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INTERNATIONAL CONGRESS OF ARTS AND SCIENCE

THE OLD CHRONICLE

Hand-painted Photogravure from the Painting by Eduard Grützner

The creator of this composition was actuated by an impulse suddenly formed while examining some antique records in Rome, the atmosphere of his environment being strongly suggestive of monkish incident and life. The painting, renowned for its faithful portraiture, is reproduced and shown here as an example of a study in the Middle Ages, before printing was in common use, as compared with the modern library, enriched with the accumulated wisdom of all time and freely accessible to even the poorest. The picture is instructive for its revelation of a phase of life many centuries ago, and it is a masterpiece of delineation.

INTERNATIONAL CONGRESS
OF
ARTS AND SCIENCE

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HOWARD J. ROGERS, A.M., LL.D.
DIRECTOR OF CONGRESSES

VOLUME VII

PHYSICS AND CHEMISTRY

COMPRISING
Lectures on Physics of Matter, Physics of Ether, Physics of
the Electron, Carbon Chemistry, Inorganic Chemistry,
Organic Chemistry, Physical Chemistry
and Physics and Chemistry in the
Nineteenth Century

UNIVERSITY ALLIANCE
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ILLUSTRATIONS

VOLUME VII

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DIVISION C—PHYSICAL SCIENCE

COLUMBUS AT SALAMANCA

Photogravure from the Painting by Niccolo Barabino

Columbus discovering a new world, which has been the theme of many artists, is the antithesis of the subject chosen by Barabino, and to the credit of this very famous painter it may be said that his wonderful composition has probably won greater sympathy and pity for the explorer than any history however eloquent in describing his wrongs. The sneer of nobles, the calumny of enemies, the disrespect of the learned, are pictured by the artist with such pathos and genius that he has left a perpetual memorial of his talent in this masterful representation of the famous discoverer's tribulations.

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DIVISION C—PHYSICAL SCIENCE

DIVISION C—PHYSICAL SCIENCE

(*Hall* 4, *September* 20, 10 *a. m.*)

SPEAKER: PROFESSOR ROBERT S. WOODWARD, Columbia University.

THE UNITY OF PHYSICAL SCIENCE

BY ROBERT SIMPSON WOODWARD

[**Robert Simpson Woodward**, Ph.D., Sc.D., LL.D., President of the Carnegie Institution of Washington. **b.** Rochester, Mich., 1849. C.E. University of Michigan, 1872; Ph.D. University of Michigan, 1892; Honorary LL.D. University of Wisconsin, 1904; Sc.D., University of Pennsylvania, and Columbia University, 1905. Assistant engineer, U. S. Lake Survey, 1872–82; assistant astronomer, U. S. Transit of Venus Commission, 1882–84; astronomer, geographer, and chief geographer, U. S. Geological Survey, 1884–90; assistant, U. S. Coast and Geodetic Survey, 1890–93; Professor of Mechanics and Mathematical Physics, Columbia University, 1893–1905; Dean of School of Pure Science, *ibid.*, 1895–1905; President of Carnegie Institution of Washington, 1905. Member of National Academy of Sciences; Past President and Treasurer (since 1894) of American Association for the Advancement of Science; Past President of American Mathematical Society and of New York Academy of Sciences; member of Astronomical and Astrophysical Society of America, Geological Society of America, Physical Society of America, and Washington Academy of Sciences. **Author of** *Smithsonian Geographical Tables ; Higher Mathematics* (with Mansfield Merriman); also of many Government reports and numerous papers and addresses on subjects in astronomy, geodesy, mathematics, mathematical physics, and education.]

THERE is a tradition, still tacitly sanctioned even by men of science, that there have been epochs when the more eminent minds were able to compass the entire range of knowledge. Amongst the vanishing heroic figures of the past it seems possible, indeed, to discern, here and there, a Galileo, a Huygens, a Descartes, a Leibnitz, a Newton, a Laplace, or a Humboldt, each capable, at least, of summing up with great completeness the state of contemporary knowledge. Traditions, however, are generally more or less mythical, and the myth in this case seems to be in flat contradiction with the fact that there never was such an epoch, that the great masters of our distinguished predecessors were, after all, much like the masters of to-day, simply the leading specialists of their times. But however this may be, if we grant the possibility of the requisite attainments, even in a few individuals at any epoch, we shall speedily conclude that there never was an epoch so much in need of them as the immediate present, when the divisional speakers of this Congress are called upon to explain the unities which pervade the ever-widening and largely diverse fields of their several domains.

The domain of physical science, concerning which I have the honor to address you to-day, presents peculiar and peculiarly formidable difficulties in the way of a summary review. While we may not be disposed to limit the wide range of inclusion specified by our programme, we must at once disclaim any attempt to speak authoritatively with respect to most of its details. There is, in fact, such a vast array of knowledge now comprehended under any one of the six Departments of our Division, that the boldest author must hesitate to enter on a limited discussion with respect to any of them. But if it is thus difficult to consider any department of physical science, it appears incomparably more difficult to contemplate all of them in the bewildering complexity of their interrelations and in the bewildering diversity of their subject-matter. What, for example, could seem more appalling to the average man of science than the duty of explaining the connections of archeology and astrophysics, or those of ecology and electrons?

Happily, however, the managers of the Congress have provided an adequate division of labor, whereby the technical details of the various Departments are allotted to experts, giving thus to a divisional speaker a degree of freedom with respect to depth in some way commensurate with the breadth of his task. Presuming, therefore, that I may deal only with the broader outlines and salient features of the subject, I invite your attention to a summary view of the present status and the apparent trend of physical science.

Whatever may be affirmed with respect to science in general, there appears to be no doubt that all of the physical sciences are characterized by three remarkable unities, — a unity of origin, a unity of growth, and a unity of purpose. Physical science originates in observation and experiment; it rises from the fact-gathering stage of unrelated qualities to the higher plane of related quantities, and passes thence on to the realm of correlation, computation, and prediction under theory; and its purpose is to interpret in consistent and verifiable terms the universe, of which we form a part. The recognition of these unities is of prime importance; for it helps us to understand and to anticipate a great diversity of perfection amongst the different branches of science, and hence leads us to appreciate the desirability of hearty coöperation on the part of scientific workers in order that progress may be ever positive towards the common goal.

Glancing rapidly *seriatim* at the different departments of physical science as specified by our programme, we come first to a consideration of formal physics, and we may most quickly orient ourselves aright in this department by trying to state in what respects the physics of to-day differs from the physics of a hundred years ago.

In spite of the extraordinary perfection of the work of Lagrange, Laplace, Fourier, Young, Fresnel, Poisson, Green, Gauss, and others of the early part of the nineteenth century, it will be at once admitted that great progress has been made. In addition to noteworthy advances and improvements along the lines laid down by these masters, there have been developed the relatively new fields of elasticity, electromagnetics, thermodynamics, and astrophysics; and there has been discovered the widest of all generalizations in physical science, — the law of conservation of energy. Whereas it was easy a century ago to conceive, as in gravitational astronomy, of action at a distance across empty space, the universe in the mean time has come to appear more and more plethoric not only with "gross matter," but with that most wonderful entity we call the ether. The astronomers have shown us, in fact, that the number of molar systems in the universe is enormously greater than was supposed possible a century ago; while the physicists have revealed to us molecular systems rivaling our solar system and its Jovian and Saturnian subsystems, and they have loaded down the ether with a burden of properties and relationships which its usual tenuity seems scarcely fitted to bear. Whereas, also, a century ago the tendency of thought, under the stimulus of the remarkable developments of the elastic solid theory of light and the fluid theories of electricity, was chiefly towards an ether whose continuity would have pleased Anaxagoras, the tendency to-day is chiefly towards an ether whose atomicity would have pleased Democritus.

On the whole, it must be said that the advances of the past century, and especially those of the past half-century, have been mainly along the lines of molecular physics. The epoch of Laplace was distinctly an epoch of molar physics; the epoch of to-day is distinctly an epoch of molecular physics. Light, heat, electricity, and magnetism have been definitely correlated as molecular and ethereal phenomena; while the recently discovered X-rays and the wonders of radioactivity, along with the "electrons," the "corpuscles" and the "electrions" of current investigations, all point towards a molecular constitution of the ether. Thermodynamics, likewise, large as it has grown in recent decades, is essentially a development of the molecular theory of gases. It would be too bold, perhaps, to assert that the trend of accumulating knowledge is towards an atomic unity of matter, but the day seems not far distant when there will be room for a new *Principia* and for a treatise which will accomplish for molecular systems what the *Mécanique Céleste* accomplished for the solar system.

One of the most important advances of recent decades is found in the fixation of ideas with respect to the units of physical science, and in the great improvements which have been wrought in metrology by the "International Bureau of Weights and Measures." Our standards of length, mass, and time are now fixed with a degree of precision which leaves little to be desired for the present; and the capital resources of measurement and calculation are now available to an extent never hitherto approached.

It should be noted, however, that confidence in the stability of our standards is by no means comparable with the perfection of their current applications. Indeed, we may raise with respect to them the question so long mooted with regard to the motions of the members of the solar system: namely, are they stable? Notwithstanding the admirable precision of the intercomparisons of the prototype meters and prototype kilograms and the equally admirable precision of Professor Michelson's determination of the length of the meter in terms of wave-lengths of cadmium light, we cannot affirm that these observed relations will hold indefinitely. Our inherited notions of mass have been rather rudely shaken, also, by the penetrating criticisms of Mach, and it appears possible even that the law of conservation of mass may need modification in the light of pending researches. But worst of all, our time-unit, the sidereal day, is so far from possessing the element of constancy that we may affirm with practical certainty that it is secularly variable. Having realized, through Professor Michelson's superb determination just referred to, the cosmic standard of length suggested by Maxwell thirty years ago, we are now much more in need of an equally trustworthy cosmic standard of time.

