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SURFACES OF SOLIDS IN SCIENCE AND INDUSTRY[1]

By Professor **WILLIAM DRAPER HARKINS**

UNIVERSITY OF CHICAGO AND UNIVERSAL OIL PRODUCTS COMPANY

I. INTRODUCTION: SOLIDS

EXCEPT for those who live on the ocean the objects observed visually by human beings are mostly solids, yet who has stopped to think that no one has actually seen a solid? All that is observed is the surface of the solid. For example, no one has ever seen anything of a house except the surfaces of its outside and of its inside walls. The surface of a solid may be considered as a two-dimensional system while the solid is itself three-dimensional. Even a single solid is, in general, made up of a very great number of small particles or crystals which are held together by surface forces. The boundary between two such crystals, or two phases, is designated as an interface, although the term surface is often used with a general meaning which includes all types of interfaces.

Surfaces are prominent in that they form the outside boundary of every phase or particle. Thus, if a thermometer is used to test the temperature of a liquid, its bulb must first be put through the surface. In vaporization every molecule must first get into and then jump out from the surface, and the condensation or adsorption of a vapor occurs upon a surface. If two particles unite, a part of their

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[1] Julius Stieglitz Memorial Lecture under the auspices of the University of Chicago and the Chicago Section of the American Chemical Society. Presented in much more extensive form to the Conference on Catalysis of the American Association for the Advancement of Science at Gibson Island, Md., June 11, 1945. Much of the work on solids has been published with Dr. George Jura in the *Journal of the American Chemical Society,* while that on liquids is given in Publications 7 and 13 of the A.A.A.S. by the writer.

surface disappears, while if a particle divides a new surface appears. A colloid system is one in which at least one of the phases exhibits a high surface area. Thus, it is evident that a high amount of surface energy is the most fundamental property which distinguishes colloids from other systems.

The tensile strength of a solid, for example a metal, is intimately related to its surface energy. Thus, the true tensile energy of a bar of steel or of a diamond one square centimeter in cross section is merely twice the free surface energy (twice the surface tension) of the iron or the diamond, since all that occurs if such a bar is pulled apart without deformation is the formation of two surfaces, each 1 square centimeter in area (Fig. 1). The energy (work) required is unknown in the case of iron, but the speaker has calculated it to be of the order of 9,000 ergs (38 times that for water) for the 111 face of the diamond and 14,000 ergs (59 times water) for the 100 face. Since the atoms in a diamond are very close together, this indicates an extremely great tensile strength for the diamond.

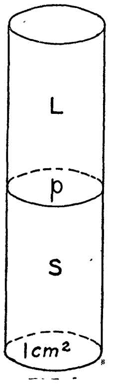

FIG. 1. Liquid (L) in contact with solid (S) to be pulled apart at the plane (p). In the text above both L and S are considered as parts of a single solid.

These values illustrate a very important difference between liquids and crystalline solids: in the latter both the tensile strength and the surface energy are highly dependent upon direction in the crystal, the structure of which may be represented by a three-dimensional lattice (Fig. 2), while that of a surface is depicted by a two-dimensional lattice (Fig. 3).

It is a remarkably unfortunate fact, which illustrates the neglect of surface chemistry both by universities and by industry, that *there is no accurate experimental value for the surface energy of any solid whatever.* The lack of such values is due, in our laboratory, to a lack of funds available for such work.

In American universities there is apparently no attempt by chemists or physicists to adjust the emphasis put upon various branches of the subjects according to their importance. Most American universities pay no attention to the physics or chemistry of surfaces; only about three do other than sporadic work in surface chemistry, and only in the University of Chicago, where the staff is small in comparison with that for organic chemistry, is there any real degree of specialization.

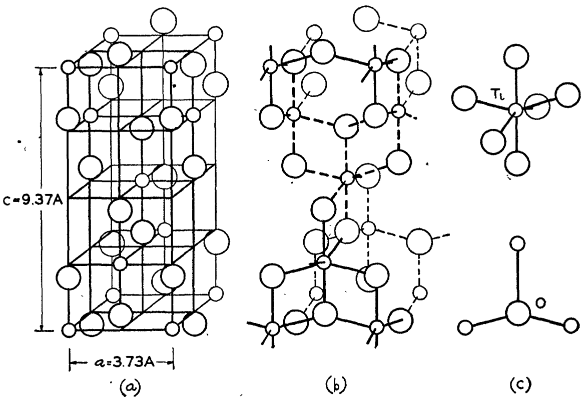

FIG. 2. Space lattice of titanium dioxide in the form of anatase.

