functions are expanded into power series in x by the multinomial theorem, by Maclaurin's series, or by La Grange's series. If, in these power series, x is made unity, the resulting series, if convergent, determine the roots of the given equation. The convergency conditions determine in advance in which two terms of the given equation the factor x is to be omitted.

It is shown that all roots of the given equation can be determined by means of infinite series, derived by that method.

The Completion of the Lunar Theory and the Tables of the Moon's Motions to be made therefrom: ERNEST W. BROWN, of Yale University. (Read by title.)

Problems of Three Bodies on Surfaces: EDGAR ODELL LOVETT, of Princeton University. (Read by title.)

Other papers of a general nature read at this meeting were the following:

The Law of Oresme, Copernicus and Gresham: THOMAS WILLING BALCH, of Philadelphia.

The Dramatic Function of Cassandre in the Oresteia of Æschylus: WILLIAM A. LAMBERTON, of the University of Pennsylvania.

Goethe's Private Library as an Index of his Literary Interests: WATERMAN T. HEWETT, of Cornell University, Ithaca, N. Y.

Art and Ethnology: EDWIN SWIFT BALCH, of Philadelphia.

A Vedic Concordance: Professor MAURICE BLOOMFIELD, of Johns Hopkins University.

On the Lost Tribes of Israel and the Aryan Ancestry of Jesus and His First Disciples: PAUL HAUPT, of Johns Hopkins University.

The Sign and Name for Planet in Babylonian: MORRIS JASTROW, JR., of the University of Pennsylvania.

Medieval German Sculpture in the Germanic Museum of Harvard University: KUNO FRANCKE, of Harvard University.

Notes on Greek Vases in the Museum of Science and Art of the University of Pennsylvania: PROFESSOR WILLIAM N. BATES, of the University of Pennsylvania.

The balloting for new members took place on Saturday morning, April 25, and those were elected whose names were printed in the last issue of SCIENCE.

The meeting concluded with a dinner at the Bellevue-Stratford, at which Vice-president William B. Scott, of Princeton, presided, and toasts were responded to by His Excellency, Mr. Wu Ting-fang, Dr. Horace Howard Furness, Professor William Gilson Farlow, Dr. Harvey W. Wiley and Hon. Hampton L. Carson.


THE APPLICATIONS OF PHYSICAL CHEMISTRY TO ORGANIC CHEMISTRY [1]

To do justice to the subject, the "Applications of Physical Chemistry to Organic Chemistry," one would have to touch on all the chapters of organic chemistry: there is no branch of it that can not be put into more precise and therefore clearer terms with the aid of physico-chemical ideas. In the time at our disposal to-day it will be necessary for me to limit myself to a few illustrations.

We might begin with the simple device which we owe to physical chemistry of identifying a solid substance most positively by taking a melting-point not only of the substance itself, but also of a mixture of it and the compound it is suspected of being: this device was hardly known or used fifteen years ago and is now considered a more reliable and, certainly, a more rapid identification test than an exact ultimate analysis: I recall that in an investigation

[1] Address before the American Chemical Society, December, 1907.

carried out a dozen years ago, two compounds were obtained, each of which melted at 245° to 247°; both had the same composition and they were at first supposed to be identical; but mixtures of the two melted 30° to 40° lower than either substance alone, and this gave us our very first warning that we were dealing with *isomers*. Again, in a more recent investigation on a new class of nitrogen *stereoisomers,* the syn and anti chlorimido compounds,

$$R—C—R' \qquad R—C—R'$$
$$\underset{ClN}{\|} \quad and \quad \underset{NCl}{\|} \;,$$
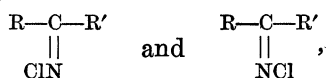
we were on the point of abandoning the search for nitrogen stereoisomers other than the long-known oximes and hydrazones, when the simple observation was made that a crude chlorimido ester, melting at 65°, gave analytical data representing a perfectly pure substance and yet could be resolved into two distinct compounds, each giving the same analytical results, but each of which melted some twenty degrees higher than the original substance, a mixture of which, however, melted again at 65°. Then we knew that we had at last stumbled on the long-sought stereoisomers, the simplest representatives of the whole type. Structural identity being proved, the rigorous proof of stereoisomerism *versus* physical or crystal isomerism was brought in part with the aid of the low melting point of the mixture of the two substances.