If the progress of physics during the past century has been chiefly in the direction of atomic theory, the progress of chemistry has been still more so. Chemistry is, in fact, the science of atoms and molecules *par excellence*, a distinction it has maintained for well-nigh a full century under the dominance of the fruitful atomic and molecular hypotheses of Dalton and of Avogadro and Ampère, and under the similarly fruitful laws of gases established by Dalton and Gay-Lussac. Perhaps the most striking feature of this progress, in a general way, is the gradual disappearance it has entailed of the imaginary lines which have been long thought to separate the fields of chemistry and physics. Through the remarkable discoveries of Faraday the two fields have been found to overlap in actual electrical contact. Through the wonderful revelations of spectrum analysis, originating with Bunsen and Kirchhoff, they have been proved to be very largely common ground. And through the broader generalizations inaugurated by Willard Gibbs, Helmholtz, and others, they are now both somewhat in danger of being annexed as a sub-province of rational mechanics.

To one whose work has fallen more especially in the fields of precise astronomy, geodesy, or metrology, it might seem a just reproach to chemistry that it is a science whose measurements and calculations demand, as a rule, no greater arithmetical resources than those of four-place tables of logarithms and anti-logarithms. The so-called "Constants of Nature" supplied by chemistry are, in fact, known with a low degree of certainty; a degree expressed, say, by three to five significant figures. A small amount of reflection, however, will convince one that the phenomena with which the chemist has to deal are usually far more complex than those which have yielded the splendid precision of astronomy, geodesy, and metrology. Moreover, it should be observed that the certainties even of these highly perfected sciences are very unequal in their different branches. It appears more correct, therefore, as well as more just, considering the central position it occupies and the wide range of its ramifications, along with the vast aggregate of qualitative and quantitative knowledge it has massed, to assert that the precision of chemistry affords the best numerical index of the present state of physical science. That is, when reduced to the most compact form of statement, the certainties of physical science are best indicated, in a general way, by a table of the combining weights of the eighty-odd chemical elements.

When one contemplates the numbers of such a table, and when one adds to its suggestions those which flow from the various periodic groupings of the same numbers, he can hardly avoid being inspired by the day-dreams of those who have looked long for the atomic unity of matter. But however the grand problem which thus obtrudes itself may be resolved finally, it appears certain that this table must stand as one of the great landmarks along the path of progress in physical science.

It was justly remarked by Laplace in his *Système du Monde* that "L'Astronomie, par la dignité de son objet et par la perfection de ses théories, est le plus beau monument de l'esprit humain, le titre le plus noble de son intelligence"; and we must all admit that subsequent progress has gone far to maintain this high position for the most ancient and interesting of the older sciences. One finds little difficulty in accounting for the early rise of astronomical science and for the universal interest in celestial phenomena. Their immanence and omnipresence appeal even to the dullest intellects. But it is not so easy to account for the remarkable fact that although astronomy deals chiefly with the relations of bodies separated by immense distances, progress in its development has thus far been at least equal to, if not in advance of, the progress of physics and chemistry, which have to deal with matter close at hand. Without attempting a full explanation of this fact, it may suffice to observe that the principal phenomena of astronomy thus far developed appear to be relatively simple in comparison with those of the other physical sciences; and that the immense distances which separate the celestial bodies, instead of being an obstacle to, are a fortunate circumstance directly in favor of, the triumphant advances which have distinguished astronomical science from the epoch of Galileo down to the present day.

Not less noteworthy than his high estimate of the position of astronomy in his time are Laplace's anticipations of the course of future progress. Our admiration is kindled by the clearness of his vision with respect to ways and means, and by the penetration of his predictions of future discoveries. Advances in sidereal astronomy, he rightly thought, would depend chiefly on improvements in telescopes; while advances in dynamical astronomy were to come along with increased precision in the observed places of the members of the solar system and along with the growing perfection of analysis. It is almost needless to say that Laplace's brilliant anticipations have been quite surpassed by the actual developments. Observational astronomy has become one of the most delicately perfect of all the sciences; dynamical astronomy easily outstrips all competitors in the perfection of its theories and in the certainty of its predictions; while the newly developed branch of astrophysics supplies the last link in the chain of evidence of the essential unity of the material universe.

The order of the dimensions and the order of the mass contents of the visible universe, at any rate, have been pretty clearly made out. In addition to the vast aggregate of direct observational evidence collected and recorded during the past century, numerous theoretical researches have gone far, also, to interpret the laws which reign in the apparent chaos of the stars. The solar system, with its magnificent subsystems, has been proved to exhibit the type of stellar systems in general.

In a profound investigation recently published, Lord Kelvin has sought to correlate under the law of gravitation the principal observed data of the visible universe. Assuming this universe to lie within a sphere of radius equal to the distance of a star whose parallax is one thousandth of a second of arc, he concludes that there must be something like a thousand million masses of the magnitude of our sun within that sphere. Light traveling at the rate of 300,000 kilometers per second would require about six thousand years to traverse the diameter of this universe, and while the average distance asunder of the visible stars is considerably less, it is still of the same order. It is only essential, therefore, to imagine our luminary surrounded by a thousand million such suns, most of which are, in all probability, attended by groups of planets, to get some idea of the quantity of matter within visual range of our relatively insignificant terrestrial abode. And the imposing range of the astronomer's time-scale is perhaps impressively brought home to us when we reflect that a million years is the smallest convenient unit for recording the life-history of a star, while the current events in that history are transmitted across the interstellar medium by vibrations which occur at the rate of about six hundred million million times per second. Measured by its accumulation of achievements, then, the astronomy of to-day fulfills the requirements of a highly developed science. It is characterized by a vast aggregate of accurately determined facts related by theories founded on a small number of hypotheses. In the past it has called forth the two greatest of all systematic treatises, the *Principia* of Newton and the *Mécanique Céleste* of Laplace. It has probably done more also than any other science, up to the present time, to illuminate the dark periods during which man has floundered in his struggle for advancement; and the indications are that its prestige will long continue.

But there are spots on every sun; and lest some may infer, even humorously, as Carlyle did seventy-odd years ago, that our system of the world is "as good as perfect," attention should be called to some noteworthy defects in astronomical data and to some singular obscurities in astronomical theory. Here, however, great caution and brevity are essential to avoid poaching on the preserves of our colleagues of the Sections. It may suffice, therefore, merely to mention, under the head of defective data, the low precision of the solar parallax, the aberration constant, the masses of the members of the solar system, and the uncertainty of our time-unit, already referred to. Two instances, likewise, which belong to the general field of physics as well, may suffice as illustrations of obscurities in astronomical theory. Stated in the order of their apparent complexity, these obscurities refer to the law of gravitation and to the phenomenon of stellar aberration. Probably both are related, and one may hope that any explanation of either will throw light on the other.

So long as no attempt is made to reconcile the law of gravitation with other branches of physics, progress, up to a certain point, is easy; and probably great advantage has resulted from the fact that dynamical astronomers have not been seriously disturbed by a desire to harmonize this law with the more elementary laws of mechanics. Perhaps they have unconsciously rested on the platform that gravitation is one of the "primordial causes" which are impenetrable to us. There are some indications that even Laplace and Fourier did so rest. However this may be, it has grown steadily more and more imperative during the past century to explain gravitation, or to discover the mechanism which provides that the force between two widely separated masses is proportional to their product directly and to the square of the distance between them inversely. All evidence seems to indicate that the ether must provide this mechanism; but, strangely enough, so far, the ether has baffled all attempts to reveal the secret. The problem has been attacked also on the purely observational side of the numerical value of the gravitation constant. But the splendid experimental researches for this purpose throw no light on the mechanism in question, and, unfortunately, they bring out values for the constant of a low order of precision.

With regard to stellar aberration, it must be at once admitted that we have neither an adequate theory nor a precisely determined fact. The astronomer has generally contented himself with the elementary view that aberration is a purely kinematical phenomenon; that the earth not only slips through the ether without sensible retardation, but that the ether slips through the earth without sensible effects. This difficulty was recognized, in a way, by Young and Fresnel, and, although the subject of elaborate investigation in recent decades, it has proved equally baffling with Newtonian gravitation. As in the case of the latter also, the numerous attempts made to determine the constant of aberration by observational methods have been rewarded by results of only meagre precision. Possibly the time has arrived when one may raise the question, Within what limits is it proper to speak of a gravitation constant or of an aberration constant?

If we agree with Laplace that astronomy is entitled to the highest rank among the physical sciences, we can accord nothing short of second place to the sciences of the earth. Most of them are, indeed, intimately related to astronomy; and some of them are scarcely less ancient in their origins, less dignified in their objects, or less perfect in their theories. Primarily, also, it should be observed, geophysics is not simply a part of, but is the very foundation of, astronomy; for the earth furnishes the orientation, the base-line, and the timepiece by means of which the astronomer explores the heavens. Geology, likewise, in the broader sense of the term, as we are now coming to see, is a fundamental science not only by reason of its interpretations of terrestrial phenomena, but also by reason of its parallel interpretations of celestial phenomena; for there is little doubt that in the evolution of the earth we may read a history which is in large degree typical of the history of celestial bodies. In any revised estimate, therefore, of the relative rank of the physical sciences, while it would be impossible to lower the science of the heavens, it would appear essential to raise the sciences of the earth to a much higher plane of importance than was thought appropriate by our predecessors of a hundred years ago.

