

CHEMISTRY

# Chemical Surface Phenomena

## "A Classic of Science"

### Langmuir, Nobel Prizeman, Shows That Adsorption Results From Chemical Forces Similar to Those Between Atoms

*THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. Part 1. Solids. By Irving Langmuir. In Journal of the American Chemical Society, Vol. 38, Nov. 1916. Part II. Liquids. Vol. 39, Sept. 1917. THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM. Vol. 40, Sept. 1918.*

THE WORK of the Braggs on crystal structure is reviewed from the viewpoint of the chemist and the relation of this work to theories of chemical constitution such as those of Werner, Stark, J. J. Thomson, and Lewis, is discussed in detail.

It is concluded that the substances whose structures have thus far been studied by the X-ray spectograph are not representative of compounds in general. Only polar compounds have been studied.

Solid polar compounds are, in general, built up of atoms bound together by secondary or residual valence. The whole crystal must be regarded as a single molecule.

Solid nonpolar compounds consist in general of "Group Molecules" in which the atoms are usually held together by primary valence. These group molecules in turn are bound together by secondary valence to form a large "Crystal Molecule," which includes the whole solid mass.

There is no present justification for dividing interatomic (or intermolecular) forces into *physical* and *chemical* forces. It is much more profitable to consider all such forces as strictly chemical in nature. Evaporation, condensation, solution, crystallization, adsorption, surface tension, etc., should all be regarded as typical chemical phenomena. The object of this paper is largely to show that *chemical knowledge already avail-*

Dr. Langmuir's three papers form so connected a whole that we have reprinted here the author's summaries rather than select a portion from any one of them alone. All those interested in surface phenomena, catalysis, or "colloid" reactions of any sort should read the three papers in their entirety, in the files of the J. A. C. S.

able is directly applicable to the study of these phenomena.

From a consideration of such properties as specific heat, compressibility, coefficient of expansion, etc., it is concluded that collisions do not take place between the atoms of solids, but that these move about equilibrium positions under the influence of both attractive and repulsive forces.

The "time of relaxation" of the atoms of solids is calculated approximately from the heat conductivity and is found to be of the order of  $10^{-14}$  to  $10^{-7}$  seconds. An independent method by which the "time of relaxation" can be calculated from the rate of evaporation of a substance in vacuum, gives substantially similar results. Thus the time necessary for an atom of a solid to reach thermal equilibrium with its neighbors is very small compared to the time necessary to make a single oscillation about an equilibrium position. The "oscillations" are thus extremely strongly damped.

Since solid substances in general are held together by secondary rather than primary valence, there are few limitations to the number of compounds that can exist in the solid state. Most of these compounds do not show a composition which could be predicted from the ordinary rules of valence. Metallic compounds, minerals, solid solutions and glasses are discussed from this point of view.

By considerations based largely on the compressibility, it is concluded that the attractive forces between atoms usually reach a maximum intensity when the distance between adjacent atoms in solids is increased by about  $0.6 \times 10^{-8}$  cm. (10-30% of the normal distance between atoms).

Since energy must be expended in breaking apart a solid, the surfaces of solids must contain more potential energy than do the corresponding number of atoms in the interior. Since this potential energy is probably electromagnetic energy in the field between atoms,

the interatomic forces are more intense on the surface than in the interior. This intense surface field of force (unsaturated chemical affinity) is one of the causes of the phenomena of condensation and adsorption.

Because of the small time of relaxation and because an atom approaching the surface is attracted by many, but later is repelled by few atoms, it follows that the surfaces of solids are almost wholly inelastic in regard to collisions of molecules impinging on the surface. There is also a great deal of experimental evidence of this inelasticity. As a result, nearly every molecule or atom striking a solid surface condenses no matter what the temperature may be. While condensed it is held to the surface by forces quite similar to those holding solids together (either primary or secondary valence). At high temperatures evaporation may take place almost immediately after condensation, but at lower temperatures, the condensed atom or molecule may remain indefinitely.

