is a project similar to those which are undertaken by the Brookings Institution, the National Industrial Conference Board, the 20th Century Fund, the Russell Sage Foundation, the Foreign Policy Association and other organizations in various fields of social and political economy. While there are foundations devoted to such thoroughly worthy objects as the promotion of good government in Philadelphia and the promotion of Henry George's writings and ideas, there is none devoted to the equally worthy studies which may be necessary to keep us from being exterminated by bombs or germs sent us from abroad, or to help us to avoid exterminating ourselves through the misuse of powers whose effects we do not yet fully understand.

It might seem that the study of the economic and social relationships of science and technology could be undertaken as a project of one of the economic research organizations or of the scientific research organizations, such as the Carnegie Institution, The Franklin Institute or the California Institute of Technology.

There is probably no basic reason why either the economic or physical science institutions should not undertake such studies. But there is the important empirical fact that a gap exists between the economists and the natural scientists in methods of thinking, approach to problems and in their contacts with each other. It might require very considerable changes in the existing research organizations to equip any one of them for studies of the place of science in our economy.

However, the gap between the natural and social scientists is narrowing. Even well before the war the Massachusetts Institute of Technology included in its curriculum studies of economics, management and industrial relationships along with the technological courses. During the war Dr. Bush and his Office of Scientific Research and Development have made great strides in bringing scientific viewpoints into the war councils not only of the military but of the civilian agencies of the government as well.

The time may be approaching when a rational and sustained attack upon the problems which science and technology have introduced into the life of the nation and of the world will not only be possible but may even seem sufficiently interesting and imposing to stimulate a major study of these things. Let us hope so, for our future security and welfare may depend upon it.

SURFACES OF SOLIDS IN SCIENCE AND INDUSTRY. II

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(*Continued from page 268*)

III. THE AREA OCCUPIED BY MOLECULES

It is now possible to calculate the area occupied by a molecule. It has been customary to measure the area (Σ) of a solid by assuming an area (σ) for the molecule and multiplying this by the number (N) of molecules in a complete monolayer. Since our new method makes it possible to obtain the area of a solid without assuming a molecular area, and the BET theory makes it possible to calculate N, the area per molecule is given by

$$\sigma = \Sigma / N$$

The extremely interesting plot (Fig. 10) results when the number (N) of solids, on which the nitrogen molecule exhibits a certain area, is plotted on the y-axis and the molecular area (σ) on the x-axis. The minimum molecular area found on 119 solids is 13.45 square A and the maximum, 17.05 square A, with peaks at 14.05, 15.25 and 16.25. Thus, the areas of nitrogen molecules vary from about that calculated from the volume relations of solid nitrogen to that obtained from liquid nitrogen.

That these areas correspond to real effects is indicated by the following interesting facts:

1. The nitrogen area on a catalyst may have *any of the above values,* but this shifts to 16.2 square A

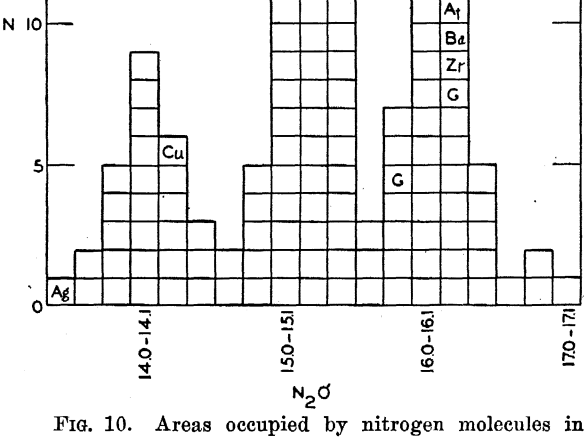

FIG. 10. Areas occupied by nitrogen molecules in complete monolayers on various solids.

after use with hydrocarbons, which results in the deposition of a solid containing both carbon and hydrogen. However, when the carbon is burned off, *the nitrogen area returns to its initial area.*

2. A silica-alumina catalyst gives a nitrogen area of 15.2 square A., if less than 8 per cent. alumina is present, but above 8 per cent, it shifts to a lower value of 14.0 square A.