As with physics, chemistry, and astronomy, the wonderful progress of the nineteenth century in geophysical science has been along lines converging towards the more recondite properties of matter. All parts of the earth, through observation, experiment, induction, and deduction, have yielded increasing evidence of limited unities amid endless diversities. Adopting the convenient terminology of geologists for the different shells of the earth, let us glance rapidly in turn at the sciences of the atmosphere, the hydrosphere or oceans, the lithosphere or crust, and the centrosphere or nucleus.

The atmosphere is the special province of meteorologists, and although they are not yet able to issue long-range predictions, like those guaranteed by our theories of tides and terrestrial magnetism, it must be admitted that they have made great progress towards a rational description of the apparently erratic phenomena of the weather. One of the peculiar anomalies of this science illustrates in a striking way the general need of additional knowledge of the properties of matter; in this case, especially, the properties of gases. It is the fact that in meteorology greater progress has been made, up to date, in the interpretation of the kinetic than in the interpretation of the static phenomena of the atmosphere. Considering that static properties are usually much simpler than kinetic properties, it seems strange that we should know much more about cyclones, for example, than we do about the mass and the mass distribution of the atmosphere. In respect to this apparently simple question meteorology seems to have made no advance beyond the work of Laplace. There are indications, however, that this, along with many other questions, must await the advent of a new *Principia.*

The geodesists, who are the closest allies of the astronomers, may be said to preside over the hydrosphere, since most of their theories as well as most of their observations are referred to the sea level. They have determined the shape and the size of the earth to a surprising degree of certainty; but they are now confronted by problems which depend chiefly on the mass and mass distribution of the earth. The exquisite refinement of their observational methods has brought to light a minute wandering in the earth of its axis of rotation, which makes the latitude of any place a variable quantity; but the interpretation of this phenomenon is again a physical and not a mensurational problem. They have worked improvements also in all kinds of apparatus for refined measurements, as of base-lines, angles, and differences of level; but here, likewise, they appear to approach limits set by the properties of matter.

The lithosphere was once thought to be the restricted province of geologists, but they now lay claim to the entire earth, from the centre of the centrosphere to the limits of the atmosphere, and they threaten to invade the region of the astronomers on their way toward the outlying domain of cosmogony. Geology illustrates better than any other science, probably, the wide ramifications and the close interrelations of physical phenomena. There is scarcely a process, a product, or a principle in the whole range of physical science, from physics and chemistry up to astronomy and astrophysics, which is not fully illustrated in its uniqueness or in its diversity by actual operations still in progress on the earth, or by actual records preserved in her crust. The earth is thus at once the grandest of laboratories and the grandest of museums available to man.

Any summary statement, from a non-professional student, of the advances in geology during the past century, would be hopelessly inadequate. Such a task could be fitly undertaken only by an expert, or by a corps of them. But out of the impressive array of achievements of this science, two seem to be especially worthy of general attention. They are the essential determination of the properties and the rôle of the lithosphere, and the essential determination of the time-scale suitable for measuring the historical succession of terrestrial events. The lithosphere is the theatre of the principal activities, mechanical and biological, of our planet; and a million years is the smallest convenient unit for recording the march of those activities. When one considers the intellectual as well as the physical obstacles which had to be surmounted, and when one recalls the bitter controversies between the Neptunists and the Vulcanists and between the Catastrophists and the Uniformitarians, these achievements are seen to be amongst the most important in the annals of science.

The centrosphere is the *terra incognita* whose boundaries only are accessible to physical science. It is that part of the earth concerning which astronomers, geologists, and physicists have written much, but concerning which, alas! we are still in doubt. Where direct observation is unattainable, speculation is generally easy, but the exclusion of inappropriate hypotheses is, in such cases, generally difficult. Nevertheless, it may be affirmed that the range of possibilities for the state of the centrosphere has been sharply restricted during the past half-century. Whatever may have been the origin of our planet, whether it has evolved from nebular condensation or from meteoric accretion; and whatever may be the distribution of temperature within the earth's mass as a whole; it appears certain that pressure is the dominant factor within the nucleus. Pressure from above, supplied in hydrostatic measure by the plastic lithosphere, supplemented by internal pressure below, must determine, it would seem, within narrow limits, the actual distribution of density throughout the centrosphere, regardless of its material composition, of its effective rigidity, or of its potential liquidity. Here, however, we are extending the known properties of matter quite beyond the bounds of experience, or of present possible experiment; and we are again reminded of the unity of our needs by the diversity of our difficulties.

In his recently published autobiography, Herbert Spencer asserts that at the time of issue of his work on biology (1864) "not one person in ten or more knew the meaning of the word . . . and among those who knew it, few cared to know anything about the subject." That the attitude of the educated public towards biological science could have been thus indifferent, if not inimical, forty years ago, seems strange enough now even to those of us who have witnessed in part the scientific progress subsequent to that epoch. But this was a memorable epoch, marked by the advent of the great intellectual awakening ushered in by the generalizations of Darwin, Wallace, Spencer, and their coadjutors. And the quarter of a century which immediately followed this epoch appears, as we look back upon it, like an heroic age of scientific achievement. It was an age during which some men of science, and more men not of science, lost their heads temporarily, if not permanently; but it was also an age during which most men of science, and thinking people in general, moved forward at a rate quite without precedent in the history of human advancement. A new, and a greatly enlarged, view of the universe was introduced in the doctrine of evolution, advanced and opposed, alike vigorously, chiefly by reason of its biological applications and implications. Galileo, Newton, and Laplace had given us a system of the inorganic world; Darwin, Spencer, and their followers have foreshadowed a system which includes the organic world as well.

The astonishing progress of biology in recent times furnishes the most convincing evidence of the unity and the efficiency of the methods of physical science in the interpretation of natural phenomena. For the biologist has followed the same methods, with changes appropriate to his subject-matter only, as those found fruitful in astronomy, chemistry, and all the rest. And whatever may be the increased complexity of the organic over the inorganic world, or however high the factor of life may seem to raise the problems of biology above the plane of the other physical sciences, there has appeared no sufficient reason, as yet, to doubt either the validity or the adequacy of those methods.

Moreover, the interrelations of biology with chemistry and physics especially are yearly growing more and more extended and intimate through the rapidly expanding researches of bacteriology, physiology, and physiological chemistry, plant and animal pathology, and so on, up through cytology to the embryology of the higher forms of life. Through the problems of these researches also we are again brought face to face, sooner or later, with the problems of molecular science.

And finally, what may be said of anthropology, which is at once the most interesting and the most novel of the physical sciences, — interesting by reason of its subject-matter, novel by reason of its applications? Some of us, perhaps, might be inclined to demur from a classification which makes man, along with matter, a fit object of investigation in physical science. Granted even that he is usually a not altogether efficient thermodynamic engine, it may yet appear that he is worthy of a separate category. Fortunately, however, it is not a rule of physical science to demand immediate answers to such ulterior questions. It is enough for the present to know that man furnishes no exception, save in point of complexity, to the manifestations of physical phenomena so widely exhibited in the animal kingdom.

But whatever may be our inherited prejudices, or our philosophic judgments, we are confronted by the fact that the study of man in all his attributes is now an established domain of science. And herein we rise to a table-land of transcendent fascination; for, to adapt a phrase of an eminent master in physical science, the instruments of investigation are the objects of research. Herein also we find the culminating unity, not only of the physical sciences, but of all of the sciences; and it is chiefly for the promotion of these higher interests of anthropology that we are assembled in this cosmopolitan congress to-day.

It has been our good fortune to witness in recent decades an unparalleled series of achievements in the fields of physical science. All of them, from anthropology and astronomy up to zoölogy, have yielded rich harvests of results; and one is prone to raise the question whether a like degree of progress may be expected to prevail during the century on which we have now entered. No man can tell what a day may bring forth; much less may one forecast the progress of a decade or a century. But, judging from the long experience of the past, there are few reasons to doubt and many reasons to expect that the future has still greater achievements available. It would appear that we have found the right methods of investigation. Philosophically considered, the remarkable advances of the past afford little cause for marvel. On the contrary, they are just such results as we should anticipate from persistent pursuit of scientific investigation. Conscious of the adequacy of his methods, therefore, the devotee to physical science has every inducement to continue his labors with unflagging zeal and confident optimism.

DEPARTMENT IX — PHYSICS

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(*Hall* 6, *September* 20, 2 *p. m.*)

CHAIRMAN: PROFESSOR HENRY CREW, Northwestern University.
SPEAKERS: PROFESSOR EDWARD L. NICHOLS, Cornell University.
PROFESSOR CARL BARUS, Brown University.

THE Chairman of the Department of Physics was Professor Henry Crew, of Northwestern University, who opened the proceedings of the Department by saying: "Whatever views we may entertain concerning the classification of the sciences which Professor Münsterberg has proposed for the guidance of this congress, we will, I believe, all concur in the opinion that it is full of suggestion and very instructive. For my own part, I think it gives a really profound glimpse into the relationships of the various departments of human learning. You will recall that the first main division is between the pure and applied sciences. We have come together this afternoon to consider a subject which lies in the former group. But physics is not the only pure science: it is merely one belonging to that subdivision which deals with phenomena. Again, there are two classes of phenomena, the mental and the physical: and physics has to do only with the latter class. Indeed, it does not cover the entire field of physical phenomena, but constitutes merely one of the six Departments in this Division. Physics is, however, the most general and most fundamental of this group of six. It is properly found, therefore, at the head of the list. Our theme this afternoon, then, is that fundamental science which deals with the general properties of matter and energy and which includes the general principles of all physical phenomena. We are fortunate in having with us men who, by wide experience gained in their own researches, and by a thorough study of the philosophy of the subject, are eminently fitted to treat this topic."