The phenomena of condensation and evaporation (sublimation) of solids is discussed at some length. In general, the rate of evaporation ( $m$ ) of a substance in a high vacuum is related to the pressure ( $p$ ) of the saturated vapor by the equation

$$m = \sqrt{\frac{M}{2\pi RTp}}$$

Red phosphorus and some other substances probably form exceptions to this rule.

The mechanism of the dissociation of a solid, such as  $\text{CaCO}_3$  is discussed. It is shown that when, according to the phase

### A Famous Patent

of an almost-human machine which is largely responsible for our great daily papers, our flood of modern literature, and for the expression, "etaoin shrdlu,"

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rule, separate phases of constant composition are present, the reaction must take place exclusively at the boundaries of these phases. This kinetic interpretation of the phase rule indicates clearly the distinction between reactions in which solid solutions are formed and those in which separate phases appear. This theory offers a ready explanation for the fact that hydrated crystals frequently fail to effloresce unless scratched and for the fact that thoroughly dehydrated substances often absorb moisture with great difficulty.

Adsorption is a direct consequence of the time lag between the condensation and the subsequent evaporation of molecules. The adsorbed substance may be held to the surface either by secondary or primary valence. In either case it is profitable to regard the phenomena as chemical in nature. A large number of experimental results are given which prove conclusively that adsorption is very frequently the result of the strongest kind of chemical union (primary valence) between the atoms of the adsorbed substance and the atoms of the solid.

It is shown that the action of a typical catalytic poison depends on the formation of a very stable film one atom deep over the surface of the catalyzer. The chemical activity of any solid surface depends upon the nature of, the arrangement of, and the spacing of the atoms forming the surface layer. There is a very close relation between the chemical activity of a surface and the electron emission from it (either thermionic or photoelectric emission).

A brief quantitative development of

this theory of heterogeneous reactions is given. A "law of surface action" analogous to but different from, the "law of mass action" is proposed. This theory is in accord with and affords an explanation of Reichstein's "Constant Sum Hypothesis". An outline is given of the application of this theory to heterogeneous gas reactions and to enzyme action.

The second part of this paper will deal with the Structure of Liquids with particular reference to surface tension phenomena. It will be shown that the surface tension of organic liquids is a characteristic chemical phenomena. It depends particularly upon the shapes of the group molecules and upon the relative intensities of the chemical activity of different portions of the molecules. A method will be described (together with experimental data) by which the cross sections, lengths and other dimensions of group molecules may be determined.

#### Mechanism of Adsorption

According to the theory previously developed, gaseous molecules impinging on a solid or liquid surface do not in general rebound elastically from the surface, but condense on it, and are held or adsorbed on the surface by forces similar to those holding the atoms or group molecules of solid bodies. If these forces are weak the "life" of the adsorbed molecules on the surface is short, so that the number of molecules adsorbed at any time is relatively small. On the other hand, when the forces are strong the rate of evaporation of the molecules may be so slow that the surface becomes practically completely covered by a monomolecular layer of adsorbed molecules. In the present paper this theory is extended and is developed along quantitative lines.

The theory requires that in typical cases of true adsorption the adsorbed film should not exceed one molecule in thickness. This is contrary to the usual viewpoint. The discrepancy is accounted for by the fact that nearly all investigators have worked with porous bodies in which the adsorbing surface is indeterminate or have used nearly saturated vapors so that condensation of liquid occurred in capillary spaces. Others have mistaken solution or absorption for true adsorption.

The mechanism of adsorption is discussed at some length. The forces causing adsorption are typically chemical and exhibit all the great differences in intensity and quality characteristic of chemical forces. The adsorptior of so-

called permanent gases by solids usually involves only secondary valence forces. A great many cases of adsorption, particularly by metals, are caused by primary valence forces. Under certain conditions stoichiometric relations should govern the amounts of gas adsorbed on saturated surfaces. These relationships may fail to hold because of steric hindrance effects between the adsorbed molecules.