The physico-chemical theory of the separation of *stereoisomers* of the asymmetric carbon type, for instance, of the separation of d and l tartaric acids, by the crystallization of their salts with optically active bases, has led to extremely important and useful developments in recent years; the theory is, in brief, that whereas two opposite forms, $+ A$ and $— A$, must have the same physical and chemical properties,

except in the rotation of the plane of polarized light, the compounds

$$\left\{ \begin{array}{c} + A \\ + B \end{array} \right\} \quad and \quad \left\{ \begin{array}{c} — A \\ + B \end{array} \right\}$$
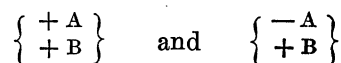
obtained when the two forms are combined with a single active component, say $+ B$, are no longer optical images and will have different physical and *chemical* properties. The recognition of this simple fact has led to the extension of the method of separation to other substances than acids and bases, namely to esters, amides, hydrazones and so forth. Most important, though, is the fact recognized first by Marckwald that for the same reason the chemical activity of two asymmetric substances, $+ A$ and $— A$ towards an asymmetric compound $+B$ may be different and that consequently, for reactions that are not instantaneous like salt formation, but involve time, like esterification, the velocity of formation of the compound, $+ A + B$, say an ester, may be quite different from the velocity of formation of $— A + B$. This must make possible a separation by chemical means, rather than by physical. But, *vice versa,* the velocity of decomposition of such esters when once formed may likewise be different. All these conclusions were confirmed by experiment and the result is of greatest importance to science, for it gives us a direct explanation of the long-known fact that enzymes will attack only one of a pair of stereoisomers and not the other, will cause, for instance, d-glucose to ferment, but not l-glucose; for in the enzymes we have asymmetrical substances (Fischer) corresponding in every way to what we have symbolized as $+ B$.

Again, the much-discussed, once hotly fought question of the true structure of so-called *tautomeric* compounds has found its rational solution with the aid of physical chemistry. Whether acid amides have the structure, $RCO.NH_2$ or $RC(OH){:}NH$,

whether a 1,3 dicarbonyl derivative, like acetoacetic ether, is a ketone, $CH_3CO.CH_2COOR$, or an alcohol, $CH_3C(OH):CH.COOR$, are questions which could not really find their final answer by the older methods of the study of derivatives, although at the time that was the best we could do. According to the present views, which J. Traube first presented, we have in solutions of the tautomeric compounds both forms in equilibrium with each other; for instance, we have

$$C_6H_5CO.NH_2 \rightleftarrows C_6H_5C(OH):NH$$

and

$$CH_3CO.CH_2COOR \rightleftarrows CH_3C(OH):CHCOOR.$$
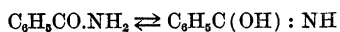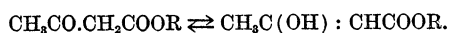
According to the laws of equilibrium and kinetics, if a given reagent, for instance an alkali, uses up the one form, say by neutralization, the whole material can be changed in the same way; the other form, inert in regard to a particular reagent, regenerates the active form continuously by a one-sided reaction. Thus, even if the unstable form existed in only minimal quantity, it could be the source of the actual product of the reaction, and that is why the old method of proof by the study of derivatives must be considered faulty. The isolation of the two closely related forms has not only confirmed this modern view by the qualitative observation that the forms are mutually convertible into each other, but Wislicenus, Claisen, Kuester and others have measured quantitatively the velocities of transformation of tautomers and have determined a number of the equilibrium constants. With the proof by Knorr, showing that in the solid phase only one tautomer can exist in stable form, the whole matter has received a definite, sharp setting. That the subject is one of interest not only to organic chemists, but to all of us, is evident from the fact that our indicators, phenolphthalein, methyl orange and others, seem to owe their valuable property of changing their tint, in passing through the neutral point, to conditions of *tautomerism* affecting the *chromophoric* groups in these compounds.

