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THE QUANTITATIVE STUDY OF ORGANIC REACTIONS[1]

BEFORE this body of chemists it is not necessary to call attention to the importance of many of the great researches in the field of so-called pure organic chemistry. The investigations of Liebig and Woehler and Fischer on uric acid derivatives, of Friedel and Kraft and others on the use of aluminium chloride, ferric chloride and zinc chloride in effecting many condensations; of Sandmeyer and Gatterman, Hantzsch, and Bamberger on the formation of diazo compounds and their derivatives; of Baeyer, Greene, Nietzki, Fischer and others on the formation of dyes; of Willstaetter, Pictet, Koenigs, and Pschorr on the alkaloids; of Wallach, Tiemann, Semmler and Harries on the terpenes; of Fischer, Kiliani, Tollens, Bruyn, Wohl and Ruff on the sugars, and of Fischer, Abderhalden, Neuberg, Curtius, Kossel, Osborne and Chittenden on the proteid compounds—all of these great researches speak for themselves in their importance to pure science, technology, medicine and the biological branches.

However much the physical chemist may turn up his nose, or hold it, in the organic laboratory and call us *pot-boilers* and *stink-producers* and *mere compound-makers;* however much the clean-working analytical or inorganic chemist may rail at us because we do not, as a rule, collect and weigh our organic precipitates accurately to within 0.10 per cent., yet these same deluded col-

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[1] Address of the chairman of the Division of Organic Chemistry in Section C of the American Association for the Advancement of Science, Baltimore, 1908.

leagues seize eagerly upon our organic solvents for use in their inaccurate methods for the determination of molecular weights, and upon our organic indicators to aid them in poor analyses. They clamor for, and would die without, our medicines, such as whiskey (*imitation* or any kind), atropine, quinine and ether, our cane sugar and glucose and our artificial breakfast foods; and their dainty daughters could not so entrancingly lure sweethearts without our beautiful dyes in their silks and cheeks, our delightful synthetic violet perfume in their handkerchiefs and our artificial pineapple, strawberry and vanilla in their dangerous embryonic pastries and ices. This same compound-making, this so-called *old style* organic chemistry, with its reactions and methods, is not only of the very greatest importance to science and economy, but is becoming more so every day.

But we have another side to organic chemistry, which appeals to the physical and inorganic chemists, and so much so, indeed, that they try to appropriate it in their text-books as part of their own domain: namely, the quantitative study of organic reactions. In pointing out the problems that busy our organic chemists, perhaps I can not do better than to bring to your attention some of the researches that have been, or are being, completed and still other problems whose solution is of the greatest importance to the chemical world.

The question of fundamental importance in any reaction, and the one that must be answered first, is: *What are the constituents that are really uniting or reacting to give the end products?* When this is known *we must then determine quantitatively the natural constants which govern the concentrations of the reacting constituents at any time and their velocity of transformation and final equilibrium.* These constants are just as characteristic as are the melting points and molecular weights for each set of substances under definite conditions, that is, in definite concentrations, in definite solvents, at definite temperatures and exposed to definite wavelengths of light of given intensity, etc.