Equations are developed which give the relation between the amount of adsorbed gas and the pressure and other variables under various assumed conditions. No single equation other than purely thermodynamic ones should be expected to cover all cases of adsorption any more than a single equation should represent equilibrium pressures for all chemical reactions.

Experiments were undertaken to measure the adsorption of several common gases by plane surfaces of mica, glass, and platinum. By using pressures of 100 bars (approximately 0.1 mm. of mercury) or less, small quantities of gas were more easily measured and the danger of condensation of liquefied gas in capillary spaces was avoided.

At room temperature the adsorption by mica and glass was negligible, certainly not over one per cent. of the surface being covered by a single layer of molecules. At  $-183^{\circ}$  and at  $-118^{\circ}$  C., relatively large amounts of gas were adsorbed, except in case of hydrogen. At the higher pressures used, the surfaces tended to become saturated with gas. The maximum quantities adsorbed even with saturated surfaces were always somewhat less than the amounts to be expected in a monomolecular layer. . . . The amounts of the different gases adsorbed by saturated surfaces of mica and glass were always in the following order: hydrogen, oxygen, argon, nitrogen, carbon monoxide, methane, and carbon dioxide.

The amounts of these gases adsorbed by mica and glass varied with the pressure in accordance with Equation 9, which was deduced for the case of simple adsorption. The adsorption of these gases was easily and quickly reversible.

The phenomena observed with platinum were quite different. No adsorption of gases could be observed even at  $-183^{\circ}$ , until the platinum had been "activated" by heating to  $300^{\circ}$  in a mixture of hydrogen and oxygen at low pressure. After this activation, hydrogen and oxygen or carbon monoxide and oxygen reacted together readily at room temperature in contact with the platinum. The platinum was then found

▼ The Science Service radio address next week will be on the subject,

**R** URANIUM AS THE EARTH'S CLOCK

by

**A** Dr. Alois Kovarik

**D** Professor of physics at Yale University and member of the National Research Council's Committee on Measurement of Geological Time.

**I** FRIDAY, DEC. 2

**O** at 12:45 P. M., Eastern Standard Time

Over Stations of

**▲** The Columbia Broadcasting System

capable of adsorbing oxygen, carbon monoxide or hydrogen. The maximum quantities of oxygen and carbon monoxide corresponded to monomolecular layers. The oxygen could not be driven off either by heat or by pumping. When the platinum was in contact with an excess of oxygen the amount of oxygen adsorbed increased as the temperature was raised, but the action was irreversible. Adsorbed carbon monoxide could not be removed by pumping at room temperature, but at 300° part of it could be pumped off. When oxygen was brought in contact with carbon monoxide adsorbed on the platinum it reacted rapidly to form carbon dioxide,

which at room temperature showed no tendency to be adsorbed on the platinum. In a similar way carbon monoxide brought into contact with adsorbed oxygen reacted immediately. These cases of adsorption are clearly due to chemical forces of the primary valence type.

Further work needs to be done to determine the cause of the activation of the platinum.

In conclusion, the writer wishes to express his appreciation of the valuable assistance of Mr. S. P. Sweetser, who carried out the experimental part of this investigation.

*Science News Letter, November 26, 1932*

## ASTRONOMY

## Earth Apparently Missed Main Leonid Meteor Swarm

**F**EARS of astronomers that the expected display of Leonid meteors might again fail to appear as it did in 1899 have been justified.

From the Flower Observatory of the University of Pennsylvania, of which he is director, Dr. Charles P. Olivier, president of the Meteor Commission of the International Astronomical Union, observed these shooting stars at the rate of thirteen per hour, during the early morning hours of Wednesday, Nov. 16. Correcting for the proximity of the bright moon, this would mean that about thirty might have been seen every hour after midnight had the sky been dark. This is far inferior to the display of last year, which it was hoped might be the forerunner of a brilliant shower this month, possibly rivalling that of 1866.