3. An alumina catalyst gives an area of 15.2 square A with less than 10 per cent. of a second component, but 16.2 square A at 10 per cent. or above.

4. Heating a catalyst for a period of 8 or 10 hours may reduce its area from 400 to 200 square meters per gram without a change of the nitrogen area, but use, with heating, for a long period gives a nitrogen area of 16.2.

The molecular areas for hydrocarbons also vary with the nature of the solid: for butane (4C) the values for a small number of solids are 56.6 for crystalline and from 37 to 52 for porous solids, and for heptane (7C) from 58 to 66. In the monolayer these molecules lie flat in the surface, but in general occupy considerably more area in the complete monolayer than corresponds to the cross-section of the molecule in this position.

Catalysts. One of the more important uses of the surfaces of solids is in catalysis. Many types of more or less porous solids are employed, and the number of chemical materials produced is so large that it is not possible to list them here. They include products from petroleum such as high octane gasoline, toluene for TNT, butadiene and styrene for rubber; from the atmosphere such products as ammonia for fertilizers and explosives; food products and soaps modified by hydrogenation, etc.

In general, the rate at which catalysts act depends upon their area and the sizes and size distribution of their pores. Cracking catalysts exhibit areas as high as 70 acres per pound with pores of the order of 10 billion miles in length. Charcoals of certain types have even higher areas, which is related to their high porosity, but carbon black, which is nonporous, may have areas as high as 80 acres per pound, owing to the fact that the spherical particles have extremely small diameters.

IV. THE SURFACES OF LIQUIDS

Measurements of the surface energy of liquids are much more simple than those of solids, and in the past investigators have not made sufficient use of the surface relations of liquids in their work with solids. At 25° C the surface tension of water is 72 dynes per centimeter, so the work used in expanding the surface of a body of water by 1 square centimeter is 72 ergs (which is the free surface energy of water), while the corresponding value for normal hexane, a hydrocarbon with 6 carbon atoms per molecule, is only 18 ergs. The high value for water is due to the polar character of its molecules, because of which it acts as though it contains positive and negative electrical charges slightly separated from each other. If the hydrogen of water is replaced by a methyl group the free surface energy is only 22 ergs, not much above that of a hydrocarbon and very much below (less than a third) that of water. The explanation of this is that in the surface the molecules of alcohol orient themselves in such a way that the hydrocarbon (methyl) groups are oriented into the surface, so the surface is nearly that of a hydrocarbon.

The theory that molecules are oriented in surfaces and interfaces has had a profound effect upon the development of surface chemistry, of colloid science and upon theories of the internal structure of liquids, particularly on the structure of soap solutions, and is of fundamental importance in biology.

With oil films on water the theory is very simple. Hydrocarbon molecules lie flat on water in a layer one molecule thick (monolayer), and this is true of alcohol molecules if sufficient area is available. However, if the alcohol film is compressed by the use of barriers, the molecules stand up like soldiers on parade. Since the polar or oxygen-containing end of the molecule is highly attracted by the water, while the nonpolar hydrocarbon and is attracted very much less, the polar groups orient themselves toward the water, while the hydrocarbon groups orient themselves toward the gaseous phase, or toward an adjacent oil phase, as at a water-hexane interface. For those who are interested in the technical aspects of the problem it may be said that "hydrogen bonds" are formed between the polar groups and the water molecules.

Oil films on water may be polymolecular in thickness (even 1 or 2 mm in thickness), but such a film is unstable and changes finally into a monolayer and lenses of oil.

V. POLAR AND NON-POLAR SOLIDS AND MOLECULAR ATTRACTION

Solids may be classified as:

1. Polar solids, with a strong attraction for water and for polar groups. These include quartz, glass, titanium dioxide, barium oxide, etc.

2. Nonpolar solids, with a small attraction for water—paraffin, graphite, carbon black, antimony trisulfide, etc.

Fig. 11 exhibits two types of molecular orientation on the surfaces of solids. The energy required to pull (energy of adhesion) water away from either of the polar solids, titanium dioxide (anatase) or quartz, is about 680 ergs, if an area of 1 square centimeter is considered, while the corresponding figure for the hydrocarbon, iso-octane, is only 155 ergs, or less than a fourth as much. The above indicated values give the total amount of energy necessary to pull the liquid from the surface of the solid. The work required (work of adhesion, w_A) is much less, and in the same units is 340 for water and 90 for the hydrocarbon (normal heptane was used).