The question as to what are the really active constituents of a given reacting mixture, whether it be one of organic or inorganic substances, is not always easily answered. Do the molecules which we put together unite or do their simple or complex ions enter into combination? Some of our prominent physical chemists tell us "that most chemical reactions, if not all, are reactions between ions; molecules, as such, do not enter into the reaction at all." On the other hand, other prominent physical chemists go perhaps too far in the other direction: they elect their colleagues with brotherly love to life membership and exalted rank in their own Ananias Club and declare that "whoever claims that the instantaneous chemical changes in aqueous, or other, conducting solutions take place because of the fact that these solutions are electrolytes (or in current phraseology, because they contain ions), must assume the burden of proving his proposition," a statement to which we must all agree. Both of these factions of physical chemists, I believe, fail to weigh judicially all of the experimental evidence at hand. The champions of the union of ions as the cause of chemical reactions argued from such facts as the failure of dry hydrochloric acid and dry ammonia to form ammonium chloride. We can challenge them to prove beyond question (1) that the molecules do not react in the presence of moisture, (2) that the gases were perfectly dry, (3) that the gases did not actually slowly unite. They could answer that no *apparent* union took place in a great length of time: but we could recall to them that neither do dry hydrogen and oxygen *apparently* unite at ordinary temperatures, even in the presence of platinum. Yet Bodenstein has proved that they *do* unite appreciably at temperatures above 500° C. in the presence of platinum, and he has calculated that if the observed temperature coefficients hold it would require the volumes of hydrogen and oxygen with which he worked *several hundred years to form a small fraction of a milligram of water at ordinary temperatures.* We sincerely hope that our ardent admirers of ions will start these experiments for their posterity to finish as a monument to them. On the other hand, the defender of the divine right of molecules to enter into instantaneous chemical reactions ignored the small minority of the ions present with the large number of molecules in such mixtures as hydrochloric acid and copper oleate in benzene solution. It does not follow that because such solutions hardly conduct the electric current there may not be present, in practically instantaneous equilibrium with the molecules, *minimal amounts of ions which react with each other with enormously high velocities.*

This point is perhaps best illustrated by the beautiful work of Whitney, Melcher, Kuester, Bodlaender and others, on solutions of the complex cyanides and ammonium compounds of copper, cadmium and silver, in which only minimal traces of the silver, copper and cadmium ions exist. A normal solution of $KAg(CN)_2$ contains so few silver ions that the dissociation constant,

$$K = \frac{Ag(CN)_2}{Ag \times (CN)^2},$$

has the enormously high value 10^{23}, which expresses in liters the volume of water which flows over the Niagara Falls in *500,000,000 years!* Yet the silver can be electrolyzed out of this same solution in a very short time. The dissociation constant of the complex cadmium cyanide ion,

$$K = \frac{Cd(CN)_4}{Cd \times (CN)^4},$$

is 10^{17} and that of hydrogen sulphide,

$$\frac{H_2S}{H \times SH} = K,$$

is 1.75×10^7, and yet in a mixture of solutions of these two substances the cadmium sulphide is precipitated almost instantaneously. Indeed it seems possible that ions with the mass which we are accustomed to ascribe to them must be so far apart in such solutions that they can not possibly migrate rapidly enough to allow all of them to come together in such a short time, and it may be that further investigation will show that these complex cyanides and ammonium compounds react in some cases through their complex ions or molecules. Kahlenberg has done great service to physical chemistry by insisting that some reactions may be those of molecules. It is quite evident then that in such inorganic reactions, which usually take place with very high velocities, it is sometimes very difficult to decide whether the constituents directly concerned are molecules or ions.

But organic chemistry offers us a rich field in which all kinds of reactions can be found. Most of these take place comparatively slowly and can be studied easily, and the values of the various constants can be determined accurately. In some reactions we have already shown that both ions and molecules undergo transformation. Of course many organic reactions do not lend themselves to quantitative work, on account of complex or disturbing side reactions which can not be followed accurately, or on account of the difficulty of finding a good analytical method for determining the concentration of each constituent at any moment. But it is certain that we could not have had the best development of the law of mass-action, of reactions of the first and second order, of the development of temperature coefficients, of Thomson's study of energy changes in combustion, etc., without the quantitative study of such organic reactions as the inversion of cane sugar, hydrolysis of methyl acetate, etc.

It will, perhaps, not be uninteresting to discuss some of the problems that are at present occupying the attention of organic chemists. The phenomena exhibited by the so-called *tautomeric compounds* are of great importance in a large number of substances, such as quinazolines, cyanides, sulphites, cyanates, amides, acetoacetic ester, pyrazolones, uric-acid derivatives, pyrimidines, all kinds of dyestuffs, such as the rosanilines, phenolphthaleins, fluoresceins, etc. In 1899 we had several theories of the action of tautomeric compounds with other substances like alkyl halides and acid chlorides. Those of Nef, Michael, Wheeler, Comstock, Knorr and Wislicenus deserve special mention.