THE FUNDAMENTAL CONCEPTS OF PHYSICAL SCIENCE

BY EDWARD LEAMINGTON NICHOLS

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All algebra, as was pointed out by von Helmholtz[1] nearly fifty years ago, is based upon the three following very simple propositions:

Things equal to the same thing are equal to each other.

If equals be added to equals the wholes are equal.

If unequals be added to equals the wholes are unequal.

Geometry, he adds, is founded upon a few equally obvious and simple axioms.

The science of physics, similarly, has for its foundation three fundamental conceptions: those of *mass, distance*, and *time*, in terms of which all physical quantities may be expressed.

Physics, in so far as it is an exact science, deals with the relations of these so-called physical quantities; and this is true not merely of those portions of the science which are usually included under the head of physics, but also of that broader realm which consists of the entire group of the physical sciences, viz., astronomy, the physics of the heavens; chemistry, the physics of the atom; geology, the physics of the earth's crust; biology, the physics of matter imbued with life; physics proper (mechanics, heat, electricity, sound, and light).

The manner in which the three fundamental quantities L, M, and T (length, mass, and time) enter, in the case of a physical quantity, is given by its *dimensional formula.*

Thus the dimensional formula for an acceleration is LT^{-2} which expresses the fact that an acceleration is a velocity (a length divided by a time) divided by a time. Energy has for its dimensional formula L^2MT^{-2}; it is a force, $LT^{-2}M$ (an acceleration multiplied by a mass), multiplied by a distance.

Not all physical quantities, in the present state of our knowledge, can be assigned a definite dimensional formula, and this indicates that not all of physics has as yet been reduced to a clearly established

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[1] Von Helmholtz, *Populäre Wissenschaftliche Vorträge*, p. 136.

mechanical basis. The dimensional formula thus affords a valuable criterion of the extent and boundaries of our strictly definite knowledge of physics. Within these boundaries we are on safe and easy ground, and are dealing, independent of all speculation, with the relations between precisely defined quantities. These relations are mathematical, and the entire superstructure is erected upon the three fundamental quantities, L, M, and T, and certain definitions; just as geometry arises from its axioms and definitions.

Of many of those physical quantities, for which we are not as yet able to give the dimensional formula, our knowledge is precise and definite, but it is incomplete. In the case, for example, of one important group of quantities, those used in electric and magnetic measurements, we have to introduce, in addition to L, M, and T, a constant factor to make the dimensional formula complete. This, the *suppressed factor* of Rücker,[1] is μ, the magnetic permeability, when the quantity is expressed in the electromagnetic system, and becomes k, the specific inductive capacity, when the quantity is expressed in terms of the electrostatic system.

Here the existence of the suppressed factor is indicative of our ignorance of the mechanics involved. If we knew in what way a medium like iron increased the magnetic field, or a medium like glass the electric field, we should probably be able to express μ and k in terms of the three selected fundamental dimensions and complete the dimensional formulæ of a large number of quantities.

Where direct mechanical knowledge ceases, the great realm of physical speculation begins. It is the object of such speculation to place all phenomena upon a mechanical basis; excluding as unscientific all occult, obscure, and mystical considerations.

Whenever the mechanism by means of which phenomena are produced is incapable of direct observation either because of its remoteness in space, as in the case of physical processes occurring in the stars, or in time, as in the case of the phenomena with which the geologist has to do, or because of the minuteness of the moving parts, as in molecular physics, physical chemistry, etc., the speculative element is unavoidable. Here we are compelled to make use of analogy. We infer the unknown from the known. Though our logic be without flaw, and we violate no mathematical principle, yet are our conclusions not absolute. They rest of necessity upon *assumptions*, and these are subject to modification indefinitely as our knowledge becomes more complete.

A striking instance of the uncertainties of extrapolation and of the precarious nature of scientific assumptions is afforded by the various estimates of the temperature of the sun. Pouillet placed this temperature between 1461°C. and 1761°C.; Secchi at 5,000,000°; Ericsson

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[1] Rücker, *Philos. Mag.*, 27, p. 104. 1889.

at 2,500,000°. The newer determinations[1] of the temperature of the surface are, to be sure, in better agreement. Le Chatelier finds it to be 7600°; Paschen, 5400°; Warburg, 6000°. Wilson and Gray publish as their corrected result 8000°. The estimate of the internal temperature is of a more speculative character. Schuster's computation gives 6,000,000° to 15,000,000°; that of Kelvin, 200,000,000°; that of Ekholm, 5,000,000°.

Another interesting illustration of the dangers of extrapolation occurs in the history of electricity. Faraday, starting from data concerning the variation between the length of electric sparks through air with the difference of potential, made an interesting computation of the potential difference between earth and sky necessary to discharge a cloud at a height of one mile. He estimated the difference of potential to be about 1,000,000 volts. Later investigations of the sparking distance have, however, shown this function to possess a character quite different from that which might have been inferred from the earlier work, and it is likely that Faraday's value is scarcely nearer the truth than was the original estimate of the temperature of the sun, mentioned above.

Still another notable instance of the errors to which physical research is subject when the attempt is made to extend results beyond the limits established by actual observation occurs in the case of the measurements of the infra-red spectrum of the sun by Langley. His beautiful and ingenious device, the bolometer, made it possible to explore the spectrum to wave-lengths beyond those for which the law of dispersion of the rock-salt prism had at that time been experimentally determined. Within the limits of observation the dispersion showed a curve of simple form, tending apparently to become a straight line as the wave-length increased. There was nothing in the appearance of the curve to indicate that it differed in character from the numerous empirical curves of similar type employed in experimental physics, or to lead even the most experienced investigator to suspect values for the wave-length derived from an extension of the curve. The wave-lengths published by Langley were accordingly accepted as substantially correct by all other students of radiation; but subsequent measurements of the dispersion of rock salt at the hands of Rubens and his co-workers showed the existence of a second sudden and unlooked-for turn of the curve just beyond the point at which the earlier determinations ceased; and in consequence Langley's wave-lengths and all work based upon them are now known to be not even approximately accurate. The history of physics is full of such examples of the dangers of extrapolation, or, to speak more broadly, of the tentative character of most of our assumptions in experimental physics.

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[1] See Arrhenius, *Kosmische Physik*, p. 131.

We have, then, two distinct sets of physical concepts. The first of these deals with that positive portion of physics, the mechanical basis of which, being established upon direct observation, is fixed and definite, and in which the relations are as absolute and certain as those of mathematics itself. Here speculation is excluded. Matter is simply one of the three factors, which enters, by virtue of its mass, into our formulæ for energy, momentum, etc. Force is simply a quantity of which we need to know only its magnitude, direction, point of application, and the time during which it is applied. The Newtonian conception of force — the producer of motion — is adequate. All troublesome questions as to how force acts, of the mechanism by means of which its effects are produced, are held in abeyance.

Speculative physics, to which the second set of concepts belongs, deals with those portions of the science for which the mechanical basis has to be imagined. Heat, light, electricity, and the science of the nature and ultimate properties of matter belong to this domain.

In the history of the theory of heat we find one of the earliest manifestations of a tendency so common in speculative physics that it may be considered characteristic: the assumption of a medium. The medium in this case was the so-called *imponderable* caloric; and it was one of a large class, of which the two electric fluids, the magnetic fluid, etc., were important members.

The theory of heat remained entirely speculative up to the time of the establishment of the mechanical equivalent of heat by Joule. The discovery that heat could be measured in terms of work injected into thermal theory the conception of energy, and led to the development of thermodynamics.

Generalizations of the sort expressed by Tyndall's phrase, *heat a mode of motion,* follow easily from the experimental evidence of the part which energy plays in thermal phenomena, but the specification of the precise mode of motion in question must always depend upon our views concerning the nature of matter, and can emerge from the speculative stage only, if ever, when our knowledge of the mechanics of the constitution of matter becomes fixed. The problem of the mechanism by which energy is stored or set free rests upon a similar speculative basis.

These are proper subjects for theoretical consideration, but the dictum of Rowland [1] that we get out of mathematical formulæ only what we put into them should never be lost from sight. So long as we put in only assumptions we shall take out hypotheses, and useful as these may prove, they are to be regarded as belonging to the realm of scientific speculation. They must be recognized as subject to modification indefinitely as we, in consequence of increasing knowledge, are led to modify our assumptions.

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[1] Rowland, *President's Address to the American Physical Society,* 1900.

The conditions with which the physicist has to deal in his study of optics are especially favorable to the development of the scientific imagination, and it is in this field that some of the most remarkable instances of successful speculative work are to be found. The emission theory died hard, and the early advocates of the undulatory theory of light were forced to work up, with a completeness probably without parallel in the history of science, the evidence, necessarily indirect, that in optics we have to do with a wave-motion. The standpoint of optical theory may be deemed conclusive, possibly final, so far as the general proposition is concerned that it is the science of a wave-motion. In a few cases, indeed, such as the photography of the actual nodes of a standing wave-system, by Wiener, we reach the firm ground of direct observation.

Optics has nevertheless certain distinctly speculative features. Wave-motion demands a medium. The enormous velocity of light excludes known forms of matter; the transmission of radiation *in vacuo* and through outer space from the most remote regions of the universe, and at the same time through solids such as glass, demands that this medium shall have properties very different from that of any substance with which chemistry has made us acquainted.

The assumption of a medium is, indeed, an intellectual necessity, and the attempt to specify definitely the properties which it must possess in order to fulfill the extraordinary functions assigned to it has afforded a field for the highest display of scientific acumen. While the problem of the mechanism of the luminiferous ether has not as yet met with a satisfactory solution, the ingenuity and imaginative power developed in the attack upon its difficulties command our admiration.