### One Was Persistent

The midwestern display of Leonid meteors was disappointing, Prof. James Van Allen of Iowa Wesleyan College at Mt. Pleasant, Iowa, reported. Bright moonlight hampered observations. Relatively few meteors were seen; one, however, left a trace that lasted fifteen seconds. The largest single count, by an observer facing the radiant or center of meteor flight, was 46 during the period from 2:30 to 5:00 A. M.

In the Southwest, observing conditions were also unsatisfactory, Prof. C. C. Wylie of the University of Iowa reported. Prof. Wylie had led an expedition to the neighborhood of Flagstaff, Ariz.

Heavy clouds blanketed the sky, rendering the astronomers' vigil almost useless for scientific purposes. However, many spectacular meteors seen through the clouds verified the prediction that the shower would start at that time.

It seems probable that the damage done to the meteor swarm by Jupiter before 1899, in pulling aside the center part so much that it missed the earth, though the beginning and end reached us in 1898 and 1901, has not yet been repaired. It had been thought that Jupiter might since have pulled the swarm into line again.

Thus it seems likely that 1933 may also be deficient in meteors of the Leonid swarm, but that in 1934 we may have one like last year's. Or we may have a shower like that of 1901, when the meteors fell at the rate of more than a hundred an hour.

But Dr. Olivier again emphasized the uncertainty of predicting meteors' behavior, since we only see them in their dying moments, and unlike other astronomical bodies cannot observe them over a large part of their orbits.

*Science News Letter, November 26, 1932*

In Massachusetts, where vaccination against smallpox is compulsory, there were 408 cases of smallpox from 1919 to 1928; in Arizona, Utah, Minnesota, and North Dakota, which have a total population about equal to Massachusetts, there is no compulsory vaccination and there were 46,130 cases of smallpox in the same period.

## PHYSIOLOGY

## Yellow Dextrin Found Harmful To Mice

**A** PARTIALLY digested food may be more harmful than a non-digested one, it appears from recent experiments by Prof. Lillias D. Francis and Dorothy F. Johnson of Wellesley College, Wellesley, Mass.

Dr. Francis and Miss Johnson found that the use of yellow dextrin, an intermediate product in the digestion of starch, in the dietaries of her mice was followed by severe diarrhea, loss of weight, and finally death. If, however, the dextrin was replaced by starch, the more complex carbohydrate from which the dextrin may be derived, the mice did not develop any abnormal symptoms and thrived. Not only that but if, after the animal was suffering with all of the typical symptoms of this "dextrin poisoning," starch was substituted for dextrin in the diet of the animal, it was cured. A return to the dextrin-containing diet at any time was always accompanied by a return of the diarrhea.

The degree of the "toxicity" of the dextrin seemed to be dependent upon the amount of it used; thus, if 38 per cent. dextrin was used as the source of carbohydrate in an otherwise adequate diet the mice suffered for five to eight days and then recovered. If 52 per cent. dextrin was used the animals suffered a great deal more and if 70 per cent. was used they lived only a few days. All control animals on similar diets but with corn starch instead of dextrin were quite normal. About 68 animals of three different ages have been tested so far.

The cause of the death, according to Dr. Francis, is not known. She has found that the caecums of the affected animals are distended by gas to almost 300 per cent. of their normal size and she has suggested that there is a possibility that a changed bacterial flora in the intestine may have been induced by the imposed dietary regime.

"It is also very interesting that young mice are more susceptible to the deleterious and lethal effects of dietary dextrin than are adult animals," says Dr. Francis. "We are investigating the condition and hope to be able to offer an explanation for it in the near future. It is particularly interesting that this seems to be the only evidence of dextrin's having such a harmful effect."

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