Comstock assumed that the potassium salt of an amide, for example, and an alkyl halide yield only one ester, the N-ester, because the potassium salt is the N-K salt (see the graphic scheme below!) and that the silver salt is an O-Ag salt and yields the O-ester. Wheeler assumed that all salts of amides are O-salts and that these salts yield the O-ester primarily, which then rearranges *per se,* or is transformed catalytically by the alkyl halides into the N-ester. Nef and Michael assumed that all salts are O-salts and that the O-ester is formed by a direct replacement of the metal, while the N-ester is formed by the primary addition of the alkyl halide to the N, or to the double bond between the N and the C. Wislicenus and Knorr believed that isomeric esters are formed by the action of alkyl halides on such so-called tautomeric salts because there are present in the molecule or ion of the salt oscillating free bonds or valences which can bind the entering alkyl group at different positions. This point of view has been used brilliantly in recent years by Lapworth.

All of these theories had much to recommend them, and each one harmonized with most of the qualitative facts known at that time. Another point of view, however, seemed to the speaker more plausible, namely, that in some cases isomeric stable esters are formed by the action of the alkylating agent on two or more tautomeric salts in equilibrium, in other cases the esters undergo rearrangement, and in other cases the anions (perhaps the molecules, too) add the alkyl halide at two different places.

Now obviously a large amount of quantitative work was an absolute necessity if we were to decide which of the above several theories is right. It was seen, too, that the chemists who undertook to solve the problem would have to work for *years* on the quantitative side before they could tell their colleagues the mechanism of these tautomeric reactions.

It may be stated that quantitative work in this particular field is very expensive, difficult and tedious, many operations being necessary to give us one set of data. If we had not been assisted so generously by the Carnegie Institution of Washington we should have made very, very slow progress. The investigations of the speaker and of Messrs. Laist, Willcox and McRae, of the University of Utah, and of Drs. Brunel, Johnson, Rogers, Shadinger and Nirdlinger, of this laboratory, during the past nine years, on the urazoles has at last brought us to the conclusion that our theory of tautomeric salts is at present the best working hypothesis for the explanation and further study of such reactions. This theory has been stated[2] as follows:

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[2] For references see *Berichte der deutschen chemischen Gesellschaft,* **41**, 3199.

The weakly acid tautomeric amides, acetoacetic ester, etc., react, as a rule, only very slowly with alkyl halides, acid chlorides, etc., at ordinary temperatures, because these weak acids furnish few *anions* of the tautomeric forms to react with the alkyl halides. The addition of bases such as pyridine, alkalies or other metallic hydroxides, or sodium ethylate, causes an *increase* in the reaction velocity, or a *catalysis,* because the base forms, to a greater or lesser extent depending upon the strength of the acid or base, tautomeric salts of the amide, acetoacetic ester, etc. These salts, because they are more highly ionized than the acid, furnish the solution with a greater concentration of the *anions* of the two or more tautomeric forms, and hence the reaction velocity is increased. This acceleration is exactly analogous to the catalysis of amides, oximes, esters and cane sugar by acids in water, in which, according to the theory developed by Kastle, Bredig, Lapworth, Acree, Goldschmidt, Stieglitz and Euler, the *cations* of these substances are hydrolyzed. The free bases (amides, oximes, etc.) are so weak that they furnish only a few *cations* ($CH_3CO\overset{+}{N}H_3+\overset{-}{O}H$, etc.). But when acids are added these weak bases unite with them and form salts to a greater or less extent. These salts are highly ionized and hence furnish the solution with a much greater concentration of *cations,* and the reaction is accelerated merely on account of this greater concentration of *cations.*

This theory has enabled us to predict mathematically and prove experimentally the following propositions:

1. The old equations used by Ostwald and modified by Hantzsch and Stieglitz, to express the dissociation constants of such tautomeric acids and salts, especially in the phenolphthalein series, were wrong because these workers embodied in them only the ionization of one of the tautomeric forms; our point of view led us to equations for these dissociation constants which are acknowledged by the other workers to be correct and which have been tested experimentally by our own work and that of Wegscheider.

