65.

Plate XX

SEE PAGE

Fig. 63.—Parallel growth of sodium nitrate crystals on a polished calcite surface. Magnification × 250 103

Fig. 64.—A thin film of sodium nitrate on a polished calcite surface. The outlines show the influence both of surface tension and of crystalline direction. Magnification × 250 103

Fig. 65.—Parallel growth of sodium nitrate crystals on an etched calcite surface, on which the deeper scratches are still visible. The parallel growth is quite unaffected by the rough and irregular texture of the surface below. Magnification × 250 103

PLATE XX

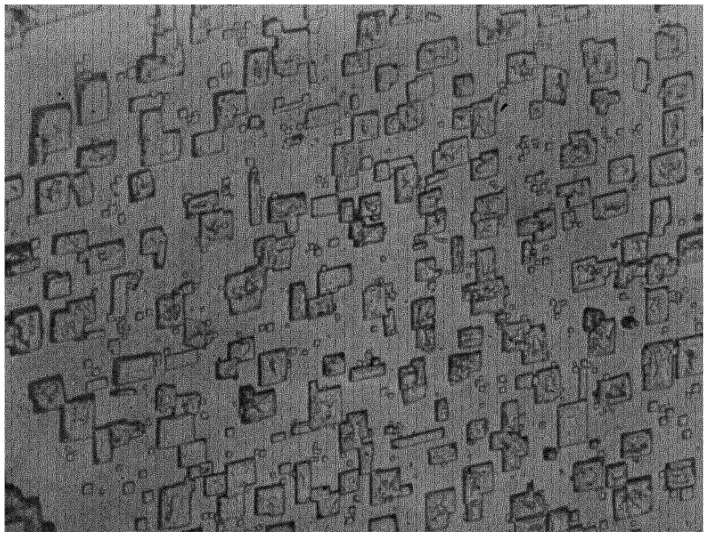

FIG. 63.

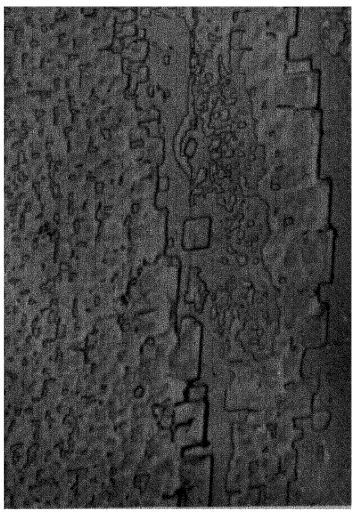

FIG. 64.

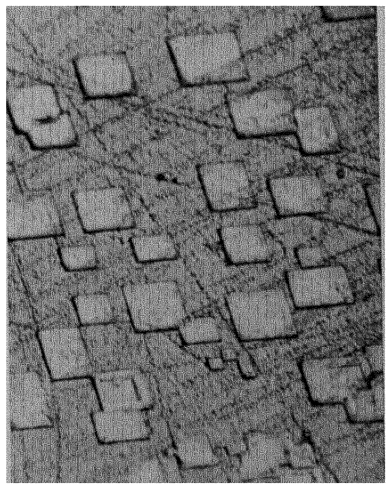

FIG. 65.

PLATE XXI

FIGS. 66, 67, 68, 69, 70, 71.

Plate XXI

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Fig. 66.—Fine flow-lines on a glass surface. Where these flow-lines cross a scratch which had been made before polishing, there are distinct signs of an attempt to bridge the gap by the flowing glass. ×700 . . 106

Fig. 67.—A splintering scratch on glass at a low magnification. ×100 . 107

Fig. 68.—Grooves ploughed on glass by drawing the edge of an uncut diamond along the surface under a light pressure 107

Fig. 69.—A piece of good commercial ground glass at a high magnification. ×700 109

Fig. 70.—Shows the first effects of moderately fine emery when applied between two glass surfaces which are being ground together. ×700 . 109

Fig. 71.—A further stage in the grinding with emery. ×700 . . 109

PLATE XXI

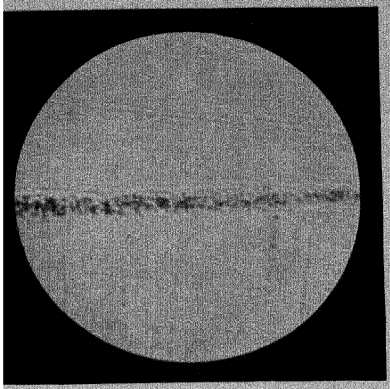

FIG. 66.

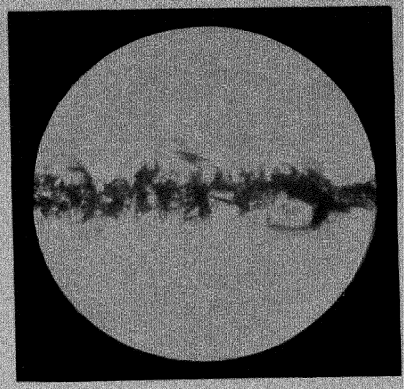

FIG. 67.

