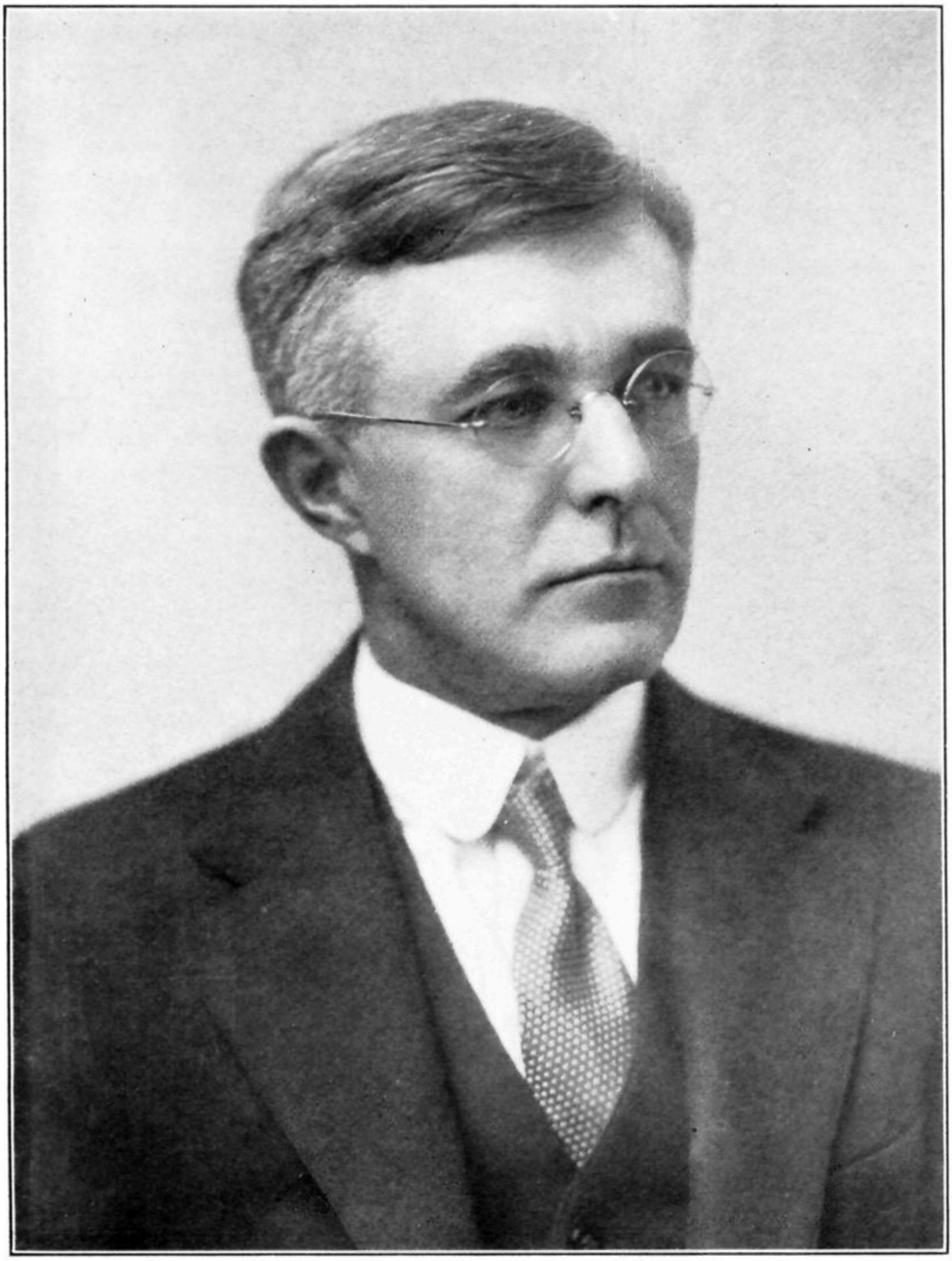

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MODERN CONCEPTS IN PHYSICS AND THEIR RELATION TO CHEMISTRY

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Only about 35 years ago, during the nineties of the last century, knowledge of the physical sciences had advanced to such a point that many of the foremost physicists and chemists began to believe that the rate of progress of fundamental knowledge must be slowing up. The concepts of length, mass, time, energy, temperature, electric and gravitational fields, etc., had been given precise meanings and were regarded as having an absolute existence quite as certain as that of matter itself. The phenomena of nature were explainable in terms of natural laws expressing relations between these absolute quantities. It seemed that the most important of these laws of physics and chemistry had already been discovered and that the work that remained to do was largely a matter of filling in the details and applying these great principles for practical purposes.

The laws of mechanics had been verified experimentally with a high degree of precision so no one doubted that they were rigorous laws of nature. Back in about 1830, Hamilton had succeeded in generalizing these laws in a few simple equations which seemed to contain all the essential truths of mechanics. It was only necessary to know how the kinetic and potential energy of any given system varied with the momentum and the coördinates of its parts in order to have at least a formal solution of the way in which the system would behave at all times. Thus all future work in mechanics need only be considered an application of Hamilton's equations.

Complete knowledge of the nature of light presented more difficulties. Hamilton, about 1820, showed that all the known laws of geometrical optics could be explained quantitatively in terms of either a corpuscular theory of light or a wave theory. The experiments of Fresnel on the interference of light, which were made about this time, seemed to disprove Newton's

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corpuscular theory, so that Hamilton's proof of the complete analogy between waves and corpuscles in the case of geometrical optics became only of academic interest. Through the study of the phenomena of interference, diffraction, polarization and absorption of light, the wave theory of light became firmly established. Light was supposed to consist of waves in some sort of an elastic medium which was called the ether.

About 1830, Faraday developed clear conceptions regarding the electric and magnetic fields and Maxwell, about 1860, by applying exact mathematical methods evolved the electro-magnetic theory of light according to which light waves consisted of fluctuating electric and magnetic fields which are propagated through space at a speed which could be calculated from electric and from magnetic measurements in a laboratory.

Although the acceptance of Maxwell's views came slowly one could not long remain skeptical after the production of electro-magnetic waves of relatively great wave length by Hertz in 1884. It may almost be said that Maxwell's theory was essentially an application of the mathematical methods which Hamilton had originated in his treatment of the laws of mechanics, to Faraday's concepts of electricity and magnetism.