And so we find physico-chemical methods of investigation of the greatest advantage in the treatment of the three important classes of organic compounds which have the same molecular weight and composition but different character and identity— namely, *isomers, tautomers* and *stereoisomers.*

But the organic compounds themselves, their structure and the arrangement of their atoms in space, represent in a way the least important side of organic chemistry—far more important are their reactions, the changes to which we can subject them, the things we can do with them. For on these changes all the scientific and technical applications and our very life depends. It is in particular to the study of some phases of this question of organic reactions that I wish to call your attention this morning. To take a concrete case, the reversible reaction of esterification and saponification

$$CH_3COOCH_3 + HOH \rightleftarrows CH_3COOH + CH_3OH$$
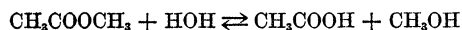
has been an important one ever since its study helped establish our fundamental law of chemical equilibrium. But the reaction has been important in other directions as well, for early investigations showed that either action is greatly accelerated by the addition of an acid like hydrochloric acid; since the acid did not seem to change or to take part in the reaction, it was said to act by its mere presence as a catalytic agent; and this is a typical reaction from which important laws regarding catalysis were laid down. There are hosts of reactions in organic as in inorganic chemistry in which we use one ingredient or the other to accelerate the action, or rather to make it go at all. It
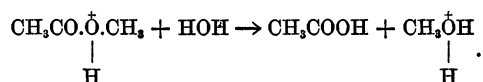
has always been a subject for speculation and investigation as to how and why a catalytic agent like hydrochloric acid does its work in actions like the saponification of methyl acetate or the inversion of cane-sugar or the digestion of food. Many chemists have believed that more reactive addition products are formed as intermediate products; but of what nature would they be to be more reactive? We know that addition products, representing more saturated compounds, very often are really less reactive than the unsaturated compounds from which they are obtained. There are, however, important exceptions to this rule: in trying to imagine just how an acid can affect the speed of the action

$$CH_3COOCH_3 + HOH + HCl \rightarrow$$
$$CH_3COOH + CH_3OH + HCl$$
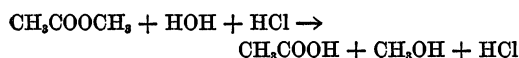
we must recall the most fundamental fact concerning acids, the fact that they have the power to form salts with bases and basic oxides. Here we have the acid and the oxide and the idea is at once suggested that *salt* formation of the ester with the acid is the cause of the acceleration or catalysis. Baeyer has shown, in fact, that acid esters in common with other oxygen compounds do form well-defined salts with acids, oxonium salts, derived from quadrivalent oxygen, salts of exceedingly weak bases, but still true salts, as shown by the electrolytic experiments of Coehn. Now, one of the most important differences between a very weak base and its salts is that almost all salts, no matter how weak the base, ionize much more readily than the weak base itself—this is a general case when the addition product, the salt, is more reactive than the unsaturated compound, the base, and it is so through the power of ionization.[2] So it was thought that the accelerating or catalytic action of

[2] Addition products often have a decomposition tension producing an action as the result of an increased potential of a component.

the acid could be readily understood as due to such salt formation, if the water reacts, not with the ester itself, but only with its positive ion, as expressed in:

$$CH_3CO.\overset{\cdot}{O}.CH_3 + HOH \rightarrow CH_3COOH + CH_3\overset{\cdot}{O}H$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | \quad .$$
$$\quad\quad H \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad H$$

The velocity of the reaction would then be simply expressed in the fundamental equation:

$$\text{Velocity} = \frac{dx}{dt} = K_{\text{velocity}} \times \text{Conc.}_{\text{Pos. Ions}} \times \text{Conc.}_{\text{HOH}}.$$

As a matter of fact, *with this single assumption* that only the positive ions are active, it is possible to deduce mathematically by the rigorous application of our simple laws of chemical equilibrium and dynamics, as applied to the salts of very weak bases, every fundamental fact that has long been known about the processes of saponification and esterification: In the first place, by the application of these laws, we find this equation resolving itself, mathematically, into the equation:

$$\text{Velocity} = \frac{dx}{dt} = K'_{\text{velocity}} \times \text{Conc.}_{\text{Ester}} \times \text{Conc.}_{\text{HOH}}$$
$$\times \text{Conc.}_{\text{H ions}},$$

the fundamental empirical equation which tells us that at a given temperature the velocity of saponification is proportional to the concentrations of the ester, the water and the hydrogen ions; the innumerable measurements which have established the correctness of this empirical equation agree, therefore, obviously also with the fundamental equation of our theory. The latter is also found to be in perfect agreement with the two other characteristic features of this catalysis—namely, that the ultimate condition of equilibrium of the reversible reaction of saponification and esterification is not sensibly modified by the addition of the acid, but is only reached more rapidly; and finally, the catalyzing acid does not appear to combine with any of the sub-

stances involved in the reaction—hence the name catalytic agent. The acid does not appear to combine with the ester simply because the salt is almost completely hydrolyzed under the conditions of equilibrium between such a weak base and a strong acid—and only very small quantities of the salt and its positive ion exist at any moment. But still, if the concentration of a component is increased, say, a thousandfold by the addition of an acid, its reactivity is increased proportionately according to the law of mass action, no matter whether a minute quantity has thus been increased a thousandfold or a larger mass.