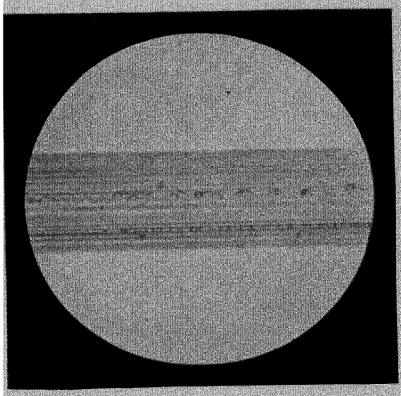

FIG. 68.

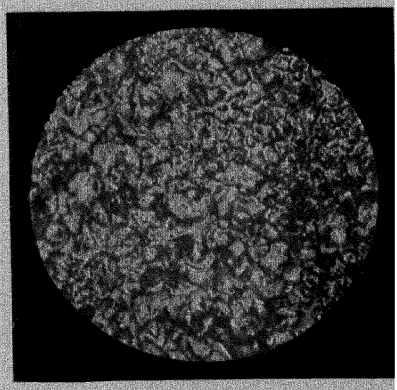

FIG. 69.

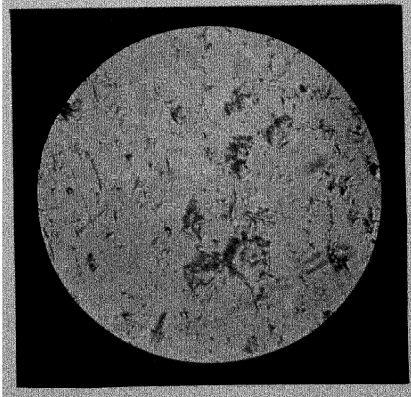

FIG. 70.

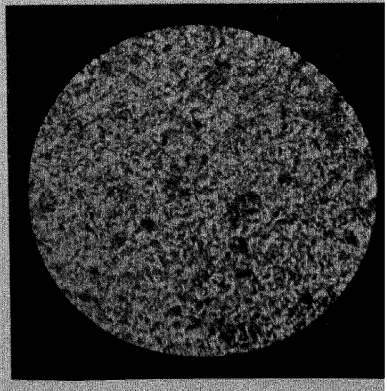

FIG. 71.

PLATE XXII

FIGS. 72, 73, 74, 75, 76, 77.

Plate XXII

SEE PAGE

Fig. 72.—At this stage the smaller pits have for the most part taken the place of the larger ones. ×700 109

Fig. 73.—In this photograph pitting has ceased and signs of flow are evident. ×700 110

Fig. 74.—Shows the remarkably quick effect of rouge polishing. The pitted effect is rapidly disappearing and is being replaced by large patches of structureless viscous-looking material. ×700 . . . 110

Fig. 75.—A further stage in the rouge polishing. The number and size of the pits is considerably reduced. ×700 110

Fig. 76.—Polished glass surface, a portion of which has been etched with hydrofluoric acid gas mixed with air. ×67. Prepared and photographed by Mr. W. D. Haigh 110

Fig. 77.—Polished quartz surface, part of which has been etched with hydrofluoric acid. ×67. Prepared and photographed by Mr. W. D. Haigh. Compare Figs. 76 and 77 with calcite in Fig. 58 . . . 115

PLATE XXII

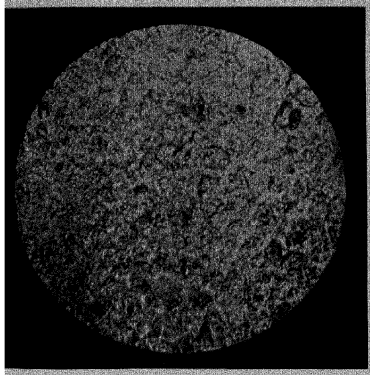

FIG. 72.

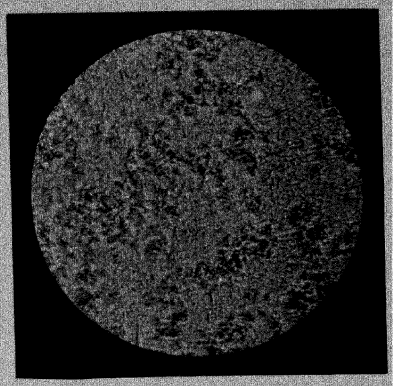

FIG. 73.

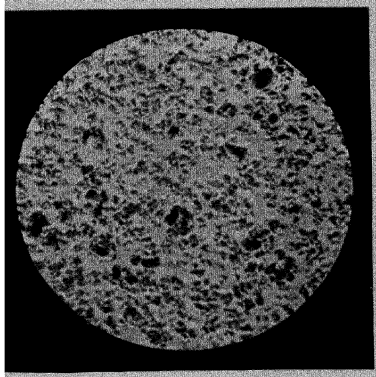

FIG. 74.