Thus in 1895, the physicists seemed to have some justification for the attitude that the most important laws had been discovered. The laws of mechanics had not been improved upon in 65 years. Faraday and Maxwell had brought in precise conceptions of electric and magnetic phenomena and had shown that by classical methods like those which had been so successful in mechanics, all the laws of optics could be derived from those of electro-magnetism.

In chemistry a somewhat similar state had been reached. After the evolution of the conception of the elements and of combining proportions based upon an atomic theory, rapid progress was made in accumulating data regarding the elements and their compounds. Faraday's laws of electrolysis and new methods for the accurate determination of atomic weights began to provide the chemist with quantitative laws almost as precise as those of the physicists. The work of J. Willard Gibbs had brought into chemistry rigorous laws as fundamental in their field of application as were those of Hamilton and Maxwell in physics.

These remarkable advances on the quantitative side seemed to overshadow in importance the more qualitative results that had previously been obtained through the stimulus of the atomic theory. Under the leadership of Ostwald, chemists began to adopt a much more critical attitude and began to distinguish carefully between what they considered experimental facts and hypotheses based upon these facts. Ostwald, although he recognized the convenience of the atomic theory, believed it must always remain impossible to prove the existence of atoms or molecules. He therefore urged that chemists avoid as far as possible the use of such hypotheses. Perhaps the chief result of this attitude was to lead physical chemists to neglect those parts of chemistry where the atomic theory would have been most helpful and to devote themselves more specially to the fields in which energy relationships and thermodynamics were directly applicable.

Physicists in general did not doubt the existence of atoms and molecules, but had by means of this theory developed the kinetic theory of gases which had led to many new quantitative laws, verified by experiment. However, the physicists in general had little to do with atoms and molecules but were more concerned with the ether, in which they believed unreservedly, although direct knowledge of the ether was far harder to obtain than knowledge of atoms and molecules.

Perhaps one of the main reasons why the physicists were so sure of the ether and the chemists so doubtful of the atoms and molecules was an unconscious belief in the respectable old adage "Natura non facit saltum," Nature makes no jumps. Certainly in those fields of physics and chemistry in which rigorous quantitative laws had been found applicable no discontinuities or jumps such as those implied by the atomic theory had been found.

The discovery of x-rays by Roentgen, in 1905, marked the beginning of an extraordinary revolution which is today still in progress. This sensational event revealed to the physicist that great and fundamental discoveries were still possible even in the field of radiation where physics had had such complete success. It immediately caused great numbers of physicists to study the phenomena of electric discharges and to look for other sources of radiation. The discovery of radium and radioactivity by Becquerel and the Curies soon showed the importance of these new forms of radiation to the chemist as well as to the physicist.

Although Stoney in 1874 had seen that Faraday's laws of electrolysis together with the atomic theory required that electricity should also have an atomic structure, and although in 1891 he proposed the name electron for these atoms of electricity, J. J. Thomson should be regarded as the discoverer of the electron. He was able to show that electrons were contained in all forms of matter and found that the electron must weigh only about $^1/_{1800}$ as much as a hydrogen atom.

The studies of radioactivity, largely by Rutherford and his students, showed that radium spontaneously disintegrated to form helium and proved to the chemist that atoms were not indestructible and even that transmutation of elements was possible.

By the application of thermodynamics to radiation processes Boltzmann proved that the total radiation, of all wave lengths, within a cavity in a heated body must increase in proportion to the fourth power of the absolute temperature; this law had already been found empirically by Stefan. By a further development of thermodynamic methods Wien, in 1896, derived an important law, known as Wien's law, by which the intensity of radiation of any particular wave length could be calculated in terms of the wave length and temperature. This law was found to agree with experiment in the case of visible radiation from incandescent solids, but serious discrepancies were observed when an attempt was made to calculate the intensity of infra-red radiation or heat waves. Lord Rayleigh and Jeans, in 1900, using what seemed to be unimpeachable methods based on the electro-magnetic theory of light, arrived at an entirely different relation between the intensity of radiation and the temperature and wave length. This equation agreed excellently with experiments on the radiation of heat where Wien's law had failed but led to absurd results when applied to the shorter wave lengths of the visible spectrum. In fact, if the total radiation including all wave lengths were calculated from the Rayleigh-Jeans equations an infinite radiation density was obtained even at low temperatures. Thus by means of the classical theories of radiation it was found on the one hand by Boltzmann that the radiation increased with the fourth power of the temperature, and on the other by Rayleigh-Jeans, that the radiation was infinite at all temperatures.

It was shown in 1905, by Planck, that this paradox could only be solved by assuming an essential discontinuity in the energies or motions of electrons whose vibrations caused the radiation. This gave birth to the Quantum Theory, which within recent years has grown to be one of the most important theories of physics and chemistry. In 1906, Einstein showed that the photo-electric effect and many photochemical reactions could be explained in terms of the Quantum Theory if light itself consisted of discrete particles of energy or quanta, now usually called photons. Although such a corpuscular theory of light seemed utterly incompatible with the accepted wave theory, an increasing number of phenomena were discovered in which it seemed necessary to resort to this corpuscular theory. The really rapid development of the Quantum Theory, however, dates from 1913, when Bohr began to develop his theory of atomic structure by applying the Quantum Theory to Rutherford's more or less qualitative theory of the nuclear atom.

Relativity Theory.—Among all the changes in the ways of thinking which were being forced upon physicists at this time, the most important by far was that which resulted from Einstein's relativity theory, first stated in 1905. In 1895, as we have seen, electromagnetic waves and matter were thought to be manifestations of the properties of an all pervading ether.

As an example of the way that the physicists thought of the ether I will quote from the preface to Lord Kelvin's "Baltimore Lectures." This preface was written in 1904, but the lectures were those that were delivered at Johns Hopkins University in 1884.

