

the side tube and the atoms combined to form molecules on the surfaces of the metallic wires which acted as catalysts.

Shortly after this correspondence it occurred to the writer that it should be possible to obtain even higher concentrations of atomic hydrogen by passing powerful electric arcs between tungsten electrodes in hydrogen at atmospheric pressure. The high heat conductivity of the gas due to the energy liberated by the recombination of the rapidly diffusing atoms should prove of particular value in the construction of electric furnaces, and for melting metals in general. Experiments of this kind were soon made. Twenty ampere arcs from a constant current transformer were passed between two tungsten rods 6 mm. in diameter mounted transversely in an alundum tube (10 cm. diam.) through which a stream of hydrogen flowed and burned at the open end.

Arcs up to 2. cm. in length were obtained with voltages ranging from 300–800. The arc, of a beautiful red color, was of small diameter (about 3 mm.) and was bowed out into a fan shape by its own magnetic field.

Iron rods 2 or 3 mm. in diameter melted within a couple of seconds when they were held 3–5 cm. above the arc. By directing a jet of hydrogen from a small tube into the arc, the atomic hydrogen could be blown out of the arc and formed an intensely hot flame of atomic hydrogen burning to the molecular form and liberating 90,000 calories per gram molecule—about 50 per cent. more than that in an oxy-hydrogen flame. To maintain these conditions the electrodes had to be brought closer together (preferably 1–3 mm.).

In this flame, even at distances of 1 or 2 cm. from the arc, it was found that molybdenum melted with ease, and tungsten rods of 3 mm. diameter could be melted when held very close to the arc itself. Quartz, on the other hand, melted with more difficulty than molybdenum, indicating that the catalytic action of the metals played an important part in the rapidity with which they could be heated.

The use of hydrogen under these conditions for melting metals has proved to have many advantages. Iron can be welded or melted without contamination by carbon, oxygen or nitrogen. Because of the powerful reducing action of the atomic hydrogen, alloys containing chromium, aluminum, silicon or manganese can be welded without fluxes without surface oxidation. The rapidity with which such metals as iron can be melted seems to exceed that in the oxy-acetylene flame, so that the process promises to be particularly valuable for welding.

The technical development of these welding processes using flames of atomic hydrogen has been the

work of several men, among whom Robert Palmer and R. A. Weinman must be particularly mentioned. Papers describing the apparatus used and the results obtained will soon be published by Mr. Weinman and the writer in the *General Electric Review*.

Mr. P. Alexander, following out a line of development suggested by Professor Elihu Thomson, has independently arrived at an arc welding process utilizing hydrogen for the purpose of improving the ductility of the weld and the speed of operation. In this process the arc is passed between an iron electrode and the material to be welded. This process also depends at least in part on the use of the high heat conductivity of atomic hydrogen.

Some joint work of Mr. Alexander and the writer has shown that particular advantages are obtained in some cases by using mixtures of nitrogen and hydrogen, and that the quality of the weld is not impaired by nitrogen unless oxygen is also present. A paper by Mr. Alexander describing his process will appear simultaneously with those dealing with the atomic flame process.

IRVING LANGMUIR

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
SCHENECTADY, N. Y.
OCTOBER 27, 1925

THE BINDING OF ACID AND ALKALI BY PROTEINS

WE have recently published¹ an extensive study of acid and alkali binding by proteins with especial reference to the mechanism involved in such binding and the relations which may exist between the chemical composition of the protein and the amount of acid or alkali which it binds at certain definite hydrogen-ion concentrations.

Inasmuch as the cited publication may not be generally available to persons interested in this subject, we have felt that it might be advantageous to briefly state certain of the conclusions which we arrived at in the course of our study.

The study included the isolation, purification and chemical analysis of a series of fourteen proteins. Twelve of these were isolated from the cereal grains and belong to the class of prolamines, the alcohol-soluble proteins of cereals. These proteins were isolated from the seeds of *Triticum vulgare*, *Triticum*

¹ Walter F. Hoffman and Ross Aiken Gortner, "Physico-chemical studies on proteins I. The prolamines—their chemical composition in relation to acid and alkali binding," Colloid Symposium Monograph, Vol. 2, pp. 209–368, 110 tables, 20 figs., 1925. The Chemical Catalog Company, New York City.

spelta, *Triticum monococcum*, *Triticum dicoccum*, *Triticum durum*, *Secale cereale*, *Avena sativa*, *Zea mays*, *Hordeum vulgare*, *Sorghum vulgare*, *Andropogon sorghum*, and *Euchlaena mexicana* Schrad. The remaining two proteins, casein from cow's milk and fibrin from blood, were included in the series for the purpose of enabling us to compare the behavior of the prolamines with proteins of a radically different type.