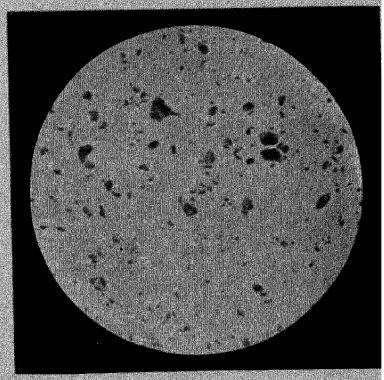

FIG. 75.

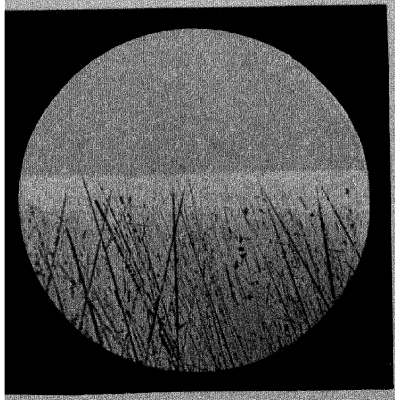

FIG. 76.

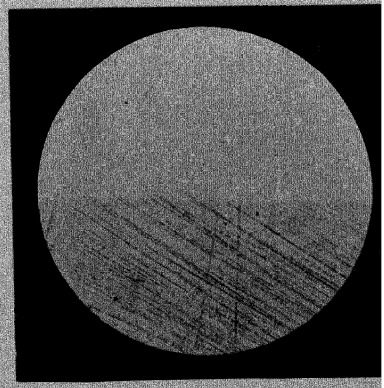

FIG. 77.

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FIGS. 78, 79, 80.

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FIG. 78.—Shows a single furrow ploughed with a diamond point on glass, along one side of which the edge has been slightly broken and distorted, but without any true splintering 107

FIGS. 79 and 80.—Cleaving or cutting scratches at a high magnification. The dark bands are the shadows caused by total reflection from the cleft which has been opened in the substance of the glass below the surface . . 108

PLATE XXIII

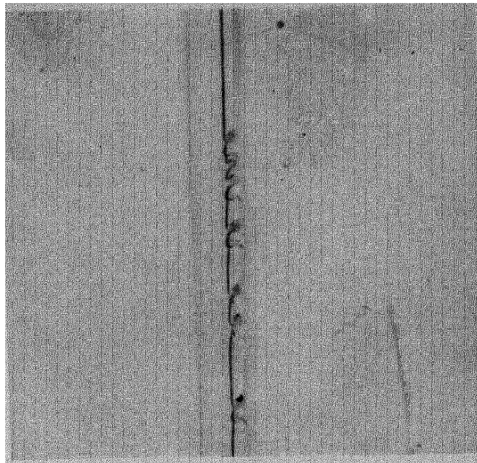

FIG 78.

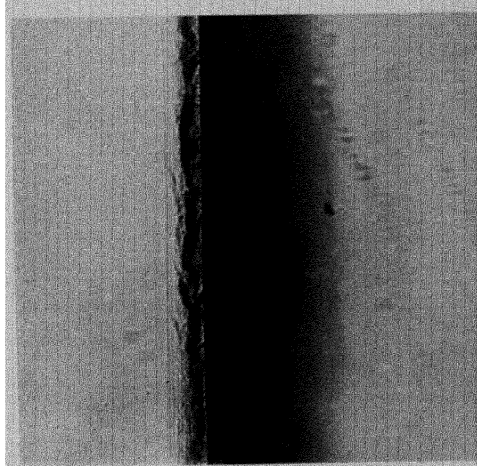

FIG. 79.

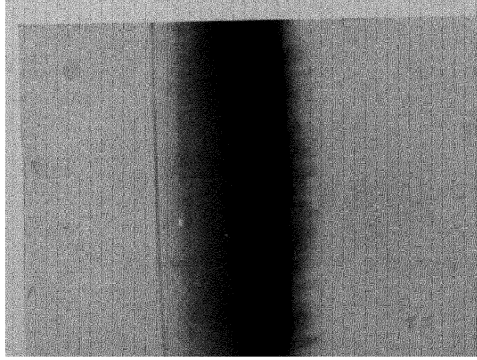

FIG. 80.

PLATE XXIV

FIG. 81.