II. THE AREA OF A FINELY DIVIDED SOLID

In three-dimensional systems, solid, liquid and gas, the fundamental quantity is the mass. However, in two dimensions the mass is not a definite quantity, since the second layer of molecules is not so much in the surface as the first, and the third not so much as the second. Thus, the area becomes the characteristic property, and, for example, the magnitude of the surface energy of a system has little meaning unless the area is known.

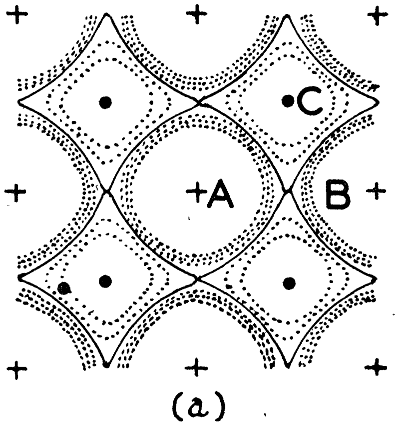

FIG. 3. Surface lattice of an ionic solid.

The relatively backward state of knowledge of the surface relations of solids is due to a considerable

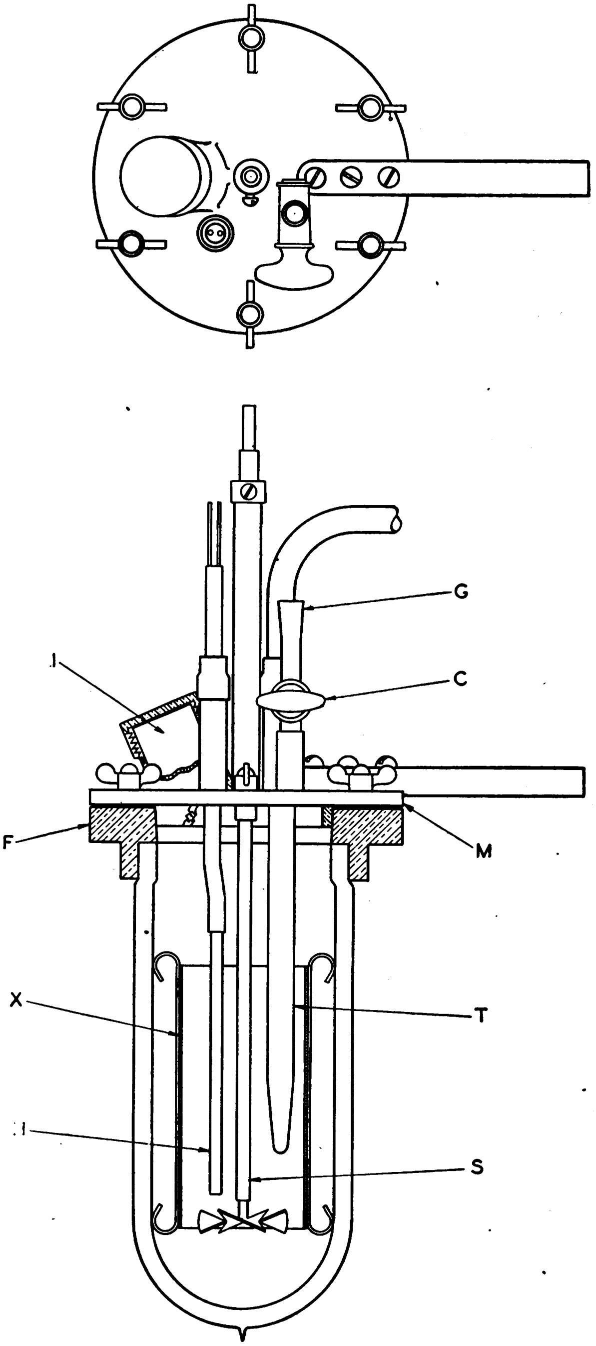

FIG. 4. Calorimeter for determination of the energy of immersion of a powder. From this the energy of adhesion can be calculated very simply.

extent to the fact that not until 1938 was there any good method for the determination of the area of a finely divided solid. This lack was serious, since the energy stored in a surface is so small that with solids a large area must be used if the energy is to be measured.