"I chose as subject the 'Wave Theory of Light' with the intention of accentuating its failures; rather than of setting forth the admirable success with which this beautiful theory had explained all that was known of light before the time of Fresnel and Thomas Young, and had produced floods of new knowledge splendidly enriching the whole domain of physical science. My audience was to consist of Professorial fellow-students in physical science. . . . I spoke with absolute freedom and had never the slightest fear of undermining their perfect faith in ether and its light-giving waves: by anything I could tell them of the imperfection of our mathematics; of the insufficiency or faultiness of our views regarding the dynamical qualities of ether; and of the overwhelmingly great difficulty of finding a field of action for ether among the atoms of ponderable matter. We all felt the difficulties were to be faced and not to be evaded; were to be taken to heart *with the hope of solving them if possible*. . . . It is in some measure satisfactory to me and I hope it will be satisfactory to all my Baltimore coefficients still alive in our world of science, when this volume reaches their hands to find in it dynamical explanations of every one of the difficulties with which we were concerned from the first to the last of our twenty lectures of 1884. All of us will, I am sure, feel sympathetically interested in knowing that two of ourselves, Michelson and Morley, have by their great experimental work on the motion of ether relatively to the earth, raised the one and only serious objection against our dynamical explanations."

This Michelson and Morley experiment of 1887, through the theoretical investigations of Lorentz and others, kept growing in importance until it finally stimulated Einstein to evolve his relativity theory.

According to this theory space and time cannot be considered as existing independently of each other. They cannot in any sense be regarded as absolute but are both dependent upon the point of view of the observer. For example, Einstein showed that it has no meaning to say that two events which took place at a great distance apart occurred simultaneously. Some observers knowing of both events would have to say that event A occurred before B, while other observers moving at a different velocity from the first observers would conclude that B occurred before A.

It is not my plan to try to explain the relativity theory to you even if I knew how to do so, but it is rather to discuss the way in which this theory and others of a somewhat similar nature have gradually brought about profound changes in the viewpoint of the physicists and how similar changes are beginning to occur in the attitude of the chemists. The importance of Einstein's work thus lies not so much in the facts or phenomena that can be explained by the relativity theory, but in the discovery of a new way of thinking as applied to physics. Somewhat similar methods of thought had, it is true, been used in some branches of mathematics and sometimes in philosophy, but Einstein subjected our elementary conceptions of space, time, mass, energy, etc., to a searching analysis quite new in the history of physics.

Concepts Involve Operations.—Professor P. W. Bridgman of Harvard University has recently written a popular book entitled "The Logic of Modern Physics," in which he analyzes the changes in our concepts that have resulted primarily from Einstein's work. Bridgman's thesis is that *physical concepts have meaning only in so far as they can be defined in terms of operations.* He shows that this new attitude toward our fundamental conceptions is perhaps one of the greatest changes that has been brought about by Einstein's work. There is no question in my mind but that the recent remarkable advances in quantum mechanics that have been made by such men as Bohr, Heisenberg, Schroedinger and Dirac have been stimulated by the desire to formulate all concepts in terms of operations. Bridgman has not originated this method, but he, more than anyone else, perhaps, has been conscious of its widespread application in modern physics.

I should like to outline to you the way in which Bridgman develops this thesis and to consider how well it applies to the most recent changes that have taken place in physics and in chemistry. I believe the chemist can derive great benefit from the conscious application of a similar critical attitude in his own science.

Bridgman points out that "hitherto many of the concepts of physics have been defined in terms of their properties." An excellent example is Newton's concept of absolute time. The following quotation from Newton's "Principia" is illuminating.

"I do not define Time, Space, Place or Motion, as being well known to all. Only I must observe that the vulgar conceive those quantities under no other notions but from the relation they bear to sensible objects. And thence arise certain prejudices, for the removing of which, it will be convenient to distinguish them into Absolute and Relative, True and Apparent, Mathematical and Common.

"(1) Absolute, True and Mathematical Time, of itself, and from its own nature flows equally without regard to anything external, and by another name is called Duration."

Thus, according to Newton, time and space have properties of a very abstract kind and are looked upon as "things" which exist independently of all other things. There is, however, as Bridgman says, "no assurance whatever that there exists in nature anything with properties like those assumed in the definition, and physics, when reduced to concepts of this character, becomes as purely an abstract science and as far removed from reality as the abstract geometry of the mathematicians." Nevertheless, these conceptions of space and time prevailed until the relativity theory was proposed.

In the development of his theory Einstein, in analyzing the concepts of space and time, considered what means are available by which an observer can measure distances between two points on a rapidly moving object. For example, imagine two planets moving past each other at high velocity and two observers, one on each planet, provided with means for observing each other and communicating with each other; such means, for example, as light signals. Einstein asks, what are the operations by which the two observers could compare their units of length and time? He finds that each observer would logically conclude that the other observer's unit of length is shorter than his own, and that the other's unit of time is longer than his own. Einstein thus proved that there can be no such thing as absolute length or time, or rather proved that the concept of absolute time has no meaning, for we have not been able to conceive of any method for determining the absolute time of any event.

In order to illustrate his thesis Bridgman considers in detail the concept of length. Probably one of the earliest concepts of length was obtained by counting the number of unit lengths that can be placed end to end between two given objects. For example, the number of paces are counted in walking from one object to another. An extension and refinement of this method is employed today when the standard meter at the Bureau of Standards is compared with a steel tape and this is then used to lay off a base line for a survey by triangulation.

As Bridgman suggests, it was one of the greatest discoveries of the human race to find that these operations performed with a measuring rod afford a useful and convenient means of describing natural phenomena.

During the transition from the earliest pacing of distances, to our modern refined measurements with the meter stick, the concept of length itself must have undergone radical modifications since the operations involved had been modified. For example, if distances are to be paced, it has no meaning to consider distances of $^1/_{1000}$ of a pace unless the concept is modified to include arbitrarily chosen methods by which a length equal to $^1/_{1000}$ of a pace may be determined. In our modern measurements with a steel tape we must measure the temperature of the tape and the force used in holding the tape taut, and then by means of the coefficient of expansion and the coefficient of elasticity, apply corrections to the observed length. It is hard to see what methods primitive man could have used in applying such corrections to his distances measured by pacing.

Why do we now apply such corrections? Merely because it has been found by experiment that the result that we get by applying such corrections is a quantity which proves to be more useful in describing natural phenomena than the results we get without these corrections. We must not think that we do it in order to obtain the "true" or "absolute" length.

Today we have many other methods of measuring length than by use of measuring rods or steel tape. For example, we use optical instruments and measure distances by triangulation, we measure heights in the atmosphere by means of a barometer, we measure the distances of spiral nebulae by measuring the brightness of the Cepheid variables observed in them by our most powerful telescopes, we measure the lengths of molecules by finding the area of a water surface over which a given amount of oil will spread, we calculate the diameters of molecules by measurements of the viscosity of gases by means of the kinetic theory, or we use x-ray diffraction patterns or, finally, we calculate the diameter of an electron from its mass and charge by means of the electro-magnetic theory assuming that all the energy of an electron lies in the electric field outside of its surface.