PLATE XXIV

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FIG. 81.—Globules of vitreous sugar, two of which have been devitrified by heating in the presence of crystalline nuclei. Globule *a* is completely vitreous. In *b* devitrification is beginning in the centre. *c* and *d* are completely devitrified 130

PLATE XXIV

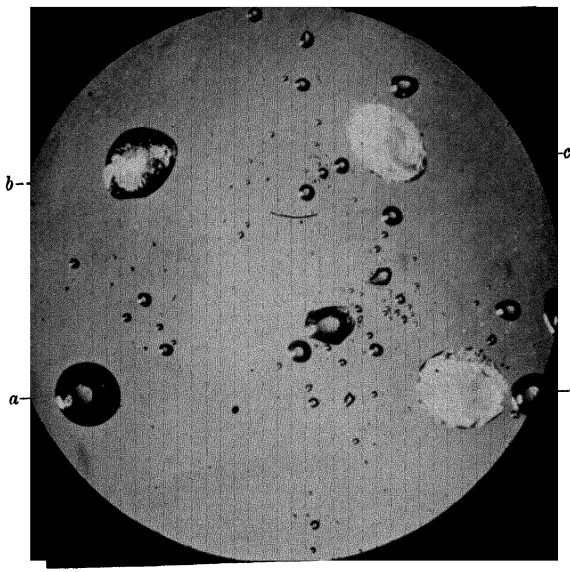

FIG. 81.

PLATE XXV

FIGS. 82, 83, 84.

Plate XXV

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Fig. 82.—Gold globule flattened by a single blow, showing the "primitive" grains, deformed but still retaining their identity. About a dozen grains cover the whole field 139

Fig. 83.—Similar globule annealed after deformation, showing structure developed by recrystallisation. The primitive grains have disappeared, and their place has been taken by a much greater number of sharply defined crystals, each with its own orientation. This shows that the original uniform orientation of each grain has been completely broken up by the deformation 140

Fig. 84.—Slip bands on outer surface of the flattened globule, Fig. 82. Magnification 700 diameters, by lens of 1·4 N.A. . 140

PLATE XXV

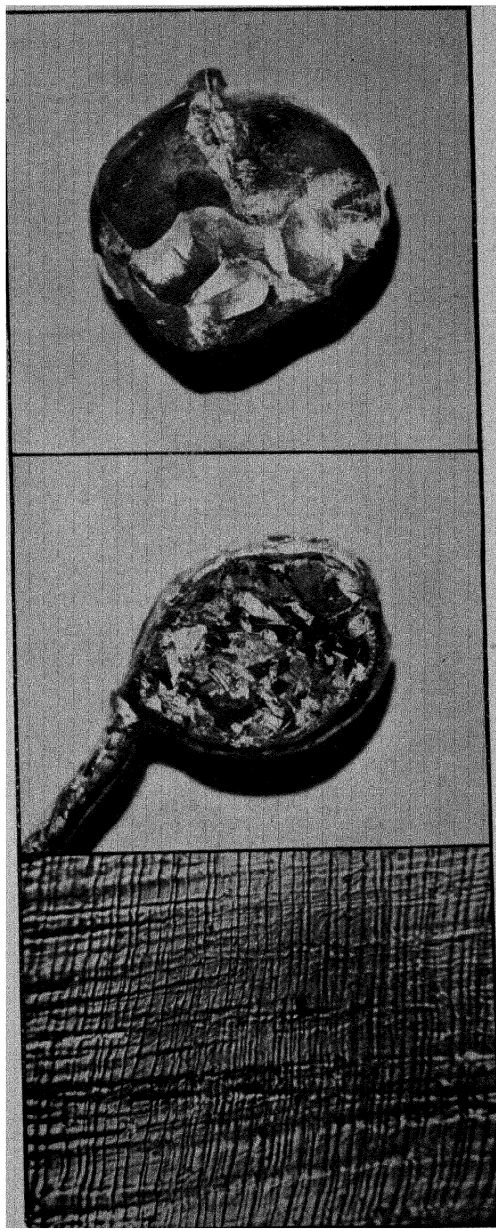

FIG. 82.

FIG. 83.

FIG. 84

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FIGS. 85, 86.

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Fig. 85.—Surface of beaten gold, lightly etched, disclosing granular structure produced by flow. Magnification × 450, by lens of ·95 N.A. Normal illumination 140

Fig. 86.—Gold globule flattened by 12 blows. The primitive grains still retain their identity. About a dozen grains can be traced . . 142

PLATE XXVI

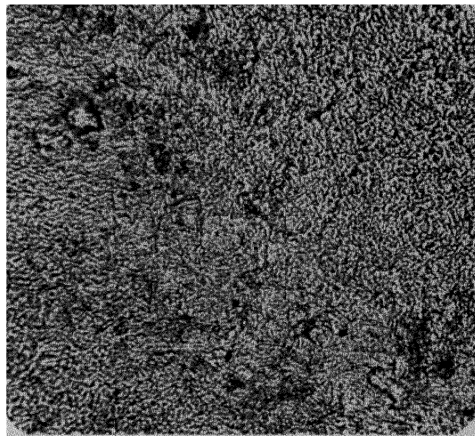

FIG. 85.