Absolute Method for the Determination of Area.—Let us undertake the development of a method which will give with certainty the area of a fine crystalline powder. In order to develop such a method it is necessary to know only a very little about the surface energy of liquids. By the measurement of the sur-

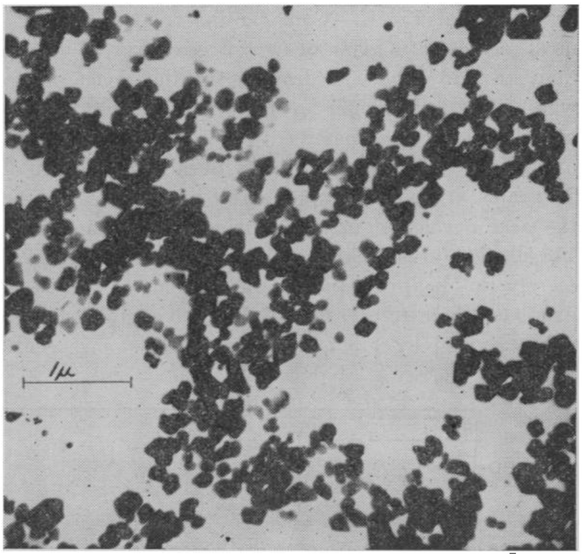

FIG. 5. Electron micrograph of finely divided crystalline titanium dioxide in the form of rutile.

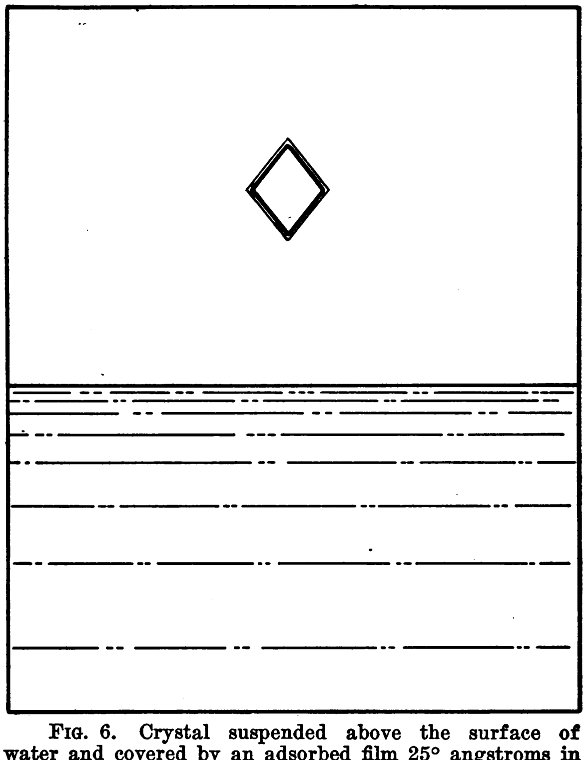

FIG. 6. Crystal suspended above the surface of water and covered by an adsorbed film 25° angstroms in thickness.

face tension of a liquid at several temperatures it is possible to obtain its total surface energy. If the liquid is water, its value is 118.5 ergs per square centimeter at 25° C. Consider the following experiment: A certain mass of water is converted into a fine mist of spherical droplets in the space above water in a calorimeter of high sensitivity (Fig. 4) and the whole calorimeter is brought to a temperature of 25° C. The water droplets of a total weight of 10 grams are now allowed to fall into the water and the heat developed in the calorimeter is found to be 118,500,000 ergs. Since what has occurred here is merely the disappearance of the surface of the water droplets, their total area is the above given energy value divided by 118.5, the energy per square centimeter, or 1,000,000 square centimeters, which, per gram of droplets, is 100,000 square centimeters or 10 square meters. The experiment cannot be carried out in just this way, because the mist cannot be sufficiently concentrated, and the water droplets fall too slowly.