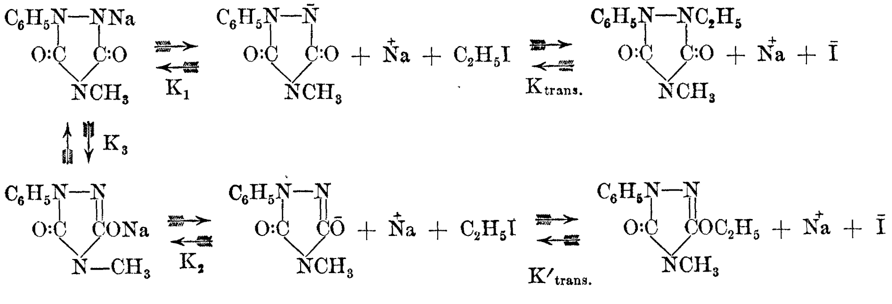
2. Our point of view on tautomeric compounds led us to a correct interpretation of the phenomena of abnormal hydrolysis which we have tested experimentally by reaction velocity methods.

3. The alkyl halide reacts with the anions and not appreciably with the molecular form of the salt.

4. The equilibrium is between the molecular forms of the salts and not between the anions as assumed by Knorr, Lapworth, Nef, Wislicenus and others. In this case, then, we have a reaction of molecules, and not of anions.

5. Our theory enabled us to predict and verify quantitatively, experimentally, the following important facts in the formation of isomeric esters from various salts of urazoles and different alkyl halides:

(*a*) Different salts and the same alkyl



halide give different ratios of N-ester to O-ester and react with different velocities because the various salts have different values for K_1, K_2 and K_3.

(*b*) The value of K_3 is not changed appreciably by a change in temperature and therefore the ratio of N-ester to O-ester is not changed. But the values of K_1 and K_2, on the one hand, and of $K_{\text{trans.}}$ and $K'_{\text{trans.}}$, on the other hand, are altered practically alike and hence the velocities of formation of both N-ester and O-ester have about the same temperature coefficients as other similar reactions.

(*c*) A change in solvent may cause a change in K_1, K_2 and K_3, and hence cause a change in the ratio of N-ester to O-ester.

(*d*) The same salt and different alkyl halides yield different ratios of esters, because $K_{\text{trans.}}$ and $K'_{\text{trans.}}$ differ for the different alkyl halides (see *g*).

(*e*) A change in the concentration of the salt and the alkyl halide does not appreciably change the ratio of the N-ester to the O-ester because there is no appreciable change in the ratio of the ions from the two salts.

(*f*) The addition of another salt with the same cation produces no appreciable change in the ratio of the N-ester to the O-ester obtained from a given salt and an alkyl halide, because the degrees of ionization of both tautomeric salts are suppressed practically alike.

(*g*) The alkyl halide reacts with the anion; but the alkyl halide does not seem to react appreciably through (1) primary dissociation into alkyl and halide ions, as was assumed by Bruyn and Steger, nor (2) through the union of the alkyl halide with the cation and the formation of a complex cation which then reacts with the anion, as was assumed by Euler, nor (3) through a preliminary dissociation into a halogen hydride and an unsaturated alkylene or alkylidene residue, as was assumed by Nef. But mathematical reasoning alone led us to the conclusion that the alkyl halide may unite to a small extent with the urazole anion and form a complex anion which then yields the ester and the halide ion. A fundamental part of this problem is: (1) to determine experimentally the relation of the amount of the free energy of the different isomeric alkyl halides to their equilibrium constants when they change into each other; (2) to connect this with the constants expressing the formation of the complex anions by the union of each alkyl halide with the urazole anion, and the velocity of transformation of the complex anions; and (3) to harmonize this with the amount of free energy, and equilibrium constants, of the corresponding isomeric urazole esters which rearrange into each other. In general, whenever an alkyl halide (*n*-propyl bromide, *n*-butyl bromide, isobutyl bromide) changes reversibly nearly completely into another one (isopropyl bromide, secondary butyl bromide, tertiary butyl bromide, respectively), as Aronstein and Gustavson have found, then the former alkyl halide reacts far more rapidly with the urazole salts than does the alkyl halide which is formed by such a reversible rearrangement. We shall study this particular problem by the use of thermodynamics.