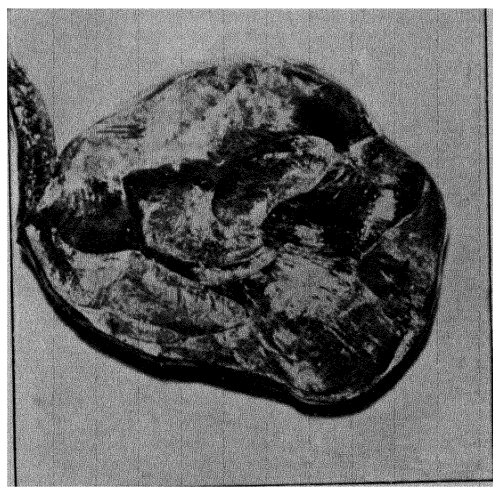

FIG. 86.

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FIGS. 87, 88.

Plate XXVII

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Fig. 87.—Microscopic crystal of antimony 144

Fig. 88.—The same flattened by a single blow from a small drop-hammer. This thin plate was in a highly strained condition. When first produced there were four or five short cracks which did not nearly reach the centre. Twenty-four hours later, when this photograph was taken, these cracks had widened, and now nearly reached the centre. A number of other cracks had also developed.

This experiment shows that the "internal strains in cold-wrought metals," which were subsequently discussed by Professor Heyn in the May Lecture of 1914 to the Institute of Metals, are due to liquefaction during flow and resolidification in the vitreous state . . . 144

PLATE XXVII

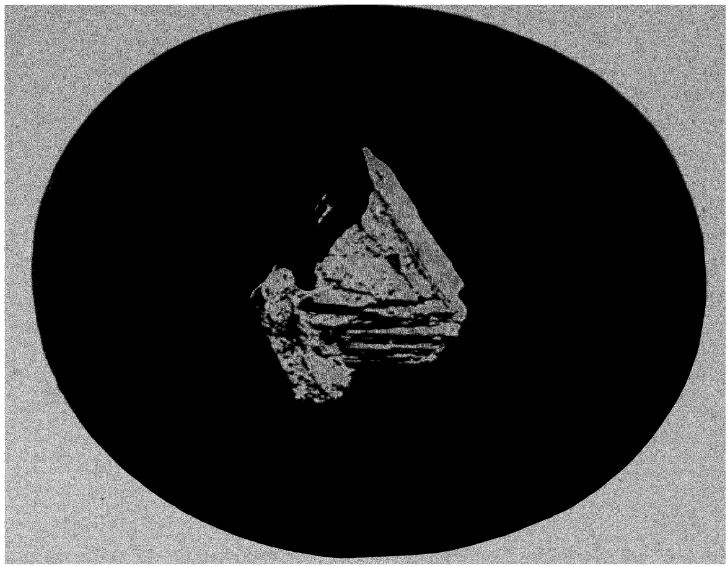

FIG. 87.

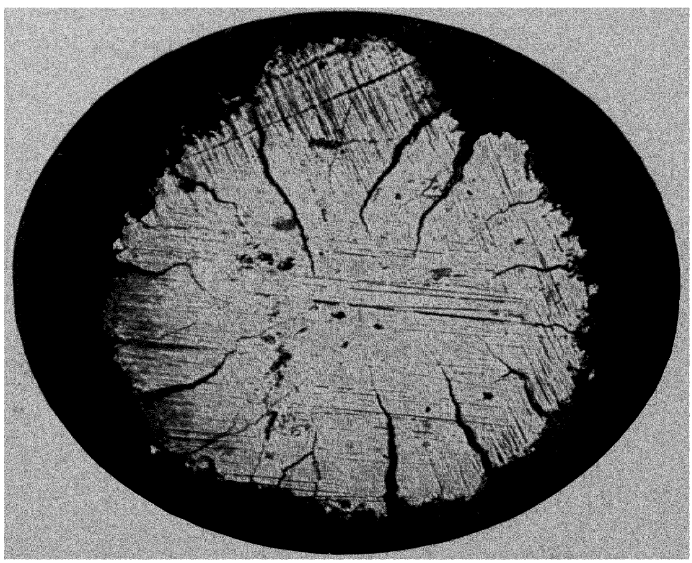

FIG 88.

PLATE XXVIII

FIGS. 89, 90.

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Fig. 89.—Silver rod notched round with a knife and sharply broken. The fractured core shows the tubular structure which results from the presence of gases in the metal, the bubbles of which are drawn out into tubes by the rolling of the rod, or by drawing, in the case of wire. Magnification ×12 155

Fig. 90.—Gold plate deeply etched with chlorine water, disclosing deformed grains and lamellae immediately below the granular layer in Fig. 9. The breaking down of the lamellae into granules is well seen. Magnification ×450, by lens of ·95 N.A. Normal illumination . . . 29