Now, an actual experiment is described in which a sample of titanium dioxide in the form of fine crystals (Fig. 5) of mass 6.94 grams is suspended above the water of the calorimeter until both thermal and adsorption equilibrium is attained (Fig. 6). A film of water is adsorbed on the surface of each crystal and the outer surface of this film at equilibrium has the same surface energy as water in bulk. Again, by the choice of a sample of just this mass the heat evolved when the film-covered crystals fall into and are immersed in the water is 118,500,000 ergs and the total area is 1,000,000 square centimeters. This, divided by 6.94, gives the area of the water-coated crystals as 14.4 square meters per gram. This is the area of the water-coated crystals. By weighing the film-covered and the dry solid the mass of the film is obtained which, when divided by the area (6.94×10^4 square centimeters), gives the thickness (τ) of the film, since the density is close to unity. Making the slight correction involved, the area comes out as 13.8 square meters per gram. Presumably this is the most accurate determination ever made of the area of a finely divided solid. Under the influence of Emmett, a theory was developed (1938) by Brunauer, Emmett and Teller by means of which it is possible to calculate the number (N) of molecules necessary to complete an adsorbed monolayer on the surface of a solid. Emmett used nitrogen as the adsorbed material. His value of the area per nitrogen molecule as calculated from liquid nitrogen is 16.2 square A, which gives an area of 13.9 square meters, while his value of 13.6 square A, as calculated from solid nitrogen gives the area as 11.65 square meters. Thus, the BET method agrees with

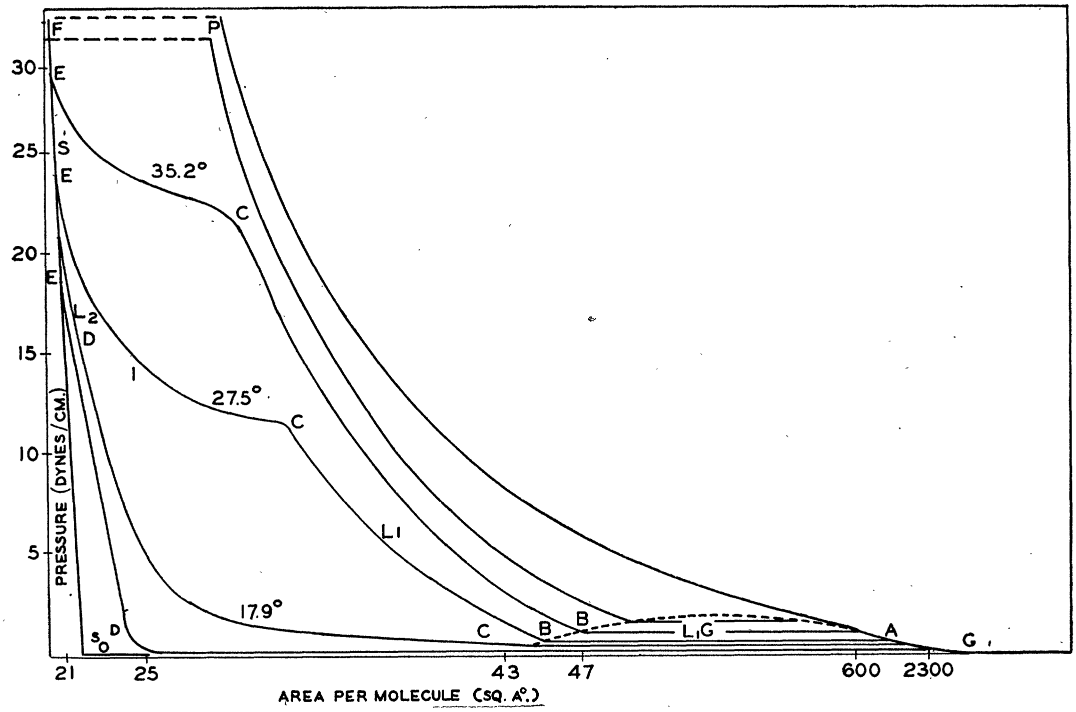

FIG. 7. Pressure-area relations of an oil film on water. The straight lines at the left represent condensed films.