Thus far the development of the subject was purely mathematical and theoretical, although no assumption was made which was not based on established facts of organic chemistry. An experimental test of the correctness of this theory necessarily was a main object. The ordinary esters were not considered suitable for the purpose; they are such weak and unstable bases that it was not considered wise to attempt to measure exactly the actual concentration of their positive ions in given cases—although this will now be attempted. Recourse was first taken to a very closely related class of compounds, the imido esters, $RC(:NH)OCH_3$, in which the stronger basic group ($:NH$) has replaced an oxygen atom of the ordinary esters. The imido esters are pronounced bases, although weak ones, and form well-defined salts. They are decomposed by water into ammonia and an acid ester according to

$$RC(:NH)OCH_3 + HOH \rightarrow RCOOCH_3 + NH_3.$$
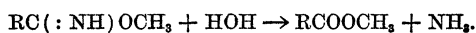
This action is enormously accelerated by the addition of acids, just as is the decomposition of an ordinary ester. On the basis of the above theory, it was thought that the acceleration of the decomposition of the imido ester would also be due wholly to the formation of the salt, and, through it, of its positive ion in larger masses; in other words, the real decomposition must be
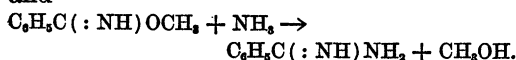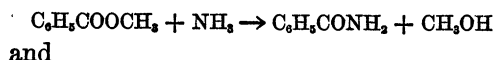
$$RC(:N\overset{+}{H}_2)OCH_3 + HOH \rightarrow RCOOCH_3 + N\overset{+}{H}_4,$$
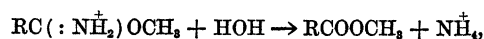
and the isothermal equation giving the velocity of the action must be

$$\text{Velocity} = \frac{dx}{dt} = K_{\text{velocity}} \times \text{Conc.}_{\text{Pos.Ions}} \times \text{Conc.}_{\text{HOH}},$$

the same as for the acid esters.

In this case the theory could be put to the test of experiment, for all the factors could be determined—the velocity of the reaction, the exact proportion of free ester, its salt and its positive ion at any moment were ascertained without difficulty. Not to weary you with experimental details, it may be said that the substance undergoing decomposition was found, as a matter of fact, to be the positive imido ester ion; the free base, the non-ionized salt do not decompose with water in this way. The deeper the investigation was carried, the more marked, too, was found the parallel between the acid esters and the imido esters, which have served for the experimental verification of the theory; there is an alkaline catalysis of imido esters, as there is of esters, and the alkaline catalysis in both cases is very much the faster one and subject to the same law; there is a salt effect or salt catalysis for the imido esters as there is for acid esters and for cane-sugar, and our measurements help to explain, we believe, the nature of salt catalysis in both cases.

The proof of the soundness of a theory is shown by the experimental verifications of predictions which can be made on the basis of it, and I would like to report two such cases. Imido esters react also with ammonia, as do ordinary esters, and the products are quite analogous; we have:

$$C_6H_5COOCH_3 + NH_3 \rightarrow C_6H_5CONH_2 + CH_3OH$$

and

$$C_6H_5C(:NH)OCH_3 + NH_3 \rightarrow$$
$$C_6H_5C(:NH)NH_2 + CH_3OH.$$

The latter reaction proceeds very slowly but is accelerated again enormously by the addition of an acid. On the basis of the general theory we supposed at once that the real action does not involve the imido ester itself at all, but only its positive ion, so that we must have

$$\text{Velocity} = \frac{dx}{dt} = K_{\text{velocity}} \times \text{Conc.}_{\text{Pos. Ion}} \times \text{Conc.}_{\text{NH}_3}.$$