Now each of these measurements of length involves an entirely different set of operations and, therefore, fundamentally, according to Bridgman, we should regard them as different concepts; logically, in fact, they should all have different names. It has, however, been found as a matter of experiment that two or more of these methods when applied to the measurement of the same distance give results which agree more or less with one another. This, then, is our justification for calling all these concepts by the same name, length.

We may, if we wish, extrapolate and predict that by applying suitable corrections to each of these methods of measuring lengths we may be able to get better and better agreement between them. Such methods of extrapolation may be useful and stimulating but we must always expect that sooner or later we will be unable to obtain agreement between these methods with more than a limited degree of accuracy. This may not be due merely to experimental difficulties but may often result from unavoidable fuzziness in the concept itself. Such concepts as the diameter of a complicated molecule, or the mean free path of a molecule in a gas are inherently fuzzy conceptions and can mean not much more than when we speak of the diameter of a tree or of the length of the waves during a storm at sea.

Perhaps the strongest reason for the general belief in the existence of an absolute space lay in the apparently perfect agreement between our measurements of length and the theorems of Euclidian Geometry. During the last century, however, mathematicians began more and more to realize that Euclidian Geometry was only one out of many possible logical geometries, and since all of these were based solely on certain axioms or postulates none of them had any real or necessary connection with physics. The apparent agreement between our physical observations and Euclidian Geometry, therefore, does not prove that space must have the properties postulated in Euclid's axioms.

Models.—As chemists we are all more or less familiar with various models of atoms and molecules that have been proposed within recent years. The structural formulas which the organic chemists have used for a good part of a century are another example of an extremely useful type of model. I want to discuss later some of the models which the physicists have used in giving more concrete forms to their theories. Logically, I believe, we should regard Euclidian Geometry as a model devised primarily to help us "explain" natural phenomena.

Observation of nature reveals great complexity. We receive enormous numbers of impressions simultaneously and if we are to make progress in understanding phenomena we must concentrate on certain aspects of the things we see about us and thus discard the less important features. This involves a process of replacing the natural world by a set of abstractions which we have become very skilful in choosing in such a way as to aid us in classifying and understanding phenomena. Thus it was found useful to develop concepts or abstractions such as shape, position, distance, etc., and separate these characteristics of the phenomena from others such as color, hardness, etc. Euclidian Geometry was found useful in correlating these concepts of shape, position, etc.

Physicists and chemists have usually felt that they understood a phenomenon best when they could explain it in terms of a model or concrete picture. The chemist explained the law of multiple combining proportions in terms of atoms which combine together to form molecules. The heat conductivity, viscosity, etc., of gases was explained in terms of the kinetic theory, with molecules making elastic collisions with one another according to the law of probability.

When we use the atomic or molecular theories to explain phenomena in this way, we assign to the atoms and molecules only those properties which seem needed to accomplish the desired result, we do not consider what the atom is made of nor what its structure is, but usually feel justified in assuming properties which are as simple as possible. For example, in the elementary kinetic theory it is assumed that the molecules are hard, elastic spheres, not because anyone really believes that molecules have these properties, but merely because these are the simplest properties we can think of which are consistent with the known facts.

What we really do, therefore, is to replace in our minds the actual gases which we observe and which have many properties which we do not fully understand by a simplified model, a human abstraction, which is so designed by us that it has some of the properties of the thing we wish to displace.

There is thus a difference of degree rather than of kind between the adoption of a mechanical model and the development of a mathematical theory such as Euclidian Geometry. When the mathematical physicist develops an abstract theory of actual phenomena, for example, Hamilton's equations to summarize the laws of mechanics, he is in reality constructing a mathematical model. Mathematical equations have certain definite properties or rather they express certain relationships between the symbols which enter them. In a mathematical theory of physical phenomena the equations are so chosen that the relation between the symbols corresponds in some simple way to that which is observed between measurable physical quantities which are the bases of our concepts of physics.

Within recent years, especially in the development of the relativity and quantum theories, physicists have been making increasing use of mathematical forms of expression, and have been giving less attention to the development of mechanical models. The older generation of physicists and chemists and those among the younger men who are less skilled in the use of mathematics are inclined to believe that this is only a temporary stage and that ultimately we must be able to form a concrete picture or model of the atom, that is, to get a picture of what the atom is really like. It seems to be felt that a mechanical model whose functioning can be understood without the aid of mathematics, even if it only gives the qualitative representation of the phenomena in question, can represent the truth in some higher sense than a mathematical theory whose symbols perhaps can be understood only by a mathematician.

There is, I believe, no adequate justification for this attitude. Mechanical models are necessarily very much restricted in scope. The relationships of their parts are limited to those that are already known in mechanics (or in electricity or magnetism). Mathematical relationships are far more flexible; practically any conceivable quantitative or qualitative relationship can be expressed if desired in mathematical form. We have no guarantee whatever that nature is so constructed that it can be adequately described in terms of mechanical or electrical models; it is much more probable that our most fundamental relationships can only be expressed mathematically, if at all.

In analyzing our attempts to describe nature, we have discussed concepts, models and mathematical theories. We find that they are all alike in that they represent human abstractions which are found convenient in describing nature. Going back a step further we must recognize that *words* themselves constitute elementary concepts. They are, it is true, much more vaguely defined than our concepts of physics and chemistry, but qualitatively they are very much like the latter; in fact, most of our misunderstandings in science arise from assigning reality to concepts whose main reason for existence is the fact that they are represented by a word. Logically we should aim to define our words in terms of operations. We should have in mind specifications by which we can test whether or not the word is properly applicable.

The progress of science depends largely upon (1) giving to words meanings as precise as possible; (2) definition of concepts in terms of operations; (3) development of models (mechanical or mathematical) which have properties analogous to those of phenomena which we have observed.

Meaningless Questions.—A great deal of time and effort is wasted in scientific circles as well as in the world at large through failure to give sufficiently definite or useful definition of words and concepts. Bridgman emphasizes this in connection with his discussion of "Meaningless Questions."

In some cases questions fail to have meaning because of the more or less inherent fuzziness of the concepts involved. For example, if we compare two trees of about the same size it may have no meaning to ask which tree has the larger diameter, for no one has defined the diameter of a tree with the necessary precision.