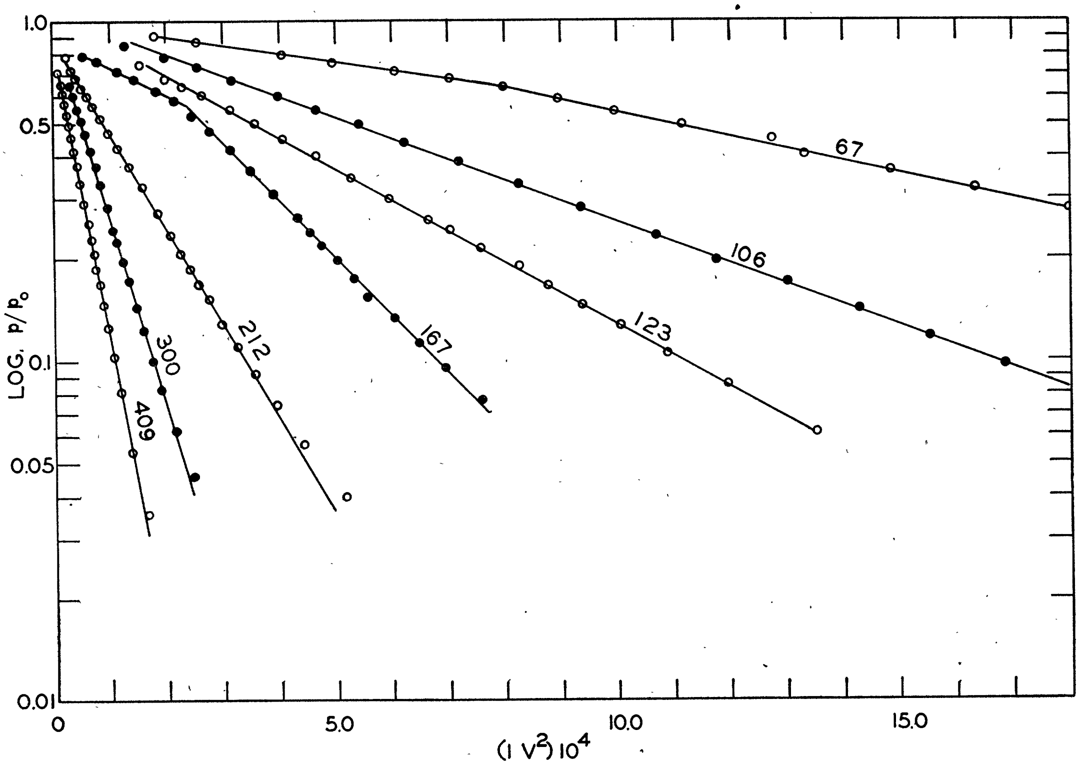

FIG. 8. Condensed films of nitrogen on the surfaces of various solids. The square root of the slope of any line when multiplied by 4.06 gives the area of the solid in square meters per gram. The figures on the straight lines give these areas for 7 solids.

our absolute method within the limits of knowledge of the area occupied per molecule on the surface.

The Relative Method. The absolute method described above is extremely simple from the standpoint of theory, but very difficult experimentally. It was developed as a standard to test other methods. A relative method, relatively easy from the experimental standpoint, has been developed. Monolayers of oil on water often exhibit at molecular areas of about 24 to 20 square A. per molecule (for a *long, single* chain alcohol, organic acid, amine, etc.) a condensed liquid phase whose pressure (π)-area (σ) relation is a straight line (Fig. 7):

$$\pi = b - a\sigma \qquad (1)$$

where *a* and *b* are constants.

Now it is desired that the area of a solid be determined from the adsorption of nitrogen or another vapor from the vapor phase. In this case π and σ cannot be obtained by direct measurement, but the pressure (p) and the volume (v) of the vapor can be measured very easily. Now, by a mere mathematical transformation equation (1) becomes:

$$\log p = B - A/v^2 \qquad (2)$$

If, now, as the pressure of the vapor is increased, the logarithm of its value is plotted on the y-axis and the reciprocal of the square of the volume (under standard conditions) of the vapor ($1/v^2$) on the x-axis (Fig. 8), then it is found that the areas of different solids vary as the square roots of the slopes

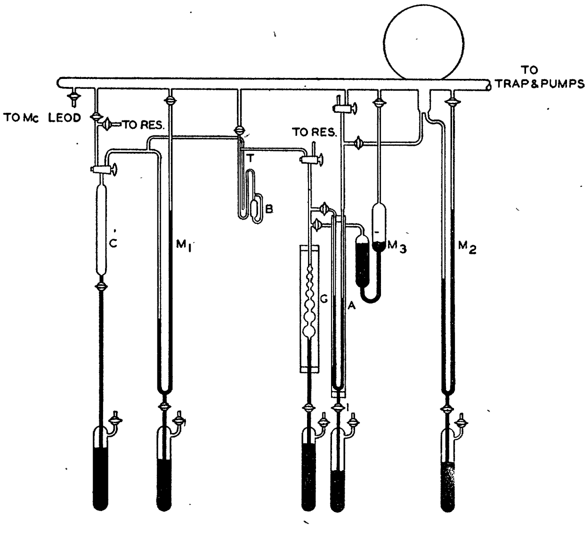

FIG. 9. Apparatus used for the determination of the area of a solid by the adsorption of a vapor.

of the straight lines, or the area is equal to a constant times the square root of the slope. Thus the area, Σ, is given by the equation

$$\Sigma = k\,A^{1/2} \qquad (3)$$

With nitrogen at $-195.8°$ C, $k = 4.06$ if the area is desired in square meters per gram. For other vapors the values are: water, 3.83 at 25° C: n-butane, 13.6 at 0°; n-heptane, 16.9 at 25° C. It is extremely simple, by the use of a solid whose area is already known, to determine the value of the constant k for any other vapor at any other temperature.