PLATE XXVIII

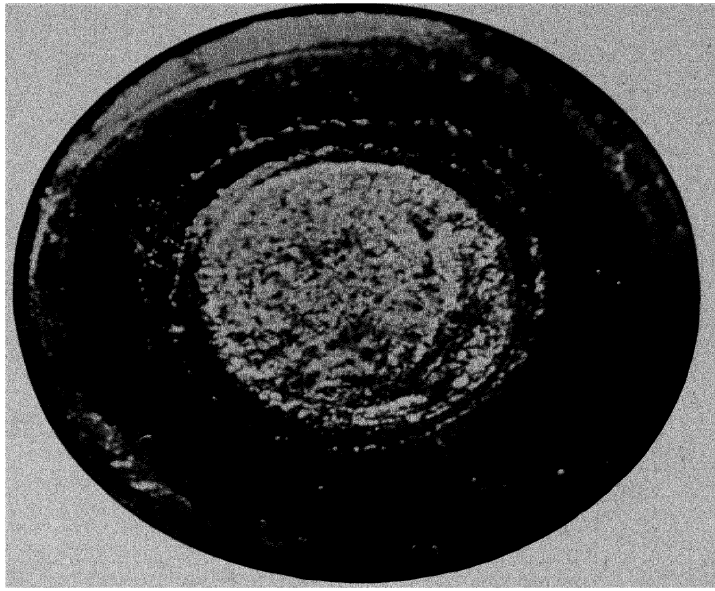

FIG. 89.

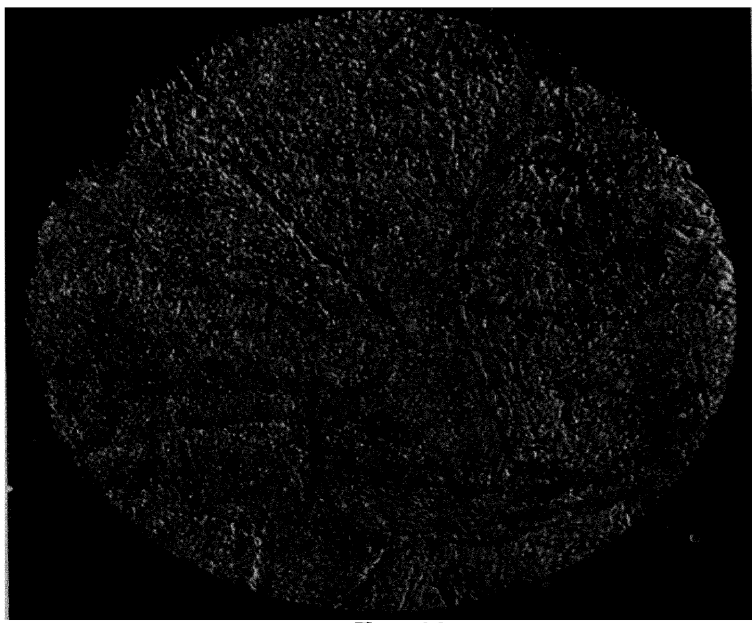

FIG. 90.

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FIGS. 91, 92.

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Fig. 91.—Half-inch bar of mild steel heated at 900° and chilled in cold water. Shows the structure of ferrite grains from the centre to the outer edge. Magnification × 250. Objective ·65 N.A. . . . 177

Fig. 92.—Half-inch bar heated for two hours in sodium cyanide at 900° C. chilled in cold water. Reheated to 900°, chilled in water, and tempered at 300°. The ferrite grains retain their identity, but the shrinkage stress due to the chilling of the hardened case has caused the lamellae of the grains to slip with the production of films in the vitreous state, which encase and cement the lamellae into a more rigid structure . 178

PLATE XXIX

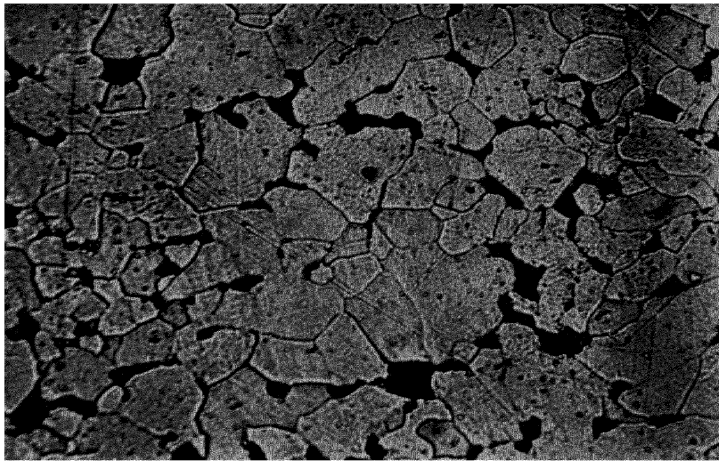

FIG. 91.

FIG. 92.

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FIGS. 93, 94.

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Fig. 93.—Individual grains in the centre portion of previous figure, showing the hardening of ferrite grains by deformation caused by the shrinkage of the hardened case. ×775. Objective 1·4 N.A. . . . 178

Fig. 94.—Surface of hardened case after repeated polishing and etching. ×250. Objective ·65 N.A. 178

PLATE XXX

FIG. 93.