The chemical analyses which were carried out included an elementary analysis of such proteins as had not previously been isolated, the nitrogen distribution in the proteins as measured by Van Slyke's method, the true amide nitrogen values, the free amino groups in the native proteins, the free carboxyl groups in the native proteins and the cystine and tryptophane content.

The analyses showed that we had selected a series of proteins which varied sufficiently among themselves to serve to demonstrate as to whether or not the chemical composition of the protein controlled the binding of acid and alkali as Loeb² contends or whether acid and alkali binding are colloidal phenomena and are largely independent of the nature of the individual amino acids in the protein molecule, as has been the contention of certain other investigators.

The analyses showed that the amide nitrogen of this series of proteins ranged from 6.93 per cent. of the total nitrogen to 25.34 per cent., the arginine nitrogen from 3.90 to 14.16 per cent., the histidine nitrogen from 1.19 to 10.36 per cent., the lysine nitrogen from 0.42 to 14.06 per cent., the total basic nitrogen from 8.24 to 33.41 per cent., the free amino nitrogen in the native protein from 1.02 to 8.95 per cent., the cystine content from 0.27 to 3.72 per cent. and the tryptophane content from none to 4.40 per cent.

The acid and alkali binding was studied, making use almost exclusively of the modern potentiometric methods for studying changes in hydrogen-ion concentration. In connection with the preliminary work using these methods, we discovered that the degree of ionization of an acid or base, or in more modern parlance, the activity of an acid or a base, had a different value when measured by potentiometric methods than when the measurements are made by the use of electrical conductivity apparatus. Inasmuch as the standard tables indicating the extent of dissociation of acids and bases at various dilutions have been calculated from conductivity data, it fol-

lows that such tables can not be utilized to calculate hydrogen-ion concentrations which are later to be compared with values of hydrogen-ion concentrations determined by the potentiometric methods. The inaccuracy of such comparisons had not previously been recognized by workers in this field, and as a result appreciable errors were introduced into their experimental findings, and they were caused to draw erroneous conclusions. The paper of Lloyd and Mays³ may be cited as a typical example.

As a result of the foregoing observation, we have not only revised the methods of experimental procedure for measuring alkali and acid binding, but we have altered the formula which has previously been used to calculate the amount of acid or alkali which was bound. We believe that our methods of measurement and of calculating the results yield as accurate data as the present state of physico-chemical knowledge permits. There is always the possibility of postulating the rôle which the "protein ions" may play in influencing the hydrogen-ion concentration of the equilibrium mixture. Certain workers insist on introducing such calculations into their formula, basing the justification for such a procedure upon theoretical or hypothetical grounds, and admitting at the same time that we have no means at the present available of proving whether or not the "protein ions" do in reality influence the "activity" of the hydrogen ions in the equilibrium mixture. Inasmuch as no exact data are available, we have preferred to believe that "protein ions," if they are present as such in the equilibrium mixture, do not influence the activity of the hydrochloric acid in the equilibrium mixture, and have made all our calculations on this assumption. The experimental readings are presented in detail in the publication referred to, and any one is at liberty to recalculate them in whatever manner he may see fit. We wish to point out, however, that we are fully aware of the possibility of calculating our data by other methods, but that we believe such calculations would introduce as many, if not more, hypothetical and possibly erroneous assumptions than the method which we have selected. The reader of this note must be referred to the original publication for a complete description of our methods and the 110 tables of experimental data and calculations.

The experimental data, interpreted on the basis of the assumptions which we have felt justified in making, indicate very clearly the following conclusions.

Approximately equivalent amounts of hydrochloric, sulfuric and phosphoric (molar) acid were bound by

² Loeb, J., "Proteins and the Theory of Colloidal Behavior," McGraw Hill Book Company, New York, 1922. See also SCIENCE 52: 449-56, 1920.