Happily the development of what may be termed the older optics did not depend upon any complete formulation of the mechanics of the ether. Just as the whole of the older mechanics was built up from Kepler's laws, Newton's laws of motion, the law of gravitational attraction, the law of inverse squares, etc., without any necessity of describing the mechanics of gravitation or of any force, or of matter itself, so the system of geometrical relations involved in the consideration of reflection and refraction, diffraction, interference, and polarization was brought to virtual completion without introducing the troublesome questions of the nature of the ether and the constitution of matter.

Underlying this field of geometrical optics, or what I have just termed the older optics, are, however, a host of fundamental questions of the utmost interest and importance, the treatment of which depends upon molecular mechanics and the mechanics of the ether. Our theories as to the nature and causes of radiation, of absorption, and of dispersion, for example, belong to the newer optics, and are based upon our conceptions of the constitution of matter; and since our ideas concerning the nature of matter, like our knowledge of the ether, is purely speculative, the science of optics has a doubly speculative basis. One type of selective absorption, for example, is ascribed to resonance of the particles of the absorbing substance, and our modern dispersion theories depend upon the assumption of natural periods of vibration of the particles of the refracting medium of the same order of frequency as that of the light-waves. When the frequency of the waves falling upon a substance coincides with the natural period of vibration of the particles of the latter, we have selective absorption, and accompanying it, anomalous dispersion. For these and numerous other phenomena no adequate theory is possible which does not have its foundation upon some assumed conception as to the constitution of matter.

The development of the modern idea of the ether forms one of the most interesting chapters in the history of physics. We find at first a tendency to assume a number of distinct media corresponding to the various effects (visual, chemical, thermal, phosphorescent, etc.) of light-waves, and later the growth of the conception of a single medium, the luminiferous ether.

In the development of electricity and magnetism, meantime, the assumption of media was found to be an essential — something without which no definite philosophy of the phenomena was possible. At first there was the same tendency to a multiplicity of media — there were the positive and negative electric fluids, the magnetic fluid, etc. Then there grew up in the fertile mind of Faraday that wonderful fabric of the scientific imagination, the electric field; the conception upon which all later attempts to form an idea of a thinkable mechanism of electric and magnetic action have been established.

It is the object of science, as has been pointed out by Ostwald, to reduce the number of hypotheses; the highest development would be that in which a single hypothesis served to elucidate the relations of the entire universe. Maxwell's discovery that the whole theory of optics is capable of expression in terms identical with those found most convenient and suitable in electricity, in a word, that optics may be treated simply as a branch of electromagnetics, was the first great step towards such a simplification of our fundamental conceptions. This was followed by Hertz's experimental demonstration of the existence of artificially produced electromagnetic waves in every respect identical with light-waves, an achievement which served to establish upon a sure foundation the conception of a single medium. The idea of one universal medium as the mechanical basis for all physical phenomena was not altogether new to the theoretical physicist, but the unification of optics and electricity did much to strengthen this conception.

The question of the ultimate structure of matter, as has already been pointed out, is also speculative in the sense that the mechanism upon which its properties are based is out of the range of direct observation. For the older chemistry and the older molecular physics the assumption of an absolutely simple atom and of molecules composed of comparatively simple groupings of such atoms sufficed. Physical chemistry and that new phase of molecular physics which has been termed the physics of the ion demand the breaking up of the atom into still smaller parts and the clothing of these with an electric charge. The extreme step in this direction is the suggestion of Larmor that the electron is a "disembodied charge" of negative electricity. Since, however, in the last analysis, the only conception having a definite and intelligible mechanical basis which physicists have been able to form of an electric charge is that which regards it as a phenomenon of the ether, this form of speculation is but a return under another name to views which had earlier proved attractive to some of the most brilliant minds in the world of science, such as Helmholtz and Kelvin. The idea of the atom, as a vortex motion of a perfect fluid (the ether), and similar speculative conceptions, whatever be the precise form of mechanism imagined, are of the same class as the moving electric charge of the later theorists.

Lodge,[1] in a recent article in which he attempts to voice in a popular way the views of this school of thought, says:

"*Electricity under strain constitutes 'charge'; electricity in locomotion constitutes light. What electricity itself is we do not know, but it may, perhaps, be a form or aspect of matter. . . . Now we can go one step further and say, matter is composed of electricity and of nothing else. . . .*"

If for the word *electricity* in this quotation from Lodge we substitute *ether*, we have a statement which conforms quite as well to the accepted theories of light and electricity as his original statement does to the newer ideas it is intended to express.

This reconstructed statement would read as follows:

Ether under strain constitutes "charge"; *ether* in locomotion constitutes current and magnetism; *ether* in vibration constitutes light. What *ether* itself is we do not know, but it may, perhaps, be a form or aspect of matter. Now we can go one step further and say: "Matter is composed of *ether* and of nothing else."

The use of the word electricity, as employed by Lodge and others, is now much in vogue, but it appears to me unfortunate. It would be distinctly conducive to clearness of thought and an avoidance of confusion to restrict the term to the only meaning which is free from criticism; that in which it is used to designate the science which deals with electrical phenomena.

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[1] Lodge, *Harper's Magazine*, August, 1904, p. 383.

The only way in which the noun *electricity* enters, in any definite and legitimate manner, into our electrical treatises is in the designation of Q in the equations—

$$Q = \int I dt,\ C = Q|E,\ W = QE, \text{ etc.}$$

Here we are in the habit — whether by inheritance from the age of the electric fluid, by reason of the hydrodynamic analogy, or as a matter of convention or of convenience merely — of calling Q the *quantity of electricity.*

Now Q is "charge" and its unit, the coulomb, is unit-charge. The alternative expression, *quantity of electricity,* is a purely conventional designation and without independent physical significance. It owes its prevalence among electricians to the fact that by virtue of long familiarity we prefer to think in terms of matter, which is tangible, rather than of ether. Charge is to be regarded as fundamental, and its substitute, quantity of electricity, as merely an artificial term of convenience; because of the former we have a definite mechanical conception, whereas we can intelligently define a quantity of electricity only in terms of *charge.*

In the science of heat the case differs, in that the term heat is used, if not as precisely synonymous with energy, at least for a quantity having the same dimensions as energy and having as its unit the erg. It might easily have happened, as has happened in electrical theory, that the ancient notion of a *heat substance* should survive, in which case we should have had for the quantity of heat not something measured in terms of energy, but, as in the case of electricity, one of the terms which enter into our expression for energy. We should then have had to struggle continually, in thermodynamics, as we now do in electrical theory, against the tendency to revert to an antiquated and abandoned view.

It would, I cannot but think, have been fortunate had the word electricity been used for what we now call electrical energy; using *charge,* or some other convenient designation, for the quantity Q. That aspect of the science in accordance with which we regard it as a branch of energetics in which movements of the ether are primarily involved would have been duly emphasized. We should have been quit forever of the bad notion of electricity as a medium, just as we are already freed from the incubus of heat as a medium. We should have had *electricity — a mode of motion* (or stress), *ether,* as we have *heat — a mode of motion of matter.* When our friends asked us: "What is electricity?" we should have had a ready answer for them instead of a puzzled smile.

One real advance which has been attained by means of the theory of ionization, and it is of extreme significance and of far-reaching importance, consists in the discovery that electrification, or the possession of charge, instead of being a casual or accidental property, temporarily imparted by friction or other process, is a fundamental property of matter. According to this newer conception of matter, the fruit of the ionic theory, the ultimate parts of matter are electrically charged particles. In the language of Rutherford:[1]

"It must then be supposed that the process of ionization in gases consists in a removal of a negative corpuscle or electron from the molecule of gas. At atmospheric pressure this corpuscle immediately becomes the centre of an aggregation of molecules which moves with it and *is* the negative ion. After removal of the negative ion the molecule retains a positive charge and probably also becomes the centre of a cluster of new molecules.

"The *electron* or *corpuscle* is the body of smallest mass yet known to science. It carries a negative charge of 3.4×10^{-10} electrostatic units. Its presence has only been detected when in rapid motion, when it has for speeds up to about 10^{10} cms. a second, an apparent mass m given by $e/m - 1.86 \times 10^{7}$ electromagnetic units. This apparent mass increases with the speed as the velocity of light is approached."

At low pressures the electron appears to lose its load of clustering molecules, so that finally the negative ion becomes identical with the electron or corpuscle, and has a mass, according to the estimates of J. J. Thomson, about one thousandth of that of the hydrogen atom. The positive ion is, however, supposed to remain of atomic size even at low pressures.

The ionic theory and the related hypothesis of electrolytic dissociation afford a key to numerous phenomena concerning which no adequate or plausible theories had hitherto been formed. By means of them explanations have been found, for example, of such widely divergent matters as the positive electric charge known to exist in the upper atmosphere, and the perplexing phenomena of fluorescence.

The evidence obtained by J. J. Thomson and other students of ionization, that electrons from different substances are identical, has greatly strengthened the conviction which for a long time has been in process of formation in the minds of physicists, that all matter is in its ultimate nature identical. This conception, necessarily speculative, has been held in abeyance by the facts, regarded as established, and lying at the foundation of the accepted system of chemistry, of the conservation of matter and the intransmutability of the elements. The phenomena observed in recent investigations of radioactive substances have, however, begun to shake our faith in this principle.