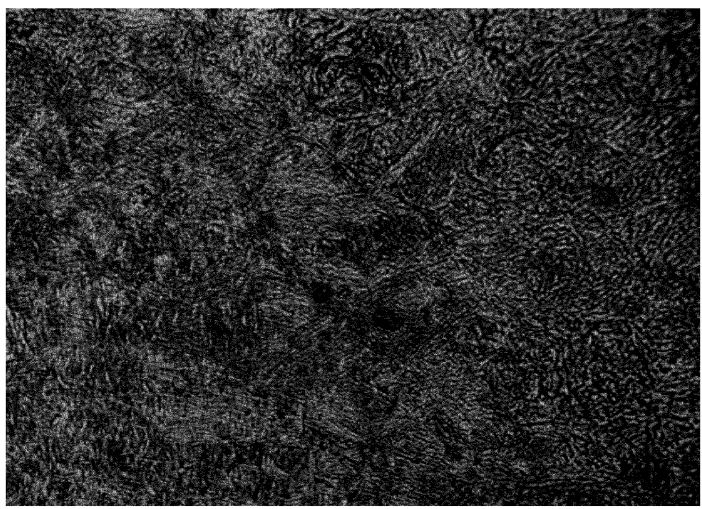

FIG. 94.

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FIGS. 95, 96, 97, 98, 99.

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Fig. 95.—Plug of compressed vitreous gold, which could withstand a compression stress of over thirty tons per square inch . . . 174

Fig. 96.—Gold wires: Fractured Ends. *c*, Etched. *d*, Unetched . 155

Fig. 97.—Gold Wires. *a*, Hard drawn. *b*, Annealed . . 148

Fig. 98.—Granular surface of *a* . . . 149

Fig. 99.—Structure of *b* shows the meeting of four crystals. The orientation of each is shown by the slope of its lamellae. Lens of 0·95 N.A. . 149

PLATE XXXI

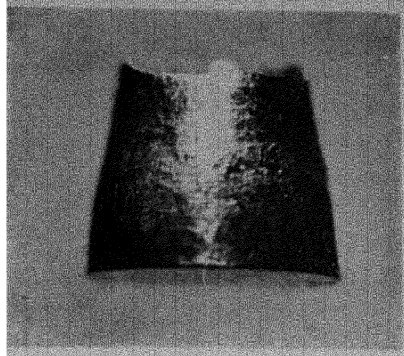

FIG. 95.

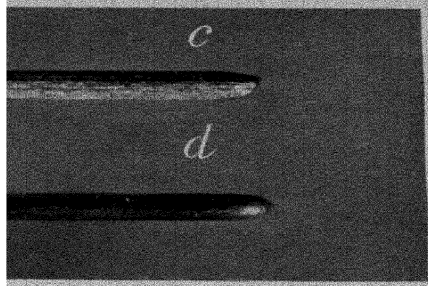

FIG. 96.

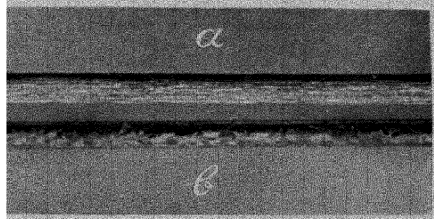

FIG. 97.

FIG. 98.

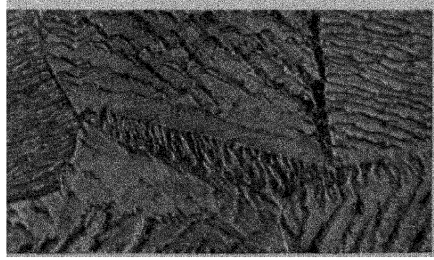

FIG. 99.

PLATE XXXII

FIGS. 100, 101.

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SEE PAGE

Fig. 100.—Hard-drawn gold wire before annealing, lightly etched. On the lighter parts of the photograph the internal structure is plainly disclosed, and it is seen that the strands or fibres are composed of grains which have been drawn out and pinched into long torpedo-like forms . 163

Fig. 101.—The same, more deeply etched. Shows the effect of etching away still more of the matrix of amorphous metal, and with it the smaller fragments of crystalline grains 163

PLATE XXXII

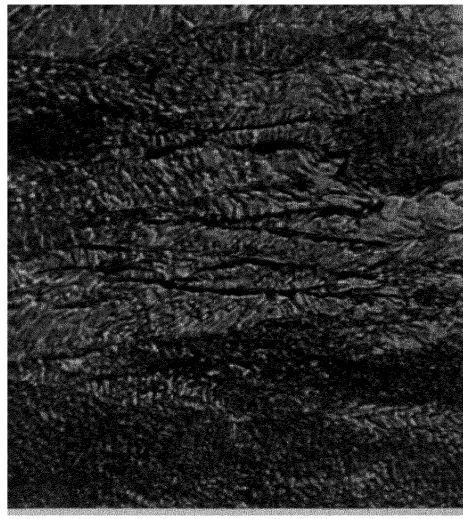

FIG. 100.