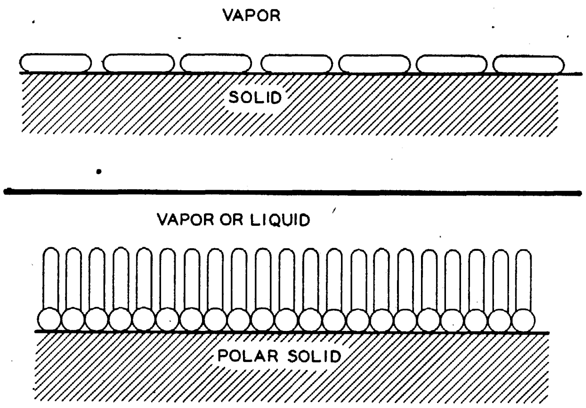

FIG. 11. Orientation of molecules in complete monolayers on the surface of a solid: *above*, hydrocarbon molecules; *below*, molecules of the type of those of an alcohol, an organic acid, a soap, etc., on the surface of a polar solid.

With a change to a relatively nonpolar solid, graphite, these values are modified: downward with water, upward with a hydrocarbon. With water the energy of adhesion is decreased from the 680 for the two polar solids to 295, while with heptane it is increased from 155 to 245. The work of adhesion is reduced from 340 to 96, while with heptane it is increased from 90 to 109.

Laminated glass. As an illustration of the use of polar groups in industry the manufacture of laminated glass may be cited. In 1929 this was a sandwich which consisted of a sheet of transparent nitrocellulose known as celluloid 0.020 inch thick between two sheets of ⅛ inch glass. Unfortunately, celluloid in the presence of sunlight, especially when water is present, is unstable and liberates oxides of nitrogen which give a yellow, brown or even red color to the lamination and causes the glass to fall apart. The celluloid was made to adhere to the glass by the use of an adhesive which consisted of gelatine dissolved in water or in glycol.

The writer suggested that cellulose acetate, which is much more stable to light than celluloid is, should be substituted for it, but it was known that ordinary adhesives did not give a good "bond" between the glass and the plastic. At that time the energy relations between organic molecules and polar solids, as given in the preceding section, were unknown, but the writer knew that glass surfaces act much like those of water, though with a much higher surface energy, and so suggested that cellulose acetate could be made to adhere well to glass by introducing into it the proper polar groups to increase the adhesion. If introduced into the whole sheet, these would change the properties of the cellulose acetate in an undesirable way. However, by making an adhesive from cellulose acetate which had been treated to give the proper polar groups, an adhesive was produced which gave an excellent bond.

Between 1932 and 1940 over two-thirds of the laminated glass used in the United States was made in this way. This illustrates the value of a scientific principle in industry, since those who employed empirical research methods were not able for years to make a really good bond between this plastic and the glass. In conclusion, it may be stated that the plastic used at present contains enough polar groups of the right kind to make a good laminated glass without the use of an adhesive.

VI. THE DISTANCE TO WHICH THE ATTRACTIVE ENERGY OF A SOLID EXTENDS INTO A LIQUID OR A FILM

One of the fundamental previously unsolved problems of physics is the distance to which molecular attraction extends. A related problem is the thickness of adsorbed films. According to one school of thought, these are never more than one molecule thick, while another believes them to attain a polymolecular thickness. This problem has been settled both by weighing the films and by determining the number of molecules adsorbed per square centimeter.

Of the 16,450 calories of energy necessary to desorb one mole of water (6.06×10^{23} molecules) from the first molecular layer on the surface of anatase (quartz and similar solids exhibit almost the same value) 9,900 (E_L) would have been used if the molecules had been separated from water, so the excess is 6,550 calories. For the second layer this excess is 1,380 and for the third 220 calories. While the effect of

TABLE 1

MOLAR ENERGY OF DESORPTION OF MOLECULAR LAYERS OF WATER FROM THE SURFACE OF TITANIUM DIOXIDE (ANATASE) MINUS THE ENERGY OF VAPORIZATION OF WATER ($E_n - E_L$)
(Calories per mole)

Layer	Heat of Desorption	$E_n - E_L$
1	16,450	6,550
2	11,280	1,380
3	10,120	220
4	9,971	71
5	9,951	51
6	9,932	32

the attraction of the solid dies off rapidly, it extends to somewhat more than 5 molecular layers.