If matter is to be regarded as a product of certain operations performed upon the ether, there is no theoretical difficulty about

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[1] Rutherford, *Radioactivity*, p. 53. 1904.

transmutation of elements, variation of mass, or even the complete disappearance or creation of matter. The absence of such phenomena in our experience has been the real difficulty, and if the views of students of radioactivity concerning the transformations undergone by uranium, thorium, and radium are substantiated, the doctrines of the conservation of mass and matter which lie at the foundation of the science of chemistry will have to be modified. There has been talk of late of violations of the principle of the conservation of energy in connection with the phenomena of radioactivity, but the conservation of matter is far more likely to lose its place among our fundamental conceptions.

The development of physics on the speculative side has led, then, to the idea, gradually become more definite and fixed, of a universal medium, the existence of which is a matter of inference. To this medium properties have been assigned which are such as to enable us to form an intelligible, consistent conception of the mechanism by means of which phenomena, the mechanics of which is not capable of direct observation, may be logically considered to be produced. The great step in this speculation has been the discovery that a single medium may be made to serve for the numerous phenomena of optics, and that, without ascribing to it any characteristics incompatible with a luminiferous ether, it is equally available for the description and explanation of electric and magnetic fields, and finally may be made the basis for intelligible theories of the structure of matter.

To many minds this seemingly universal adaptability of the ether to the needs of physics almost removes it from the field of speculation; but it should not be forgotten that a system, entirely imaginary, may be devised, which fits all the known phenomena and appears to offer the only satisfactory explanation of the facts, and which subsequently is abandoned in favor of other views. The history of physics is full of instances where a theory is for a time regarded as final on account of its seeming completeness, only to give way to something entirely different.

In this consideration of the fundamental concepts I have attempted to distinguish between those which have the positive character of mathematical laws and which are entirely independent of all theories of the ultimate nature of matter, and those which deal with the latter questions and which are essentially speculative. I have purposely refrained from taking that further step which plunges us from the heights of physics into the depths of philosophy.

With the statement that science in the ultimate analysis is nothing more than *an attempt to classify and correlate our sensations* the physicist has no quarrel. It is, indeed, a wholesome discipline for him to formulate for himself his own relations to his science in terms such as those which, to paraphrase and translate very freely the opening passages of his recent *Treatise on Physics*, Chwolson [1] has employed.

"For every one there exist two worlds, an inner and an outer, and our senses are the medium of communication between the two. The outer world has the property of acting upon our senses, to bring about certain changes, or, as we say, to exert certain stimuli.

"The inner world, for any individual, consists of all those phenomena which are absolutely inaccessible (so far as direct observation goes) to other individuals. The stimulus from the outer world produces in our inner world a subjective perception which is dependent upon our *consciousness*. The subjective perception is made objective, viz., is assigned *time* and *place* in the outer world and given a name. The investigation of the processes by which this objectivication is performed is a function of philosophy."

Some such confession of faith is good for the man of science, —*lest he forget;* but once it is made he is free to turn his face to the light once more, thankful that the *investigation of objectivication* is, indeed, *a function of philosophy*, and that the only speculations in which he, as a physicist, is entitled to engage are those which are amenable at every step to mathematics and to the equally definite axioms and laws of mechanics.

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[1] Chwolson, *Physik*, vol. I, Introduction.

THE PROGRESS OF PHYSICS IN THE NINETEENTH CENTURY

BY CARL BARUS

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You have honored me by requesting at my hands an account of the advances made in physics during the nineteenth century. I have endeavored, in so far as I have been able, to meet the grave responsibilities implied in your invitation; yet had I but thought of the overwhelmingly vast territory to be surveyed, I well might have hesitated to embark on so hazardous an undertaking. To mention merely the *names* of men whose efforts are linked with splendid accomplishments in the history of modern physics would far exceed the time allotted to this address. To bear solely on certain subjects, those, for instance, with which I am more familiar, would be to develop an unsymmetrical picture. As this is to be avoided, it will be necessary to present a straightforward compilation of all work above a certain somewhat vague and arbitrary lower limit of importance. Physics is, as a rule, making vigorous though partial progress along independent parallel lines of investigation, a discrimination between which is not possible until some cataclysm in the history of thought ushers in a new era. It will be essential to abstain from entering into either explanation or criticism, and to assume that all present are familiar with the details of the subjects to be treated. I can neither popularize nor can I endeavor to entertain, except in so far as a rapid review of the glorious conquests of the century may be stimulating.

In spite of all this simplicity of aim, there is bound to be distortion. In any brief account, the men working at the beginning of the century, when investigations were few and the principles evolved necessarily fundamental, will be given greater consideration than equally able and abler investigations near the close, when workers (let us be thankful) were many, and the subjects lengthening into detail. Again, the higher order of genius will usually be additionally exalted at the expense of the less gifted thinker. I can but regret that these are the inevitable limitations of the cursory treatment prescribed.

As time rolls on, the greatest names more and more fully absorb the activity of a whole epoch.

Metrology

Finally, it will hardly be possible to consider the great advances made in physics except on the theoretical side. Of renowned experimental researches, in particular of the investigations of the constants of nature to a degree of ever-increasing accuracy, it is not practicable to give any adequate account. Indeed, the refinement and precision now demanded have placed many subjects beyond the reach of individual experimental research, and have culminated in the establishment of the great national or international laboratories of investigation at Sèvres (1872), at Berlin (1887, 1890), at London (1900), at Washington (1901). The introduction of uniform international units in cases of the arts and sciences of more recent development is gradually, but inexorably, urging the same advantages on all. Finally, the access to adequate instruments of research has everywhere become an easier possibility for those duly qualified, and the institutions and academies which are systematically undertaking the distribution of the means of research are continually increasing in strength and in number.

Classification

In the present paper it will be advisable to follow the usual procedure in physics, taking in order the advances made in dynamics, acoustics, heat, light, and electricity. The plan pursued will, therefore, specifically consider the progress in elastics, crystallography, capillarity, solution, diffusion, dynamics, viscosity, hydrodynamics, acoustics; in thermometry, calorimetry, thermodynamics, kinetic theory, thermal radiation; in geometric optics, dispersion, photometry, fluorescence, photochemistry, interference, diffraction, polarization, optical media; in electrostatics, Volta contacts, Seebeck contacts, electrolysis, electric current, magnetism, electromagnetism, electrodynamics, induction, electric oscillation, electric field, radioactivity.

Surely this is too extensive a field for any one man! Few who are not physicists realize that each of these divisions has a splendid and voluminous history of development, its own heroes, its sublime classics, often culled from the activity of several hundred years. I repeat that few understand the unmitigatedly fundamental character, the scope, the vast and profound intellectual possessions, of pure physics; few think of it as the one science into which all other sciences must ultimately converge — or a separate representation would have been given to most of the great divisions which I have named.

Hence even if the literary references may be given in print with some fullness, it is impossible to refer verbally to more than the chief actors, and quite impossible to delineate sharply the real significance and the relations of what has been done. Moreover, the dates will in most instances have to be omitted from the reading. It has been my aim, however, to collect the greater papers in the history of physics, and the suggestion is implied that science would gain if by some august tribunal researches of commanding importance were formally canonized for the benefit of posterity.

Elastics

To begin with elasticity, whose development has been of such marked influence throughout the whole of physics, we note that the theory is virtually a creation of the nineteenth century. Antedating Thomas Young, who in 1807 gave to the subject the useful conception of a modulus, and who seems to have definitely recognized the shear, there were merely the experimental contribution of Galileo (1638), Hooke (1660), Mariotte (1680), the elastic curve of J. Bernoulli (1705), the elementary treatment of vibrating bars of Euler and Bernoulli (1742), and an attempted analysis of flexure and torsion by Coulomb (1776).

The establishment of a theory of elasticity on broad lines begins almost at a bound with Navier (1821), reasoning from a molecular hypothesis to the equation of elastic displacement and of elastic potential energy (1822–1827); yet this startling advance was destined to be soon discredited, in the light of the brilliant generalizations of Cauchy (1827). To him we owe the six component stresses and the six component strains, the stress quadric and the strain quadric, the reduction of the components to three principal stresses and three principal strains, the ellipsoids, and other of the indispensable conceptions of the present day. Cauchy reached his equations both by the molecular hypothesis and by an analysis of the oblique stress across an interface, — methods which predicate fifteen constants of elasticity in the most general case, reducing to but one in the case of isotropy. Contemporaneous with Cauchy's results are certain independent researches by Lamé and Clapeyron (1828) and by Poisson (1829).

Another independent and fundamental method in elastics was introduced by Green (1837), who took as his point of departure the potential energy of a conservative system in connection with the Lagrangian principle of virtual displacements. This method, which has been fruitful in the hands of Kelvin (1856), of Kirchhoff (1876), of Neumann (1885), leads to equations with twenty-one constants for the æolotropic medium reducing to two in the simplest case.

The wave-motion in an isotropic medium was first deduced by Poisson in 1828, showing the occurrence of longitudinal and transverse waves of different velocities; the general problem of wave-motion in æolotropic media, though treated by Green (1842), was attacked with requisite power by Blanchet (1840–1842) and by Christoffel (1877).

Poisson also treated the case of radial vibrations of a sphere (1828), a problem which, without this restriction, awaited the solutions of Jaerisch (1879) and of Lamb (1882). The theory of the free vibrations of solids, however, is a generalization due to Clebsch (1857–58, *Vorlesungen*, 1862).

Elasticity received a final phenomenal advance through the long-continued labors of de St. Venant (1839–55), which in the course of his editions of the work of Moigno, of Navier (1863), and of Clebsch (1864), effectually overhauled the whole subject. He was the first to assert adequately the fundamental importance of the shear. The profound researches of de St. Venant on the torsion of prisms and on the flexure of prisms appeared in their complete form in 1855 and 1856. In both cases the right sections of the stressed solids are shown to be curved, and the curvature is succinctly specified; in the former Coulomb's inadequate torsion formula is superseded, and in the latter flexural stress is reduced to a transverse force and a couple. But these mere statements convey no impression of the magnitude of the work.