$$\overset{-}{\mathrm{An}}+\overset{+}{\mathrm{K}}+C_2H_5I \rightleftarrows \overset{-}{\mathrm{An}}\cdot C_2H_5I+\overset{+}{\mathrm{K}} \rightleftarrows \mathrm{An}C_2H_5+\overset{-}{\mathrm{I}}+\overset{+}{\mathrm{K}}.$$

This complex anion theory has now been accepted by others and has been put on a firm basis by the isolation of several double compounds, such as $AgNO_3\cdot ICH_2CN$, which seem to have all the properties demanded by the theory.

Another problem of interest to us is the study of the action of acids, or alkalies, and water on amides, hydrazides, semicarbazides, oximes, esters, etc. According to our theory the hydrolysis of these substances should be analogous to the catalysis produced by alkalies on the reaction between alkyl halides and acids. According to this theory only the cations formed by the union of the H ion with the amide, oxime, hydrazide, etc., should be *appreciably* hydrolyzed.

$$CH_3CONH_2+\overset{+}{H}+\overset{-}{Cl}+H_2O \rightleftarrows CH_3CO\overset{+}{N}H_3+\overset{-}{Cl}+H_2O \rightleftarrows CH_3COOH+\overset{+}{N}H_4+\overset{-}{Cl}.$$

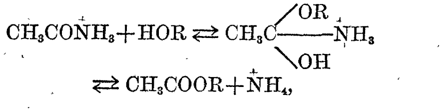
This has been amply verified in this laboratory by Mr. Nirdlinger, and here we have a reaction of ions. We are studying, too, the *reverse* reactions: viz., the *formation* of amides, hydrazides, etc., by the action of ammonia, amines and hydrazines on the organic acids, esters or acid chlorides, with and without catalyzers, in different solvents, etc. We shall study especially the velocity of the reaction and the equilibrium in the gaseous phase.

In the case of the oxime, in which we have a reversible change as follows:

$$(CH_3)_2CO+\overset{+}{N}H_3OH \rightleftarrows (CH_3)_2C{=}\overset{+}{N}HOH \rightleftarrows (CH_3)_2C{=}NOH+\overset{+}{H},$$

Dr. Johnson and Mr. Desha have discovered the first reversible reaction in which the so-called third law of catalysis fails to hold, in which the equilibrium point is changed by a change in the concentration of the catalyzer.

This theory of acid-catalysis allows us to predict that such cations will be found to react with alcohol, phenols, amines, hydrazines, etc. Dr. E. E. Reid has been able to show by the necessary quantitative measurements that the amides react with alcohols in the presence of acids and form quantitative yields of esters,



$$CH_3CO\overset{+}{N}H_3+HOR \rightleftarrows CH_3C\begin{cases}OR\\ \overset{+}{N}H_3\\ OH\end{cases} \rightleftarrows CH_3COOR+\overset{+}{N}H_4,$$

and that excellent yields of esters may be obtained also from anilides and hydrazides under the same conditions. This suggests that the ordinary Fischer esterification method for the isolation of amino acids in the form of their esters from casein, horn, hair, polypeptides, etc., might be effectively modified in some cases by boiling the substance in alcoholic hydrochloric acid instead of in aqueous solutions. The ester would then be formed directly instead of through the present indirect destructive methods.

$$\begin{array}{r|r|r|l} NH_2CH_2CO & NHCH_2CO & NHCH_2CO & NH_2 \\ RO & H \qquad RO & H \qquad RO & H \end{array}$$

The chief disadvantage would be the insolubility of the proteid in the alcohol, but we find that our difficultly soluble compounds seem to work well.