Table 1 indicates that it requires 6,550 calories more to vaporize a mole of water from the first monolayer of water on the surface of anatase than from water itself. For the second layer the excess is 1,380 calories and for the third, 220 calories, and none of these is negligible.

A nitrogen film attains a thickness at −195.6° C. of 10 molecular layers, or 36 A, butane 64 A, and heptane from 50 to over 100 A, depending upon the subphase.

Thus, experiment decides in favor of the polymolecular nature of adsorbed films, and, contrary to the views of a certain group of scientists, in a film or liquid on a solid the attractive interaction extends much farther than to the adjacent molecules. However, it does not agree with the views of those who believe the film to be very thick.

VII. PHASES AND PHASE CHANGES IN ADSORBED FILMS ON SOLIDS

Five phases have been discovered in films on solids. These seem to be: (1) gas, (2) expanded, (3) intermediate, (4) condensed, (5) second condensed. These designations are those used for films on liquids.

Solid films on water melt without the adsorption of heat. Thus, there is no latent heat of fusion. Such changes are considered to be of the second order, and phase changes of the second order are much more common in films on either solids and water than first order changes, which exhibit a latent heat. Certain oil films on water which are in the liquid state vaporize without the absorption of any heat (second order), while others involve a heat of vaporization (first order). In three dimensions isothermal vaporization is always accompanied by the absorption of heat, and, contrary to the opinion of experts on adsorption that such first order changes do not occur in films on solids, we have recently discovered such changes, both on metals and non-metals.

On account of the great importance of surface films on solids in both industry and agriculture, the subject discussed in this lecture should advance rapidly, since some of the fundamental relations have now been developed.

OBITUARY

GEORGE ARGALE HARROP, JR.

Eheu fugaces, Postume, Postume

THE years slip away and our friends are lost to us, but they will live forever in our hearts and memories.

Born in Peru, Illinois, in 1890, George Argale Harrop enjoyed a world-wide reputation as a scientific investigator, particularly in metabolism and nutrition. In such work lay his greatest delight and happiness, and the achievements in the brief span allotted to him were so great that little need be said here.

He had a very large circle of friends and acquaintances throughout the scientific world. This was due not only to his repute but also to the extent of his wanderjahra. Following two years in the University of Wisconsin he went to Harvard and received an A.B. in 1912. Going thence to the Johns Hopkins University to study medicine, he obtained his M.D. in 1916 and became in succession interne, resident and instructor in medicine. One of the happiest years of his life followed when he went to Europe and studied in Copenhagen under Professor Krogh. His admiration for his teacher was very great, and he was delighted when Professor Krogh came to the United States in 1938 to take part in the dedication of the Squibb Institute. On his return to this country, he spent two years at Columbia University and then went to China as associate professor of medicine in the Peking Union Medical College.

While in China, in 1924, he married Esther Caldwell. To one who knew Dr. Harrop in later life there was no more outstanding characteristic than his deep affection for his wife and for the four children—three boys and a girl.

Returning to the United States in 1924, Dr. Harrop was appointed associate professor of medicine at Johns Hopkins. Here he carried on his studies on nutrition and metabolism and took a leading part in the work of the department of medicine, where one of his greatest pleasures was his contacts with the internes and students.

He made two trips to South America. One of these in 1921–22 was a purely scientific expedition with the Royal Society to Peru and the high Andes, and the other was in 1939 when he paid a visit to all the medical centers in Mexico and South America. These trips added to the evergrowing circle of scientific friends. They left him with a deep interest in the countries he had visited and he would frequently recall, with enthusiasm, his experiences.

During his eight years in New Brunswick many of his old friends—from Europe, from Asia, from Mexico, from South America and from the United States—visited him there or at his home in Princeton to his delight. Old friendships were renewed, old scientific discussions reopened and the new work and surroundings critically examined.

After the founding of the Squibb Institute for