Among other notable creations with a special bearing on the theory of elasticity there is only time to mention the invention and application of curvilinear coördinates by Lamé (1852); the reciprocal theorem of Betti (1872), applied by Cerruti (1882) to solids with a plane boundary — problems to which Lamé and Clapeyron (1828) and Boussinesq (1879–85) contributed by other methods; the case of the strained sphere studied by Lamé (1854) and others; Kirchhoff's flexed plate (1850); Rayleigh's treatment of the oscillations of systems of finite freedom (1873); the thermo-elastic equations of Duhamel (1838), of F. Neumann (1841), of Kelvin (1878); Kelvin's analogy of the torsion of prisms with the supposed rotation of an incompressible fluid within (1878); his splendid investigations (1863) of the dynamics of elastic spheroids and the geophysical applications to which they were put.

Finally, the battle royal of the molecular school following Navier, Poisson, Cauchy, and championed by de St. Venant, with the disciples of Green, headed by Kelvin and Kirchhoff, — the struggle of the fifteen constants with the twenty-one constants, in other words, — seems to have temporarily subsided with a victory for the latter through the researches of Voigt (1887–89).

Crystallography

Theoretical crystallography, approached by Steno (1669), but formally founded by Haüy (1781, *Traité*, 1801), has limited its development during the century to systematic classifications of form. Thus the thirty-two type sets of Hessel (1830) and of Bravais (1850) have expanded into the more extensive point series involving 230 types due to Jordan (1868), Sohncke (1876), Federow (1890), and Schoenfliess (1891). Physical theories of crystalline form have scarcely been unfolded.

Capillarity

Capillarity antedated the century in little more than the provisional, though brilliant, treatment due to Clairaut (1743). The theory arose in almost its present state of perfection in the great memoir of Laplace (1805), one of the most beautiful examples of the Newton-Boscovichian (1758) molecular dynamics. Capillary pressure was here shown to vary with the principal radii of curvature of the exposed surface, in an equation involving two constants, one dependent on the liquid only, the other doubly specific for the bodies in contact. Integrations for special conditions include the cases of tubes, plates, drops, contact angle, and similar instances. Gauss (1829), dissatisfied with Laplace's method, virtually reproduced the whole theory from a new basis, avoiding molecular forces in favor of Lagrangian displacements, while Poisson (1831) obtained Laplace's equations by actually accentuating the molecular hypothesis; but his demonstration has since been discredited. Young in 1805 explained capillary phenomena by postulating a constant surface tension, a method which has since been popularized by Maxwell (*Heat*, 1872).

With these magnificent theories propounded for guidance at the very threshold of the century, one is prepared to anticipate the wealth of experimental and detailed theoretical research which has been devoted to capillarity. Among these the fascinating monograph of Plateau (1873), in which the consequences of theory are tested by the behavior both of liquid lamellæ and by suspended masses, Savart's (1833), and particularly Rayleigh's, researches with jets (1879–83), Kelvin's ripples (1871), may be cited as typical. Of peculiar importance, quite apart from its meteorological bearing, is Kelvin's deduction (1870) of the interdependence of surface tension and vapor pressure when varying with the curvature of a droplet.

Diffusion

Diffusion was formally introduced into physics by Graham (1850). Fick (1855), appreciating the analogy of diffusion and heat conduction, placed the phenomenon on a satisfactory theoretical basis, and Fick's law has since been rigorously tested, in particular by H. F. Weber (1879).

The development of diffusion from a physical point of view followed Pfeffer's discovery (1877) of osmotic pressure, soon after to be interpreted by van 't Hoff (1887) in terms of Boyle's and Avogadro's laws. A molecular theory of diffusion was thereupon given by Nernst (1887).

Dynamics

In pure dynamics the nineteenth century inherited from the eighteenth that unrivaled feat of reasoning called by Lagrange the *Mécanique analytique* (1788), and the great master was present as far as 1813 to point out its resources and to watch over the legitimacy of its applications. Throughout the whole century each new advance has but vindicated the preëminent power and safety of its methods. It triumphed with Maxwell (1864), when he deduced the concealed kinetics of the electromagnetic field, and with Gibbs (1876–78), when he adapted it to the equilibrium of chemical systems. It will triumph again in the electromagnetic dynamics of the future.

Naturally there were reactions against the tyranny of the method of "liaisons." The most outspoken of these, propounded under the protection of Laplace himself, was the celebrated *Mécanique physique* of Poisson (1828), an accentuation of Boscovich's (1758) dynamics, which permeates the work of Navier, Cauchy, de St. Venant, Boussinesq, even Fresnel, Ampère, and a host of others. Cauchy in particular spent much time to reconcile the molecular method with the Lagrangian abstractions. But Poisson's method, though sustained by such splendid genius, has, nevertheless, on more than one occasion — in capillarity, in elastics — shown itself to be untrustworthy. It was rudely shaken when, with the rise of modern electricity, the influence of the medium was more and more pushed to the front.

Another complete reconstruction of dynamics is due to Thomson and Tait (1867), in their endeavor to gain clearness and uniformity of design, by referring the whole subject logically back to Newton. This great work is the first to make systematic use of the doctrine of the conservation of energy.

Finally, Hertz (1894), imbued with the general trend of contemporaneous thought, made a powerful effort to exclude force and potential energy from dynamics altogether — postulating a universe of concealed motions such as Helmholtz (1884) had treated in his theory of cyclic systems, and Kelvin had conceived in his adynamic gyrostatic ether (1890). In fact, the introduction of concealed systems and of ordered molecular motions by Helmholtz and Boltzmann has proved most potent in justifying the Lagrangian dynamics in its application to the actual motions of nature.

The specific contributions of the first rank which dynamics owes to the last century, engrossed as it was with the applications of the subject, or with its mathematical difficulties, are not numerous. In chronological order we recall naturally the statics (1804) and the rotational dynamics (1834) of Poinsot, all in their geometrical character so surprisingly distinct from the contemporary dynamics of Lagrange and Laplace. We further recall Gauss's principle of least constraint (1829), but little used, though often in its applications superior to the method of displacement; Hamilton's principle of varying action (1834) and his characteristic function (1834, 1835), the former obtainable by an easy transition from D'Alembert's principle and by contrast with Gauss's principle, of such exceptional utility in the development of modern physics; finally the development of the Leibnitzian doctrine of work and *vis viva* into the law of the conservation of energy, which more than any other principle has consciously pervaded the progress of the nineteenth century. Clausius's theorem of the *Virial* (1870) and Jacobi's (1866) contributions should be added among others.

The potential, though contained explicitly in the writings of Lagrange (1777), may well be claimed by the last century. The differential equation underlying the doctrine had already been given by Laplace in 1782, but it was subsequently to be completed by Poisson (1827). Gauss (1813, 1839) contributed his invaluable theorems relative to the surface integrals and force flux, and Stokes (1854) his equally important relation of the line and the surface integral. Legendre (published 1785) and Laplace (1782) were the first to apply spherical harmonics in expansions. The detailed development of volume surface and line potential has enlisted many of the ablest writers, among whom Chasles (1837, 1839, 1842), Helmholtz (1853), C. Neumann (1877, 1880), Lejeune-Dirichlet (1876), Murphy (1833), and others are prominent.

The gradual growth of the doctrine of the potential would have been accelerated, had not science to its own loss overlooked the famous essay of Green (1828), in which many of the important theorems were anticipated, and of which Green's theorem and Green's function are to-day familiar reminders.

Recent dynamists incline to the uses of the methods of modern geometry and to the vector calculus with continually increasing favor. Noteworthy progress was first made in this direction by Moebius (1837–43, *Statik*, 1838), but the power of these methods to be fully appreciated required the invention of the *Ausdehnungslehre*, by Grassmann (1844), and of *quaternions*, by Hamilton (1853).

Finally the profound investigations of Sir Robert Ball (1871, *et seq.*, *Treatise*) on the theory of screws with its immediate dynamical applications, though as yet but little cultivated except by the author, must be reckoned among the promising heritages of the twentieth century.

On the experimental side it is possible to refer only to researches of a strikingly original character, like Foucault's pendulum (1851) and Fizeau's gyrostat; or like Boys's (1887, *et seq.*) remarkable quartz-fibre torsion-balance, by which the Newtonian constant of gravitation and the mean density of the earth originally determined by Maskelyne (1775–78) and by Cavendish (1798) were evaluated with a precision probably superior to that of the other recent measurements, the pendulum work of Airy (1856) and Wilsing (1885–87), or the balance methods of Jolly (1881), König, and Richarz (1884). Extensive transcontinental gravitational surveys like that of Mendenhall (1895) have but begun.

Hydrodynamics

The theory of the equilibrium of liquids was well understood prior to the century, even in the case of rotating fluids, thanks to the labors of Maclaurin (1742), Clairaut (1743), and Lagrange (1788). The generalizations of Jacobi (1834) contributed the triaxial ellipsoid of revolution, and the case has been extended to two rotating attracting masses by Poincaré (1885) and Darwin (1887). The astonishing revelations contained in the recent work of Poincaré are particularly noteworthy.

Unlike elastics, theoretical hydrodynamics passed into the nineteenth century in a relatively well-developed state. Both types of the Eulerian equations of motion (1755, 1759) had left the hands of Lagrange (1788) in their present form. In relatively recent times H. Weber (1868) transformed them in a way combining certain advantages of both, and another transformation was undertaken by Clebsch (1859). Hankel (1861) modified the equation of continuity, and Svanberg and Edlund (1847) the surface conditions.