This action is interesting because almost all of the added acid is taken by the stronger base, the ammonia, to form an ammonium salt, the weaker base, the imido ester, taking only a very small share of it. The same catalytic effect can, therefore, be produced also by adding an ammonium salt to the mixture; the weaker base will also take a small part of the acid; but this small share, however minute, can be rigorously ascertained with the aid of the equilibrium law and of the experimentally ascertained affinity constants of the two bases. The mathematical development led to the rather startling prediction that the reaction velocity would be found to be independent of the concentration of free ammonia—one of the reacting components—a result which no one would anticipate from the old view as expressed in the first equation. That is, while accelerating the action proportionately to its mass, the ammonia, according to our view, should also retard it to a like degree by driving the imido ester proportionately out of its combination with the acid and thus its concentration would not affect the reaction. As a matter of experiment, the velocity of the reaction was found, as predicted, to be practically independent of the concentration of free ammonia. In the second place the degree of ionization a of the ammonium salt figures in the final mathematical equation—the velocity constant referred to the positive imido ester ions being K_v/a. Now, ammonium sulphate is ionized considerably less than ammonium chloride in equivalent solutions. When we determined the velocity of the action for methyl imido benzoate, first using ammonium chloride as the catalyzer, we found that it is 281 if a is left out of consideration, and for the sulphate solution it is 212. The respective degrees of ionization of the salts in the concentrations used are 80 per cent. and 61 per cent., respectively, and for K_v/a we have $281/0.80 = 351$ and $212/0.61 = 351$. The third point of especial interest is that in this reaction the actual concentration of the reacting substance, the positive ester ion, is exceedingly small; for instance, only 0.000,018 gram molecules at the beginning of our first series, and still smaller as the reaction proceeds, but it is rigorously calculable and it is noteworthy that the velocity is really found proportionate to this small but vital component. This, I believe, also justifies completely the conception that the catalysis of ordinary esters is also due to a very small but vital component, which has hitherto escaped measurement, but the assumption of whose presence enables us to give a rational explanation of catalytic action of acids which is in complete agreement with all experimental facts and with the laws of dynamics.

Another fact discovered as a result of applying the theory is this: in all our determinations we have found the rule to hold that in the presence of an acid catalyzer the tendency for action is for the ion of a weaker base to change into the ion of a stronger one—that is true for the amidine reaction, for the action of water on imido esters and on ordinary esters, and even for the formation of esters from an acid and alcohol; the rule is probably de-

pendent on the law of maximum work and should lead to the recognition of what may be called the driving force of the actions— I have not time to discuss it here. In our experience there was only one notable exception to the rule: years ago we found that urea esters would not react with amines to give guanidines, a reaction which would correspond entirely to the formation of amidines from imido esters:

$$NH_2C(NH)OCH_8 + NH_8 \rightarrow$$
$$NH_2C(NH)NH_2 + CH_8OH.$$
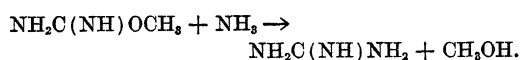
And, yet, the guanidines are much stronger bases than are the urea esters. Now it happened that in our older work we had almost invariably used the free esters and amines, no salts. In a reinvestigation of the action from the new point of view, hydrochloric acid was added to help the ionization of the urea ester. With this simple modification, the method works beautifully, excellent yields of guanidines are obtained and the action falls into line with the others. Quantitative measurements showed too that the reaction proceeds with a velocity proportionate to the concentration of the positive urea ester ion. The result was interesting not only because it represents a successful synthesis predicted by the theory, but also because in this case the stronger base is the urea ester and it takes the major part of the catalyzing acid—for the imido esters and ammonia the conditions were reversed. And so the theory is found to work, whether the reacting positive ions are present in very minute or in larger masses, whether the catalyzer combines in minimal or in larger proportion with the substance undergoing catalysis!

We thus find that it is possible by physico-chemical methods to determine the mode of action of reagents, so-called catalyzers, which we add to mixtures in organic chemistry to make the actions "go." By entirely analogous methods and properly chosen conditions the active component may be ascertained by velocity determinations in a large variety of organic reactions, methods which are applicable not only in chemistry proper, but also particularly in the domain of biochemistry, where catalytic action by acids, alkalies and enzymes is of foremost importance.