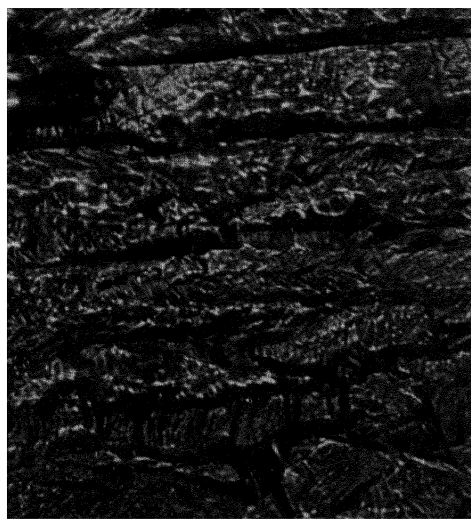

FIG. 101.

PLATE XXXIII

FIGS. 102, 103.

PLATE XXXIII

SEE PAGE

FIG. 102.—Hard-drawn gold wire No. 3 after annealing for one hour at 225-230°, and deeply etched. The distorted structure of Figs. 102-103 is disappearing, and minute crystalline aggregates are forming. Magnification × 770. Oil immersion lens of 1·4 N.A. 165

FIG. 103.—Hard-drawn gold wire No. 5 after annealing for one hour at 278-284°, and deeply etched. The differently oriented grains and lamellae now cover the whole field. Magnification × 700. Lens of ·95 N.A. . 165

PLATE XXXIII

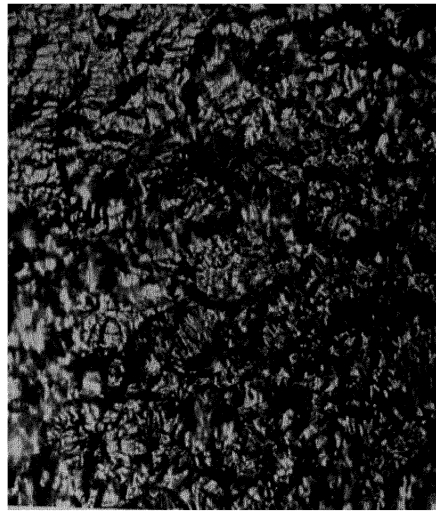

FIG. 102.

FIG. 103.

PLATE XXXIV

FIGS. 104, 105, 106.

PLATE XXXIV

SEE PAGE

FIG. 104.—Gold leaf annealed by heating on glass. Transmitted light with green screen. Magnification × 440. Objective 12 mm. Apo. N.A. 0·65. Compare with Figs. 15 and 16 220

FIG. 105.—Silver leaf on glass, made transparent by heating at 350°. Direct photograph, natural size. Compare with Figs. 17 and 18 . 40, 221

FIG. 106.—Barium platino-cyanide crystals, showing the change from the crystalline to the vitreous state due to flow. The yellow colour is changed to a deep brownish-red wherever the pressure has acted so as to cause flow. This specimen was prepared and photographed by Mr. W. D. Haigh 238

PLATE XXXIV

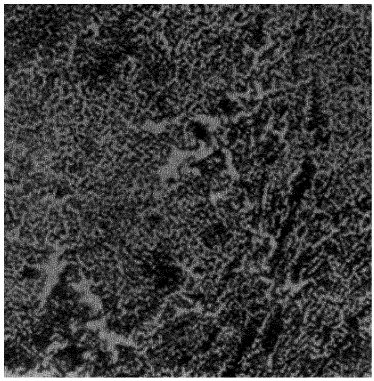

FIG. 104.

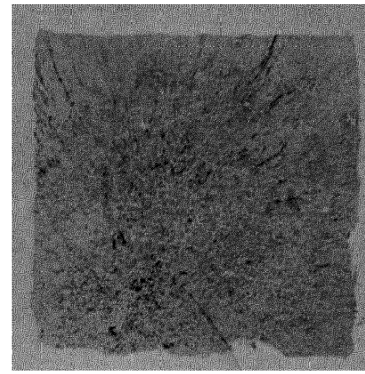

FIG. 105.

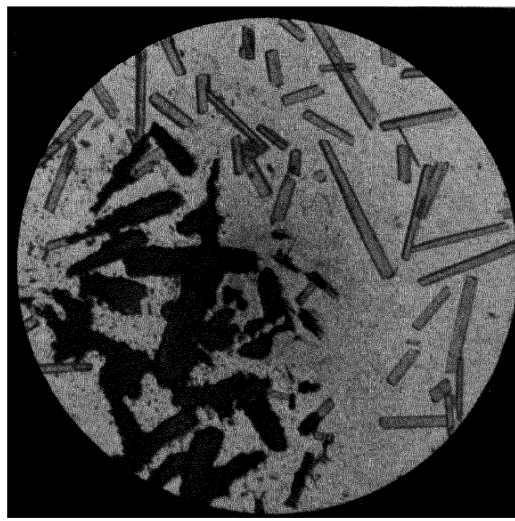

FIG. 106.