A more important class of meaningless questions arises when there are no conceivable operations that could be performed to arrive at a decision. For example, what is the meaning of the question, "Would the United States have ended the World War if the Lusitania had not been sunk?" Such a question may be a good subject for a school debating society, but no one is apt to think that the question has thereby been answered.

A study of meaningless questions may serve a very useful purpose in science. A statement that a certain question has no meaning may be equivalent to stating a fundamental law of nature; for example, to say that the question "What is the true velocity of the north star through space?" has no meaning is a fairly good statement of at least a part of the relativity theory.

In some cases it may have no meaning to ask whether or not there is a magnetic field in a certain portion of space. For example, suppose an observer, stationary on the earth, studies an electron in motion. The motion of an electron constitutes an electric current and experimentally he will observe the characteristic magnetic field surrounding this electron corresponding to this current. If another observer moves along with the electron, it will appear to him to be at rest, and, of course, he can observe no magnetic field. Otherwise, the presence or absence of a magnetic field around an electron or group of electrons could be used to determine absolute motion through space, which would be contrary to the relativity theory. The relativity theory thus requires that a magnetic field can have no real existence in any absolute sense.

We have seen that there are fundamentally as many different concepts of length as there are different ways in which length may be measured; nevertheless, we find approximate agreement between different ways of measuring the diameter of molecules and therefore are justified in assigning some *reality* to the concept diameter of molecule. When, however, we ask what is the diameter of an electron, we find that the question is practically without meaning. It is true that we can calculate a diameter by assuming that the electron behaves like a charged sphere and that the classical laws of electrodynamics can be applied in this case. However, since we have no independent way of measuring this diameter, the process is one which involves reasoning in a circle.

There are many meaningless questions which afflict the chemist. It clearly has no meaning to ask what is the molecular weight of sodium chloride in a crystal. It is very doubtful whether it has any meaning to ask what is the molecular weight of water in liquid water. There are many cases where the concept of temperature has no definite meaning. Strictly speaking, temperature acquires meaning in terms of operations only in so far as an approach is made to equilibrium conditions. When the motions of molecules or atoms follow Maxwell's Distribution Law, that is, a random or probability distribution of velocity among the molecules, the concept of temperature becomes very definite. If, however, we deal with mercury vapor streaming into a high vacuum, or the conditions near a hot tungsten filament in a gas of low pressure, temperature has very little meaning. The same is true of the conditions frequently existing in an electric discharge tube such as a mercury arc, where the electrons act as though they had a temperature of perhaps 50,000°, whereas the atoms have motions corresponding to far lower temperatures. Strictly speaking, neither the electrons nor atoms have well-defined temperatures, for the conditions are far removed from equilibrium.

In much of the recent discussion of the Radiation Hypothesis of chemical reactions, chemists have been discussing meaningless questions usually without realizing it. At first it was proposed that the radiation is absorbed by the reacting gas to form excited molecules in accordance with Einstein's photochemical law. When this is found not to be in accord with experiment, the concept of radiation is altered repeatedly as new experimental facts are found so as to make the modified theory continue to fit the facts. After this process has been carried on sufficiently, it no longer has any meaning to ask whether the reaction is caused by radiation or whether the radiation hypothesis is true.

In the studies of the properties of liquids, questions of the degree of ionization and of association and in some cases of internal pressures have been discussions of questions without meaning. A great deal of such discussion might be simplified or even avoided entirely if chemists would agree in defining these concepts in terms of operations.

Theories of valence within recent years have been afflicted with the same difficulties. As long as chemists deal with the ordinary valence rules of organic chemistry, they are dealing with concepts of valence which are actually defined in terms of operations; that is, the organic chemists know how to conduct experiments to prove that the valence of nitrogen in dimethylaniline is 3. The types of operations needed to establish the valence of magnesium in magnesium chloride are in many ways quite different, and they are still different if we consider the case of so-called quinquevalent nitrogen in ammonium chloride or heptavalent chlorine in perchloric acid. I believe that the chemist has much to learn from the physicist in regard to the proper method of attacking such problems as these.

The electrochemist has been troubled in locating the source of electromotive force in cells. The physicist has similar difficulty in finding the origin of the contact potential between metals. Fundamentally it must be recognized that unless or until there are methods by which these quantities can be measured, questions involving them have no meaning.

A practical example of the meaninglessness of some questions involving electric potential has recently arisen in the numerous proposals that have been made to construct a speed indicator for airplanes which will give the speed with respect to the earth's surface independently of that of the wind surrounding the plane. It is reasoned that since the plane is moving through the earth's magnetic field a potential will be set up between the ends of a wire stretched between the wing's tips. It is only necessary to measure this potential difference in order to calculate the speed of the plane with respect to the earth. Careful analysis shows that the concept of the potential difference under these conditions is meaningless except with reference to a particular reference system. If this system is referred to the plane itself, this potential difference is zero quite regardless of what the speed of the plane may be with reference to the earth. A contrary result would conflict with the relativity theory.

Meaningless questions will assume far greater importance in future years. We shall see that the latest forms of the quantum theory now give us the best of reasons for believing that the identity of separate electrons within atoms or molecules may be partly or wholly lost, so that it may have no meaning to ask whether a particular electron we find as a result of experiment is the same electron which has previously produced an observed phenomenon. Even more far-reaching in its consequences is the Bohr-Heisenberg Uncertainty Principle according to which it has no meaning to ask what is the precise position and velocity of an electron or atom. An electron may have a definite position or a definite velocity but it cannot in any exact sense have both. This doesn't mean merely that there are experimental difficulties in measuring them, it means that the concepts themselves (position and velocity) are relative to one another in a sense somewhat analogous to that of time and space in the relativity theory.

One's instinctive reaction when first questioned as to the objective reality of space, time, position, velocity, etc., is to object to such consideration on the grounds that they are too metaphysical. The recent advances in physics demonstrate that these methods of thinking are eminently practical; they represent, in fact, an attempt to get away from the metaphysical character of much of our thinking in the past. Instead of taking for granted objective realities corresponding to our concepts, we now deal with things which can be measured in the laboratory, the concrete data that we have to start from.