Two other reactions, worked out by Dr. J. M. Johnson in our laboratory, are recalled, the simplest explanation of which is that *non-ionized salts* are transformed into other products. Acetyl chloraminobenzene and hydrochloric acid react with a velocity proportional to the concentration of the undissociated salt present, or to the *square* of the concentration of the hydrogen ions. Two other explanations of this reaction are to be considered, but as they are at present very improbable, they will be discussed in a later communication.

$$CH_3CONClC_6H_5+\overset{+}{H}+\overset{-}{Cl} \rightleftarrows CH_3CONHCl_2C_6H_5 \rightarrow CH_3CONHC_6H_4Cl+\overset{+}{H}+\overset{-}{Cl}.$$

The other reaction is one in which imido-esters of various types yield alkyl halides when heated with halogen hydrides. In this case, too, an undissociated salt seems to be decomposed.

$$ROCH_3+\overset{+}{H}+\overset{-}{Cl} \rightleftarrows R\overset{+}{O}CH_3\cdot HCl \rightarrow ROH+CH_3Cl.$$

This work disproves the validity of the so-called second law of catalysis, which postulated that there must be direct proportionality between the reaction velocity and the concentration of the hydrogen ions in acid catalysis.

Professor Bredig, who, with his students, has made the chief contributions to the theoretical and experimental development of the idea that the catalyzer forms an intermediate compound, has written me that he too has recently discovered some reactions in which the non-ionized salt seems to be transformed into other substances.

We see, then, that the question whether the *anion* or *cation* (simple or complex) or the *molecular form* of a given acid, base, salt or other neutral substance, is the *chief* constituent transformed directly into the end products depends entirely upon the relative magnitudes of the various constants, and therefore varies widely in the different problems.

Occupying our attention in this connection is another phase of this work which should certainly be a great help to us in the solution of such problems. There is no method to-day for determining the concentrations of the constituents of such a reacting system as a mixture of acetamide, hydrochloric acid and water, in which

$$\mathrm{CH_3CONH_2}+\overset{+}{\mathrm{H}}+\overset{-}{\mathrm{Cl}}+\mathrm{CH_3CO}\overset{+}{\mathrm{N}}\mathrm{H_3}+\overset{-}{\mathrm{Cl}}+$$
$$\mathrm{CH_3CONH_3Cl}+\mathrm{H_2O}\rightleftarrows\mathrm{CH_3COOH}+\overset{+}{\mathrm{N}}\mathrm{H_4}+\overset{-}{\mathrm{Cl}},\ \text{etc.},$$

the salt undergoing transformation is very greatly hydrolyzed. The decrease in conductivity produced by adding acetamide to hydrochloric acid does not give us sufficient *knowns* to solve for the *unknowns* in the above equation. If some method were devised for determining the concentration of the hydrogen ions *nearly instantaneously*, then these problems could be solved. A colorimetric method involving the use of indicators seems to be out of the question with such concentrated solutions, but it may, in certain cases, work well in dilute solutions. But the use of the hydrogen electrode for the determination of the changing hydrogen ion concentration at any moment would seem to be very effective in those cases in which no disturbing side reactions take place, and this problem is engaging Mr. Desha's attention. Such a method, if successful, would be of great help in the study of a large number of reactions in acid, alkaline and other solutions.

Finally, organic chemistry is to-day a ripe field for the study of energy changes in reacting systems, as has been emphasized especially by Michael. The total energy of a system can in some cases be measured by studying the rate of formation or absorption of heat during the reaction in an adiabatic system. This has been done very satisfactorily by Bredig and Epstein in the decomposition of hydrogen peroxide by potassium iodide. Especially important is the study of free energy by the use of equilibrium and electrometric methods. A large number of organic reactions can be very easily arranged to take place in concentration cells in such a manner that the electromotive force can be readily and accurately measured. In order to study such cases completely the mechanism of the reaction must be known, and the values of all the constants, especially the equilibrium constant, must be determined accurately.