In conclusion, I should like to call attention to one other important method of physical chemistry which has been extensively applied in inorganic fields and is now being used in organic work with the largest promise of valuable results. It is the method of studying chemical reactions with the aid of potential differences produced by a logical arrangement of reacting substances—a method which Ostwald seems to have originated and which he has developed into a chemometric method. One of the most valuable applications is in the study of oxidation and reduction, and it was, in fact, first used by Ostwald in such reactions in an investigation carried out with Bancroft. Such potential differences, according to the theory of Nernst, amply confirmed by experience, are a function, in the first place, of characteristic constants of the reacting substances and, in the second place, also, of the concentrations of the reacting substances, the ions, around the electrodes. The application to an organic problem will become clear by the consideration of a specific case. We remember that the oxidation of a great many organic compounds like aldehydes and sugars is most vigorous in alkaline solutions. We use ammoniacal silver solution and even sodium hydroxide with it as a most delicate test for such aldehydes, and alkaline Fehling solution for sugars. Is the alkali necessary to liberate silver oxide or copper oxide as the true oxidizing agent, as is often sup-

posed? The physico-chemical method of investigation shown here easily leads to a correct analysis of the action; as a matter of fact, we find silver nitrate a far more powerful oxidizing agent than is ammoniacal silver oxide, and it is so because in both cases the oxidation is due to the tendency of the silver ions to discharge their positive electricity and that positive electricity is the real oxidizing agent here just as it is at the positive pole in every case where a current is passed through any solution whatever. In the silver-nitrate solution there is a far greater concentration of these discharging silver ions than in the ammoniacal solution, in which most of the silver is present in the rather stable complex ion, $[Ag(NH_3)_2]$. But the alkali is used to increase the concentration of the active reducing component of the aldehyde—which probably is a methylene salt $\pm CH(ONa)$ or its ion[3]—the alkali added to the silver nitrate is positively detrimental to the latter's oxidizing power. (Illustrated by an experiment with silver nitrate against formaldehyde and sodium nitrate; then alkali is added to the alde-

[3] The oxidation of an aldehyde is best interpreted as being due to the oxidation of sodium oxymethylene $(NaO)CH\pm$, the two free valences of which may justly be considered to consist of a positive and a negative electric charge. Any oxidizing agent, *e. g.*, the positive current of electricity resulting from the discharge of the silver ions, would oxidize this as follows:

$(NaOCH)\pm$ and 2 positive charges $\rightarrow (NaO)CH{+\atop+}$

and the hydroxyl ions of the alkaline solution would by uniting with this residue give sodium formate:

$$(NaO)HC{+\atop+} + 2\overline{OH} \rightarrow NaO(HCO) + H_2O.$$
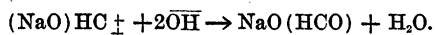
The two sodium ions belonging to the two hydroxyl ions used migrate to the silver nitrate cell in the chemometer, replacing the two silver ions which have been discharged—all of which corresponds to actual observation. (Views developed by Nef, W. A. Noyes and others are in part applied in this interpretation.)

hyde, and finally ammonia to the silver nitrate.) It could be shown in the same way that the alkali used with Fehling's solution in the oxidation of glucose is used wholly for its action on glucose, and is rather a disadvantage than helpful as far as the copper is concerned. This method of investigation enables us, therefore, to analyze the action of our oxidizing and reducing agents, and it promises to lead us ultimately to a mathematical solution of the problem.

<div align="right">JULIUS STIEGLITZ</div>

UNIVERSITY OF CHICAGO

SCIENTIFIC BOOKS

Psychology: General Introduction, pp. 389. *Laboratory Manual of Psychology*, pp. 127. *Laboratory Equipment for Psychological Experiments*, pp. 257. By CHARLES HUBBARD JUDD, Professor of Psychology at Yale University. New York, Charles Scribner's Sons. 1907.

Professor Judd's contribution to the available facilities for the teaching of psychology is a notable one. The plan is consistent, the execution capable, the result distinctive. The text becomes part one of the series of three volumes; a brief laboratory manual makes possible the performance of a considerable range of demonstrations and individual experiments, all reduced to as simple a material basis as is compatible with convenience; while the third volume furnishes the instructor with a *vade mecum* for management and equipment of his modest instrumental plant. The general plan thus provides for the " object lesson " conduct of an introductory course in psychology, suitable at once to colleges and universities and to normal schools that are ready to give psychology a prominent place in their schedules. The text becomes available alike with such illustrative experimentation and without it, or with such portion of it as meager facilities make possible.

In distinction from the more conventional text which implies and as a rule receives the supplementary exposition of demonstration,