It is, however, very useful to retain the concept of reality. Bridgman suggests that reality should be measured by the number and the accuracy of the independent ways in which we arrive at similar measures of the concept in question. For example, owing to the fact that we have so many concordant methods of measuring the distance between the ends of a base line used for triangulation, we attribute great reality to the concept of length or, rather, to those concepts of length which are applicable in cases of this kind. We thus have some justification in saying that two points are really one kilometer apart. We do not attribute, however, much reality to the concept of the diameter of an electron.

Thirty years ago the physical chemist doubted the existence of atoms or believed the concept was useless if not pernicious. A few years later the leader of this movement, Ostwald, in the preface of one of his books stated that he believed that the existence of atoms had been proved experimentally beyond question, although in previous books he had stated that there are always an infinite number of hypotheses that could be advanced to explain any given set of experimental facts.

Today, what can we say in answer to the question "Does matter really consist of atoms?" Must we say that this is one of those meaningless questions?

Of course, the amount of meaning that can be attached to any such question depends upon the definitions of the words and concepts which it contains. If we mean by atoms indivisible and indestructible infinitely hard, elastic spheres, we are compelled to answer the question in the negative. In accordance with modern usage, however, we do not attribute any such properties to the atom. If, by the use of the word atom, we mean to imply principally the concept that matter consists of discrete particles which can be counted by the various methods which are now known for this purpose, we have the very best of reasons for answering the question in the affirmative. If in our studies of nature we discover evidences of discontinuities or of the presence of discrete natural units which can be correlated in a definite way with the numerical integers, we have come, it would seem, about as close to something absolute in nature as we can hope to get. Einstein in the relativity theory has taught us to look upon the intersections of world lines as the data upon which our observations of nature rest. Such points of intersections, which can be called events, are essentially discontinuities. In general they are all unlike one another. When we find in nature discrete units which in many respects appear to be identical with one another, and we can count these units, it would seem that the number of these units which obtain as a result is apt to be independent of our system of reference; therefore, they have in general, a certain kind of absolute significance.

In this respect, therefore, it seems that the atomic theory and the quantum theory in which integers play such a fundamental role may be considered as representing reality to a higher degree than almost any other of our physical and chemical theories.

Skepticism in regard to an absolute meaning of words, concepts, models or mathematical theories should not prevent us from using all these abstractions in describing natural phenomena. The progress of physical chemistry was probably set back many years by the failure of the chemists to take full advantage of the atomic theory in describing the phenomena that they observed. The rejection of the atomic theory for this purpose was, I believe, based primarily upon a mistaken attempt to describe nature in some absolute manner. That is, it was thought that such concepts as energy, entropy, temperature, chemical potential, etc., represented something far more nearly absolute in character than the concept of atoms and molecules, so that nature should preferably be described in terms of the former rather than the latter. We must now recognize, however, that all of these concepts are human inventions and have no absolute independent existence in nature. Our choice, therefore, cannot lie between fact and hypothesis, but only between two concepts (or between two models) which enable us to give a better or worse description of natural phenomena. By better or worse we mean, approximately, simpler or more complicated, more or less convenient, more or less general. If we compare Ostwald's attempts to teach chemistry without the use of the atomic theory with a good modern course based upon the atomic theory, we get an understanding of what should be meant by better or worse.

The more recent advances in atomic theory which have resulted from the development of the quantum theory and which have given us our present knowledge of atomic structure, afford us interesting applications of the new methods of thought, first introduced into physics and chemistry by the relativity theory.

The older atomic and molecular theories of the chemists took on more definite form through the development of the kinetic theory of gases, and through the electron theory and the study of radioactivity developed to a point where the atom is conceived of as consisting of a definite number of electrons revolving around the nucleus. The atom ceased to be indestructible and was no longer the smallest particle of matter which could take part in a chemical reaction. The nucleus, rather than the atom, became characteristic of the chemical elements. The chemical properties of the atom, however, depended upon the number and arrangement of electrons.

Bohr, in 1913, developed a marvellous new theory of the atom by combining Planck's quantum theory with a relative theory of the nuclear atom. He evolved several new quantitative mathematical relationships with new concepts such as energy levels, quantum states, etc., and showed how the spectra of elements could be explained in terms of these new concepts. He also gave a mechanical model consisting of electrons revolving in orbits about the nucleus according to laws which were partly classical and partly inconsistent with classical laws. This model enabled him to derive certain mathematical equations from which he was able to calculate the frequencies corresponding to the different lines in the spectra of hydrogen and other elements, these frequencies being obtained from fundamental quantities such as the charge and mass of the electron and the quantum constant h, and did not involve any quantities dependent on the properties of the elements in question. The agreement between the theory and experiment was practically perfect, often enabling the frequency to be calculated with an accuracy of one part in two hundred thousand.

Such remarkable success made most physicists and chemists believe that Bohr's model, for the hydrogen atom at least, was substantially correct. That is, they believed that Bohr's work proved that in a normal hydrogen atom the electron really described a circular orbit around a nucleus having a diameter and a frequency given by Bohr's model. Bohr himself never attached any such importance to the mechanical model, realizing that the important steps that he had taken consisted mainly in the introduction of new concepts and more particularly in the mathematical equations by which the observed frequencies in the spectral lines could be calculated.

Within recent years, largely through the work of Bohr himself and his students, and Sommerfeld, Schroedinger, and others, this theory of the hydrogen atom has undergone changes. According to Bohr's original model the radiation of energy corresponding to a spectral line resulted from transition in which the electron passed from one stationary orbit to another. No physical picture of this transition seemed possible. To account for the known phenomena it seemed necessary that the transition should occur so rapidly that the electron would have to move from one orbit to another with a velocity greater than that of light, and yet the train of waves in the resulting radiation lasted for relatively long periods of time, about 10^{-8} seconds. Radiant energy could be absorbed by the atom only if the frequency was just that which was capable of transferring an electron from one orbit to another definite orbit. Thus only one frequency could be absorbed at a time by an atom. It was found, however, that the frequencies corresponding to many lines could be scattered by a single atom. This seemed to require the presence within any given atom of a number of oscillators as great as the number of lines in the spectrum. One of the greatest arguments in favor of the original Bohr theory was that it avoided just this sort of complication in the atom.

To get rid of difficulties such as these, Heisenberg and Born realized that it was necessary to sweep out of the theories of atomic structure the many concepts which were characteristic of the mechanical models that had been proposed and to develop a mathematical theory of the atom which would involve only concepts that were definable in terms of operations. That is, the theory was one that dealt more directly with measurable quantities such as the frequencies of spectral lines. New methods of matrix calculus had to be evolved, a kind of calculus of discontinuities or discrete quantities instead of the calculus of continuous quantities which had characterized classical mechanics.