We are further using electrometric methods in the study of the question whether in the presence of platinum, iridium, etc., such substances as methane, ethylene, trimethylene, etc., can be made to dissociate as follows in substitution and addition reactions:

$$\mathrm{CH_2{=}CH_2}+2\oplus\rightarrow\overset{+}{\mathrm{C}}\mathrm{H_2}\text{—}\overset{+}{\mathrm{C}}\mathrm{H_2}+2\overset{-}{\mathrm{B}}\mathrm{r}\rightarrow\mathrm{C_2H_4Br_2},$$
$$\mathrm{CH_2{=}CH_2}+2\ominus\rightarrow\overset{-}{\mathrm{C}}\mathrm{H_2}\text{—}\overset{-}{\mathrm{C}}\mathrm{H_2}+2\overset{+}{\mathrm{H}}\rightarrow\mathrm{C_2H_6},$$
$$\mathrm{CH_4}+2\oplus\rightarrow\overset{+}{\mathrm{C}}\mathrm{H_3}+\overset{+}{\mathrm{H}}+2\overset{-}{\mathrm{B}}\mathrm{r}\rightarrow\mathrm{CH_3Br}+\mathrm{HBr},$$
$$\mathrm{CH_4}\rightarrow\overset{-}{\mathrm{C}}\mathrm{H_3}+\overset{+}{\mathrm{H}}.$$

We see, then, that organic chemistry presents a large number of interesting problems that can and must be studied quantitatively. The solution of these problems will be not only of the greatest importance to abstract science and to industry, but will take first rank in giving an insight into the fundamental processes in plant and animal life, which involve both chemical and physical phenomena in homogeneous and heterogeneous systems.

These problems will, in my opinion and that of some of my physical chemical colleagues, be solved most easily by organic chemists, and not by physical chemists. The worker who would do great service to this branch of the science must have *as the great essential* such a broad and deep knowledge of organic chemistry that he can recognize wrong interpretations of reaction mechanisms almost by *intuition:* he must not make wrong postulations regarding reactions as Ostwald did in the *theory of indicators* and in the *catalysis of amides,* and as Euler did in the *saponification of esters,* mistakes which were corrected by *organic chemists.* Then he must turn to his physical chemistry and learn *three things well*—the mass law, thermodynamics and electrochemistry; even then he must constantly advise with some well-trained *real* physical chemist, and with some mathematician, who can to some extent understand the problems.

No man can do *trustworthy* work in physico-organic chemistry with half-way preparation, but the chemist who is well equipped will render great service to the science.

S. F. ACREE
JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.,
December 30, 1908

BACTERIOLOGY AS A NON-TECHNICAL COURSE FOR PUBLIC SCHOOLS[1]

BACTERIOLOGY, a biological science as distinct from a useful art, has hardly received any material recognition as yet in this country. The writer would advocate the academic study of certain of its phases as illustrating the general bases of life, as a mental training, and as furnishing a field for thought.

Again realizing that sociology, in ultimate analysis, is strictly dependent upon and limited by biological laws, sociological teaching which neglects the biology and physiology of the individual neglects the study of its primal units. Hence the value of, even necessity for, the elementary biological training of the prospective sociologist. But sociology is more than the study of certain units in multiple. It is the study of the interrelations of these units. Therefore, the study of the anatomy and physiology of a single example of man (or for convenience and by analogy of the frog or the plant) furnishes no actual laboratory biological study analogous to the study of the interrelations of man in the world. Bacteriology supplies this missing link, for bacteriology deals hardly at all with the individual—almost wholly with aggregations of individuals. Symbiosis, antagonism—the effect of overcrowding, the survival of the fittest—coordination of partial efforts of different cooperating species to produce a sum total result—all these phases of sociology, chosen from many more for this address at random, can be illustrated in a bacteriological course—and with materials directly under control, subject to experimental variation and, from the rapidity of bacterial development, without waste of time.

Finally, beyond these purely scholastic views lies a practical value of bacteriology as a general study, especially for women, in that it furnishes an armamentarium in dealing with certain every-day problems of household life which come into play during at least one half of the conscious waking life of man and almost the whole of the conscious waking life of the alma mater of the family—the housekeeper and actual food provider, as the wife and mother must always be in nine tenths of the population. The writer will discuss the third of these phases, *i. e.,* bacteriology for its

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[1] Presented at the Baltimore meeting of the Society of American Bacteriologists, December 31, 1908.