³ Lloyd, D. J., and Mays, C., *Proc. Roy. Soc.* 93 B, 69-85, 1922.

a unit amount of protein, when the acids are compared on the normality basis. Equal amounts were not bound at the same equilibrium hydrogen-ion concentration as is claimed by Loeb, much more phosphoric acid than hydrochloric acid being bound.

A marked negative temperature coefficient was obtained when the experiments on the binding of hydrochloric acid and sodium hydroxide were carried out at 15°, 25° and 35° C. and when the final hydrogen-ion concentration was more than pH 2.5 and the hydroxyl-ion concentration was more than pH 10.5. The ratio was approximately 1:2:3 where the amount bound at 35° is 1. When the logarithms of the equivalents of acid or alkali bound at the different temperatures were plotted against the logarithms of the equivalents of acid or alkali added, the lines for a single protein passed through common points. For acid this point represented a hydrogen-ion concentration of about pH 2.5 and for alkali, a hydroxyl-ion concentration of about pH 10.5.

Experiments were carried out where more dilute acid and alkali were used, in an attempt to determine the behavior of acid and alkali binding between the hydrogen-ion concentrations represented by pH 2.5 and pH 10.5. Here the amount of acid or alkali bound apparently depends on the chemical composition of the protein. The buffer curve does not form a smooth line. When the logarithms of the equivalents of acid or alkali bound in this pH region are plotted against the final pH, the curves do not form a straight line. It is suggested that there are two types of combinations between proteins and acid or alkali: (1) chemical type of combination which takes place when the hydrogen-ion concentration is between pH 2.5 and pH 10.5 and (2) an adsorption type of combination which takes place when the hydrogen-ion concentration is greater than pH 2.5 or the hydroxyl-ion concentration is greater than pH 10.5.

Evidence of a chemical type of combination⁴ between a hydrogen-ion concentration of pH 2.5 and pH 10.5 is presented by:

- (1) The logarithms of the amount of acid or alkali

⁴ Certain workers, of whom Loeb was the outstanding exponent, prefer to call such compounds formed between proteins and hydrochloric acid "protein-chlorides," and between proteins and sodium hydroxides "sodium proteinates." Such terminology may correctly indicate the nature of the compounds formed. Proof to that effect, however, is not at present forthcoming and accordingly we have purposely avoided such terminology, preferring to state that a "chemical type of combination" takes place and not making any assumptions at present as to the nature of the compounds formed.

bound plotted against the original concentrations do not form a straight line.

- (2) The buffer curves do not form a smooth, regular line.

- (3) The amount of acid or alkali bound at any hydrogen-ion concentration between pH 2.5 and pH 10.5, depends on the chemical composition of the protein. This is not true where the pH is less than 2.5 or greater than 10.5.

Evidence of the adsorption type of combination is furnished by:

- (1) At the higher concentrations of acid and alkali, all the proteins used in this work, *regardless of their chemical composition*, bind approximately the same amount of acid or of alkali.

- (2) There is a marked negative temperature coefficient of the acid or alkali binding at the higher concentrations of acid and alkali.

- (3) The logarithms of the amount of acid or alkali bound plotted against the logarithms of the original acid or alkali concentration or against the final pH form a straight line.

- (4) There is more alkali bound when the original concentration is 0.500 normal than can be accounted for by chemical combination assuming that there is an available carboxyl group for each nitrogen atom, an assumption far in excess of possibility.

The analytical data in regard to the amino acid content of prolamines are not sufficiently accurate to enable final conclusions to be drawn as to the chemical groups responsible for the chemical binding of alkali. In the case of acid binding, however, a correlation of $r = 0.9923 \pm 0.00275$ was found between the free amino nitrogen of the protein as determined in the Van Slyke apparatus and the equivalents of acid bound at pH 2.8, and a correlation of 0.9918 ± 0.00312 was obtained between the sum of the free amino nitrogen plus one fourth of the arginine nitrogen (the free amino group of the guanidine nucleus) and the equivalents of acid bound at pH 2.5. As already noted, the character of acid binding changes at pH 2.5.