Only a little later Schroedinger, by developing DeBroglie's wave theory of quantum phenomena, was able to build up a theory that we will now refer to as the wave mechanics, according to which the whole atom with all its electrons can be looked upon as a wave phenomenon. The electrons are no longer considered to be moving in orbits. For example, the hydrogen atom is found to have spherical symmetry instead of the axial symmetry of the old Bohr model of the atom. Yet this theory leads to identically the same equations for the frequencies of the lines in the hydrogen spectrum. We must not say that Bohr's theory of the hydrogen atom has been overthrown. Bohr's *mechanical* model has been superseded, but the more important model which is represented by the equations and the concepts which he evolved is even better today than it was when it was first proposed.

The wave mechanics which involves the calculus of continuous variables is not now in conflict with the Born matrix calculus of discrete quantities. The two theories are essentially merely different mathematical methods applied to a single fundamental problem. The resulting mathematical equations always agree with one another. One begins to believe that the mathematical theory is a far better model of the atom than any of the mechanical models which are possible.

The long-standing conflict between the wave theory of light and the corpuscular quantum theory now disappears with the new wave mechanics, the two aspects of light being somewhat analogous to the two aspects of the quantum theory, the wave mechanics and the matrix mechanics. In fact, the quantum theory now indicates that the electron itself can be regarded as a particle, or as a wave, just as light can be thought of as a photon or a wave. Whatever remained of the conflict between the wave and corpuscular theory of light and of the electron seems now to be fundamentally removed by the Bohr-Heisenberg Uncertainty Principle. To ask whether an electron is a particle or a wave is a meaningless question; the same is true of the question whether light consists of corpuscles or waves. One must answer that both of these are particles or waves according to the kind of operations that we may perform in observing them. If we make an experiment which proves that an electron has a very definite position, then it would seem to prove that it is a particle. In that case, however, according to the Uncertainty Principle, we are not able to determine accurately the velocity and therefore cannot predict where the particle will go.

Bohr has emphasized that the essential reason that the classical theory falls down in any detailed description of atomic phenomena is that our knowledge of such atomic systems can only be obtained through an act of observation which makes the observer inherently a part of the system. On the classical theory we assume that we could have knowledge of a completely closed system as though it were possible to know anything of what would go on in a strictly closed system. In order to make an observation some signal must be transmitted from the system to ourselves, and if we take this interaction completely into account we are forced to the quantum theory with its Uncertainty Principle.

An interesting feature of this new quantum mechanics is that the original conception of the relation between cause and effect which was universally accepted in science has lost its meaning. Atomic processes seem to be governed fundamentally by the law of probability. It has no meaning to ask when a particular radium atom will disintegrate, for no operation is conceivable by which such an event could be predicted. The same is true of every individual quantum process. We have no guarantee whatever that the expulsion of an α-particle from an atom of radium has any immediate cause. In chemistry the formation of nuclei in supercooled liquids, etc., must be essentially quantum phenomena in which no cause can be assigned for the formation of the individual nucleus. By varying the conditions we may alter the probability that a nucleus will appear at a given point, but in no absolute sense can we ever make a nucleus form through a direct cause.

By a deeper analysis of this question of causality Bohr concludes that we have an option of two alternative descriptions of natural phenomena. If we choose to describe phenomena in terms of ordinary space and time then we must abandon causality. We may, however, retain the conception of causality if we are willing to describe atomic phenomena in terms of what the mathematician calls configuration space. Consider, for example, a helium atom with its two electrons. If we attempt to give the position of both of these electrons in space we would need a set of three coördinates, x, y, z, for each of the electrons, that is, six coördinates in all, three of which belong to one and three to the other electron. The mathematician, however, finds that the two electrons in general could also be described by one point in six-dimensional space, for such a point has six coördinates. This is a representation of two electrons as a single point in a configuration space of six dimensions. Now it turns out from Schroedinger's theory that the motion of electrons, or rather of the waves corresponding to them, can be completely described in the case of the helium atom by a quantity which has a particular value at each point in this six-dimensional space or configuration space. The helium atom, however, can be described in terms of the motion of two electrons in three-dimensional space if we are content merely to know the probabilities that the electrons may be found at any point in this space.

These matters undoubtedly seem very abstract to those of you who have not previously become familar with them. I give them here mainly in order to illustrate how far the modern concepts of physics differ from those of twenty years ago.

If we must thus abandon our ordinary ideas of cause and effect, it may be asked why have the physicist and chemist so long believed that the whole teaching of science gave proof that every phenomenon resulted inevitably from the causes that led to it. I think the answer is that in the past scientists chose as the subjects for their investigations almost wholly those phenomena in which such definite relations as cause and effect could be found. These phenomena are those in which such enormous numbers of individual quantum phenomena are grouped together that the result is determined only by their averages. For example, when we study the variation of the pressure with the volume of a gas, the forces that we measure result from the impacts of great numbers of molecules, the average force remaining steady and definite. If, however, we only had one molecule in a small volume, the pressure exerted on the walls would be zero except for those instants at which the molecules struck the wall. It would then be impossible to predict in advance what the pressure would be at a particular time.

I think in trying to estimate the reliability of any of our scientific knowledge we should keep in mind that the whole complexion of a science may be made to change by the psychology of the investigators which governs the choice of the subjects that are investigated.

Our best knowledge of time and its relation to other concepts is that which we have obtained through Einstein. Yet in the whole relativity theory there is nothing to distinguish between positive and negative time, that is, between future and past, any more than there is between different directions in space, such as right and left. There thus appears to be something curiously incomplete in our knowledge of time, for every one of us knows the vast practical difference between past and future. Eddington, in his recent book, "The Nature of the Physical World," discusses the "arrow of time" at some length. He suggests that the second law of thermodynamics is the only fundamental law of nature which provides us with any distinction between future and past. One way of stating this law is that all spontaneous processes that occur in nature involve an increase in entropy. Eddington thus proposes that the positive direction of time can be defined as that direction in which the entropy increases. If we had a system in absolute equilibrium the entropy would be constant, and there would then be no arrow of time. This is in accord with the fact that in such a system there are no changes with time.