The apparatus used for the measurement of the pressures and volumes, that is, for the determination of an adsorption isotherm, is shown in Fig. 9. With this, pressures up to 100 mm of mercury can be measured to 0.002 mm, up to 400 mm, to 0.1 mm, and up to 1,000 mm to 0.5 mm.

(To be concluded)

OBITUARY

HAROLD HIBBERT

IN the passing of Harold Hibbert on May 13, the world has lost a foremost specialist in the chemistry of lignin and cellulose, a gifted and beloved teacher and a scientist of international renown. Hibbert was born in Manchester, England, on August 27, 1877. He attended Victoria University College at Manchester, graduating in 1897 with a B.Sc. degree and first class honors in chemistry. In further recognition of his marked ability, Hibbert was awarded the Levinstein Exhibition Fellowship for research in organic chemistry at Owens College of the University of Manchester under William H. Perkin, Jr., son of Sir William, the inventor of mauve. Perkin, Jr., was in his fortieth year and was attracting research students from far and near. He was the first of three great leaders in organic chemistry to exert a marked influence on Hibbert's career. His alma mater's public recognition of his talents was a great stimulus towards higher goals. Hibbert's very active career extended over a period of almost fifty years, years crowded with achievements.

Completing his studies at Owens in 1900, and receiving the degree of M.Sc., Hibbert next accepted a post as teacher in chemistry at the University of Wales. But in 1904, anxious to broaden his knowledge of organic chemistry, he left Wales and arrived at Leipzig in October, 1904, to work under Arthur Hantzsch, who had recently taken over the laboratory and classes of Johann Wislicenus. Hantzsch was a born scholar and philosopher. His lectures on organic chemistry were an inspiration. They were accompanied by numerous experiments and were unparalleled in interest and originality. What appealed to his classes and to Hibbert in particular was Hantzsch's keen sense of humor. In tackling a research problem Hantzsch preferred the physical rather than the chemical attack. Hibbert's sincere respect for his professor and Hibbert's natural charm and cordial manner brought him into intimate contact with Hantzsch and his family, a distinction which but few other students could boast of. Hantzsch was an ideal host, well versed in art, poetry and music.

Leipzig awarded Hibbert the Ph.D. degree "summa cum laude" in 1906. At Leipzig Hibbert met a small group of American chemistry students—Lind, Lamb, Bray and Fink—who urged him to visit America and to accept the post of research assistant in chemistry at Tufts College, Boston. The two years (1906–1908) under Arthur Michael at Tufts, Hibbert always regarded as his most valued and stimulating experiences. He returned to England in 1908 and researched for a little over a year at the Imperial College of Science. Hibbert then decided to go back to America and was appointed research chemist at the Wilmington laboratories of the duPont company (1910–1914). His work on the isolation of the two solid isomeric forms of nitroglycerine was one of the outstanding discoveries in the field of explosives and threw new light on the underlying causes for the instability of frozen dynamites.

In 1914 Hibbert joined the ever-growing group of skilled research chemists at the Mellon Institute in Pittsburgh and concentrated his attention on new methods for the manufacture of acetic acid and acetaldehyde from acetylene, products badly needed during World War I. His association with the Mellon Institute continued until 1919, when he was made assistant (and two years later associate) professor of chemistry at Yale University. Here he concentrated his studies on the chemistry of cellulose. He was instrumental in organizing the Cellulose Division of the American Chemical Society, with which he was intimately identified until the last.

In 1925 Hibbert accepted the crowning appointment of his career, the E. B. Eddy professorship of industrial and cellulose chemistry at McGill University, Montreal. Here he taught and inspired students from all parts of the country. Almost one hundred had the rare privilege of working in Hibbert's laboratories. Upon his retirement in 1943 a large bronze plaque was presented to him engraved with the signatures of seventy-five men and women who had received their advanced training under Hibbert.