If the isoelectric points are calculated by extrapolating the logarithmic curves of the second type, the acid and alkali curves intersect in the neighborhood of pH 7, the neutral point as referred to water. This is the case when the isoelectric point was calculated from, (1) the logarithms of the amount of acid or alkali bound by the proteins and the logarithms of the original concentration of acid or alkali, (2) the logarithms of the amount of acid or alkali bound and the equilibrium pH and (3) the logarithms of the amounts of acid or alkali added, and the equilibrium pH. The isoelectric point of the protein, *i.e.*, the hydrogen-ion concentration of the protein sus-

pended in water, determined potentiometrically, does not in a number of instances agree with these extrapolated values but is found to be in the neighborhood of the values reported in the literature as determined directly by cataphoresis or other methods. The measured isoelectric "point" of a protein probably is not a definite point but should in all probability be referred to as an "isoelectric range." *The position of this isoelectric range on the pH scale is dependent on the chemical composition of the protein.* The calculated isoelectric point is very near the hydrogen-ion concentration of neutral water. This is what would be predicted on the theory that at the higher concentrations of acid and alkali the binding of acid and alkali follows the adsorption law. *The calculated isoelectric points are not related to the chemical composition of the proteins.*

From these findings we conclude that the chemical nature of a protein and the power of a protein to bind acid and alkali in stoichiometrical relationships depends upon the chemical groups within the protein molecule and is therefore limited to the range between pH 2.5 and pH 10.5. Thus our findings afford a logical explanation for the divergent views of Loeb *et al.* and other workers who hold that acid and alkali binding are of a stoichiometrical chemical nature and those workers who insist that colloidal adsorption is the predominating factor. *Both are correct*, and we have shown in what regions (in terms of hydrogen-ion concentration) one or the other phenomenon may be expected to predominate.

ROSS AIKEN GORTNER
WALTER F. HOFFMAN

DIVISION OF AGRICULTURAL BIOCHEMISTRY,
UNIVERSITY OF MINNESOTA

**AMERICAN ASSOCIATION FOR THE
ADVANCEMENT OF SCIENCE
ANNUAL REPORT OF THE PERMANENT
SECRETARY FOR THE FISCAL
YEAR 1924-25¹**

THE permanent secretary reports as follows concerning the work of the association during the year 1924-25 and plans for the year 1925-26.

PUBLICATIONS

A special issue of *SCIENCE* (February 6, 1925) was arranged to present the general reports of the fifth Washington meeting. Special reports of associated societies were presented in subsequent issues of

¹ Presented to the Executive Committee on October 25, 1925.

SCIENCE. The issue of February 6 was sent to all members, including those who receive *The Scientific Monthly*. The usual booklet on the organization and work of the Association was revised and was again used in the circularization of new members of the affiliated societies. About 7,000 circular letters inviting such persons to join the Association were sent out October 1, 1925. About 4,000 more letters are to be sent out. The official statement of the Association on the status of the Evolution Theory was printed as a leaflet for use at the time of the Scopes trial and later. Additional copies of this leaflet are available if needed. The new volume of summarized proceedings is nearly off the press. Its publication is expected within the next few weeks. The work of proof-reading has been in the hands of Dr. Sam F. Trelease, of Columbia University. In the preparation of the manuscripts the permanent secretary has been greatly assisted by the Washington staff. One new feature of the volume is an annotated list of all the organizations that are associated with the Association, each name being followed by a brief statement concerning the organization, secured from its secretary. With the help of the editor of *SCIENCE* plans have been made by which the preliminary announcement of the Kansas City meeting is to appear in *SCIENCE* for Friday, November 27, 1925. This issue is to be sent to those who receive *The Scientific Monthly* as well as to the regular subscription list of *SCIENCE*. It is hoped that this arrangement will prove to be an improvement. A considerable expense will be thereby avoided.

DIVISION AND ACADEMY RELATIONS

The arrangements with the two divisions have been continued as heretofore. The new arrangement with affiliated academies is going into effect smoothly. Division allowances amounted to \$1,746 for the fiscal year 1924-25. The allowances to the affiliated academies and the local branch amounted to \$1,540; this item will probably be only about half as large for next year, under the new arrangement.

MEETINGS

The fifth Washington meeting was by far the largest in the history of the Association and it was successful in many ways. Full reports concerning it have been published. There were two summer meetings of the Association in 1925, one held jointly with the Southwestern Division (at Boulder, Colo., June 8-11) and the other held jointly with the Pacific Division (at Portland, Ore., June 17-20). The two summer meetings cost the association the sum of \$782.42,