It is improbable that there are two independent fundamental factors which provide an arrow for time, so that it would seem that Eddington in having found one such factor has found the only one. There are, however, grave difficulties with this view. An arrow is a vector quantity which should have magnitude as well as direction. Now the rate of change of entropy does not seem to give us any measure of time. For this purpose we use phenomena which are as nearly reversible as possible, such as the swinging of a pendulum in a vacuum.

Fundamentally entropy is a measure of randomness. A random distribution of molecules in space and velocity is a system having the maximum entropy. If we throw a pack of cards out of the window and collect them from the ground they have become effectively shuffled. We would not expect by this process, starting with a shuffled pack of cards, to find them at the end in the order in which they come from the manufacturer. The direction in which the randomness increases thus provides an arrow for time. This arrow is, however, equivalent to that involving the increase of entropy.

It is still an open question, however, whether processes directed by intelligent beings may not involve a decrease in entropy. In fact it seems conceivable that the evolution of organic life on the earth is in some measure fundamentally contrary to the second law of thermodynamics. The inherent tendency of evolution seems to be to bring about an ordered rather than a random arrangement of parts, and in the future perhaps forms of life may evolve which cause a decrease of entropy on a large scale. Are we then to have some parts of the universe in which the arrow of time points in the opposite direction from that in neighboring parts?

Such speculations may seem fantastic. It is, however, I believe, of the utmost importance for the chemists and the physicists to evolve fundamentally sound conceptions of such things as time and entropy.

The profound changes in physical thought, particularly those represented by the Quantum Theory, are rapidly bringing about a revolution in physical chemistry. The third law of thermodynamics involving chemical constants has changed radically our methods of studying chemical equilibria. The application of the Quantum Theory to band spectra promises to be of the utmost importance in chemistry. By enabling us to determine the moments of inertia of chemical molecules, the actual distances between the nuclei of the atoms in molecules can be found. Apparently our most accurate determinations of the heats of dissociation of elementary gases can be obtained from the band spectra through a knowledge of the energy levels of the various possible states of the molecules. In recent numbers of the "Journal of the American Chemical Society," particularly in the paper of Giauque and Johnston, we see the beginnings of what promises to be the most accurate and fertile source of knowledge of chemical equilibria. From a detailed knowledge of the spectrum, for example, of oxygen, and without recourse to any other experimental determinations, the specific heat at all temperatures can be calculated, and the entropy of oxygen at all temperatures is thus found. This, together with the heats of reactions, which may be found by a similar method, makes possible the calculation of the degree of dissociation of oxygen and will ultimately make possible the calculation of all chemical equilibria.

The remarkable work of Dennison, Bonhoeffer and Eucken in predicting and isolating para-hydrogen should prove to the chemist how many of his chemical discoveries will be obtained in the future by the application of these new theories of physics.

Gurney and Condon have recently derived from the wave mechanics an explanation of the fundamental law of radioactivity. Similar methods will probably before long enable us to understand the processes involved in chemical reactions far better than we ever have before.

Physics and chemistry are being inevitably drawn closer together. It seems that there has never been a time when we can predict with such certainty rapid progress in fundamental chemistry, for the new theories of physics have as yet scarcely begun to be applied in the field of chemistry. The physicist on the other hand has much to learn from an increased knowledge of chemical phenomena which should provide him with a richness of experimental data far greater than any he has yet had an opportunity to use.

Unfortunately, although theoretical physics and chemistry are thus supplementing each other and in many respects are being merged into a new science, there are remarkably few men as yet that have received adequate training in both sciences. Before long, I hope, sharp distinctions between physics and chemistry will no longer exist, but at present there seems to be a very practical distinction.

In order to find approximately how many chemists are also active as physicists and *vice versa*, I have selected at random 100 pages of the fourth edition of American Men of Science (1927) which contains the names of 13,500 American scientists. Of these, approximately 2700 are classed as chemists and 760 as physicists. Of the chemists 87% are members of the American Chemical Society, while only 2.5% belong also to the American Physical Society. Seventy-seven per cent. of the physicists are members of the American Physical Society, while 3.3% are also members of the American Chemical Society. Thus only about 3% of the physicists and chemists of the United States, whose names are given in the American Men of Science, belong to both of the national societies. This leaves far too small a number of men who are capable or are properly prepared to carry on the important work of bringing these two sciences closer together.

To pave the way for the coming revolutionary changes in chemistry we must be prepared to modify our methods of thinking, probably along lines now so prevalent in physics. But above all we must urge young chemists in the universities and after graduation to become thoroughly well trained in mathematics and in modern physics.

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THE MOLECULAR STRUCTURE OF THE TUNGSTOSILICATES AND RELATED COMPOUNDS

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1. Introduction

The molecular structure of the heteropolyacids[1] such as 12-tungstosilicic acid, $H_4SiW_{12}O_{40}{\cdot}xH_2O$, has long been the subject of speculation. A structure based upon Werner's coördination theory, suggested by Miolati,[2] has been developed and extensively applied in the systematization of heteropolyacids by Rosenheim,[3] and now is generally used in the discussion of these acids.[4] The Miolati-Rosenheim conception is, however, far from satisfactory. It provides no explanation for the characteristic properties of these acids and their salts, and the single definite pre-

[1] A historical summary of work on the heteropolyacids, with complete references to the papers of C. Marignac, F. Kehrmann, H. Copaux, W. Gibbs and many other investigators, is given by A. Rosenheim and J. Jaenicke, *Z. anorg. Chem.*, **100**, 304 (1917).

[2] A. Miolati, *J. prakt. Chem.*, [2] **77**, 417 (1908).

[3] (a) A. Rosenheim and co-workers, *Z. anorg. Chem.*, **69**, 247 (1910); (b) **69**, 261 (1910); (c) **70**, 73 (1911); (d) **70**, 418 (1911); (e) **75**, 141 (1912); (f) **77**, 239 (1912); (g) **79**, 292 (1913); (h) **84**, 217 (1913); (i) **89**, 224 (1914); (j) **91**, 75 (1915); (k) **93**, 273 (1915); (l) **96**, 139 (1916); (m) **100**, 304 (1917); (n) **101**, 215 (1917); (o) **101**, 235 (1917).

[4] F. Ephraim, "Inorganic Chemistry," Gurney and Jackson, London, **1926**, pp. 405–419; J. N. Friend, "A Textbook of Inorganic Chemistry," Griffin, London, **1926**, Vol. VII, Part III, pp. 251–268; etc.