Helmholtz in his epoch-making paper of 1858 divided the subject into those classes of motion (flow in tubes, streams, jets, waves) for which a velocity potential exists and the vortex motions for which it does not exist. This classification was carried even into higher orders of motion by Craig and by Rowland (1881). For cases with a velocity potential, much progress has been made during the century in the treatment of waves, of discontinuous fluid motion, and in the dynamics of solids suspended in frictionless liquids. Kelland (1844), Scott Russel (1844), and Green (1837) dealt with the motion of progressive waves in relatively shallow vessels, Gerster (1804) and Rankine (1863) with progressive waves in deep water, while Stokes (1846, 1847, 1880), after digesting the contemporaneous advances in hydrodynamics, brought his powerful mind to bear on most of the outstanding difficulties. Kelvin introduced the case of ripples (1871), afterwards treated by Rayleigh (1883). The solitary wave of Russel occupied Boussinesq (1872, 1882), Rayleigh (1876), and others; group-waves were treated by Reynolds (1877) and Rayleigh (1879). Finally the theory of stationary waves received extended attention in the writings of de St. Venant (1871), Kirchhoff (1879), and Greenhill (1887). Early experimental guidance was given by the classic researches of C. H. and W. Weber (1825).

The occurrence of discontinuous variation of velocity within the liquid was first fully appreciated by Helmholtz (1868), later by Kirchhoff (1869), Rayleigh (1876), Voigt (1885), and others. It lends itself well to conformal representations.

The motions of solids within a liquid have fascinated many investigators, and it is chiefly in connection with this subject that the method of sources and sinks was developed by English mathematicians, following Kelvin's method (1856) for the flow of heat. The problem of the sphere was solved more or less completely by Poisson (1832), Stokes (1843), Dirichlet (1852); the problem of the ellipsoid by Green (1833), Clebsch (1858), generalized by Kirchhoff (1869). Rankine treated the translatory motion of cylinders and ellipsoids in a way bearing on the resistance of ships. Stokes (1843) and Kirchhoff entertain the question of more than one body. The motion of rings has occupied Kirchhoff (1869), Boltzmann (1871), Kelvin (1871), Bjerknes (1879), and others. The results of C. A. Bjerknes (1868) on the fields of hydrodynamic force surrounding spheres, pulsating or oscillating, in translatory or rotational motion, accentuate the remarkable similarity of these fields with the corresponding cases in electricity and magnetism, and have been edited in a unique monograph (1900) by his son. In a special category belong certain powerful researches with a practical bearing, such as the modern treatment of ballistics by Greenhill and of the ship propeller of Ressel (1826), summarized by Gerlach (1885, 1886).

The numerous contributions of Kelvin (1888, 1889) in particular have thrown new light on the difficult but exceedingly important question of the stability of fluid motion.

The century, moreover, has extended the working theory of the tides due to Newton (1687) and Laplace (1774), through the labors of Airy, Kelvin, and Darwin.

Finally the forbidding subject of vortex motion was gradually approached more and more fully by Lagrange, Cauchy (1815, 1827), Svanberg (1839), Stokes (1845); but the epoch-making integrations of the differential equations, together with singularly clear-cut interpretations of the whole subject, are due to Helmholtz (1858). Kelvin (1867, 1883) soon recognized the importance of Helmholtz's work and extended it, and further advance came in particular from J. J. Thomson (1883) and Beltrami (1875). The conditions of stability in vortex motion were considered by Kelvin (1880), Lamb (1878), J. J. Thomson, and others, and the cases of one or more columnar vortices, of cylindrical vortex sheets, of one or more vortex rings, simple or linked, have all yielded to treatment.

The indestructibility of vortex motion in a frictionless fluid, its open structure, the occurrence of reciprocal forces, were compared by Kelvin (1867) with the essential properties of the atom. Others like Fitzgerald in his cobwebbed ether, and Hicks (1885) in his vortex sponge, have found in the properties of vortices a clue to the possible structure of the ether. Yet it has not been possible to deduce the principles of dynamics from the vortex hypothesis, neither is the property which typifies the mass of an atom clearly discernible. Kelvin invokes the corpuscular hypothesis of Lesage (1818).

Viscosity

The development of viscous flow is largely on the experimental side, particularly for solids, where Weber (1835), Kohlrausch (1863, *et seq.*), and others have worked out the main laws. Stokes (1845) deduced the full equations for liquids. Poiseiulle's law (1847), the motion of small solids in viscous liquids, of vibrating plates, and other important special cases, has yielded to treatment. The coefficients of viscosity defined by Poisson (1831), Maxwell (1868), Hagenbach (1860), O. E. Meyer (1863), are exhaustively investigated for gases and for liquids. Maxwell (1877) has given the most suggestive and Boltzmann (1876) the most carefully formulated theory for solids, but the investigation of absolute data has but begun. The difficulty of reconciling viscous flow with Lagrange's dynamics seems first to have been adjusted by Navier.

Aeromechanics

Aerostatics is indissolubly linked with thermodynamics. Aerodynamics has not marked out for itself any very definite line of progress. Though the resistance of oblique planes has engaged the attention of Rayleigh, it is chiefly on the experimental side that the subject has been enriched, as, for instance, by the labors of Langley (1891) and Lilienthal. Langley (1897) has, indeed, constructed a steam-propelled aeroplane which flew successfully; but man himself has not yet flown.

Moreover, the meteorological applications of aerodynamics contained in the profound researches of Guldberg and Mohn (1877), Ferrel (1877), Oberbeck (1882, 1886), Helmholtz (1888, 1889), and others, as well as in such investigations as Sprung's (1880) on the inertia path, are as yet rather qualitative in their bearing on the actual motions of the atmosphere. The marked progress of meteorology is observational in character.

Acoustics

Early in the century the velocity of sound given in a famous equation of Newton was corrected to agree with observation by Laplace (1816).

The great problems in acoustics are addressed in part to the elastician, in part to the physiologist. In the former case the work of Rayleigh (1877) has described the present stage of development, interpreting and enriching almost every part discussed. In the latter case Helmholtz (1863) has devoted his immense powers to a like purpose and with like success. König has been prominently concerned with the construction of accurate acoustic apparatus.

It is interesting to note that the differential equation representing the vibration of strings was the first to be integrated; that it passed from D'Alembert (1747) successively to Euler (1779), Bernoulli (1753) and Lagrange (1759). With the introduction of Fourier's series (1807) and of spherical harmonics at the very beginning of the century, D'Alembert's and the other corresponding equations in acoustics readily yielded to rigorous analysis. Rayleigh's first six chapters summarize the results for one and for two degrees of freedom.

Flexural vibration in rods, membranes, and plates become prominent in the unique investigations of Chladni (1787, 1796, *Akustik*, 1802). The behavior of vibrating rods has been developed by Euler (1779), Cauchy (1827), Poisson (1833), Strehlke (1833), Lissajous (1833), Seebeck (1849), and is summarized in the seventh and eighth chapters of Rayleigh's book. The transverse vibration of membranes engaged the attention of Poisson (1829). Round membranes were rigorously treated by Kirchhoff (1850) and by Clebsch (1862); elliptic membranes by Mathieu (1868). The problem of vibrating plates presents formidable difficulties resulting not only from the edge conditions, but from the underlying differential equation of the fourth degree due to Sophie Germain (1810) and to Lagrange (1811). The solutions have taxed the powers of Poisson (1812, 1829), Cauchy (1829), Kirchhoff (1850), Boussinesq (1871–79), and others. For the circular plate Kirchhoff gave the complete theory. Rayleigh systematized the results for the quadratic plate, and the general account makes up his ninth and tenth chapters.

Longitudinal vibrations, which are of particular importance in case of the organ-pipe, were considered in succession by Poisson (1817), Hopkins (1838), Quet (1855); but Helmholtz in his famous paper of 1860 gave the first adequate theory of the open organ-pipe, involving viscosity. Further extension was then added by Kirchhoff (1868), and by Rayleigh (1870, *et seq.*), including particularly powerful analysis of resonance. The subject in its entirety, including the allied treatment of the resonator, completes the second volume of Rayleigh's *Sound.*

On the other hand, the whole subject of tone-quality, of combination and difference tones, of speech, of harmony, in its physical, physiological, and æsthetic relations, has been reconstructed, using all the work of earlier investigators, by Helmholtz (1862), in his masterly *Tonempfindungen.* With rare skill and devotion König contributed a wealth of siren-like experimental appurtenances.

Acousticians have been fertile in devising ingenious methods and apparatus, among which the tuning-fork with resonator of Marloye, the siren of Cagniard de la Tour (1819), the Lissajous curves (1857), the stroboscope of Plateau (1832), the manometric flames of König (1862, 1872), the dust methods of Chladni (1787) and of Kundt (1865–68), Melde's vibrating strings (1860, 1864), the phonograph of Edison and of Bell (1877), are among the more famous.

Heat: Thermometry

The invention of the air thermometer dates back at least to Amontons (1699), but it was not until Rudberg (1837), and more thoroughly Regnault (1841, *et seq.*) and Magnus (1842), had completed their work on the thermal expansion and compressibility of air, that air thermometry became adequately rigorous. On the theoretical side Clapeyron (1834), Helmholtz (1847), Joule (1848), had in various ways proposed the use of the Carnot function (1894) for temperature measurement, but the subject was finally disposed of by Kelvin (1849, *et seq.*) in his series of papers on temperature and temperature measurement.

Practical thermometry gained much from the measurement of the expansion of mercury by Dulong and Petit (1818), repeated by Regnault. It also profited by the determination of the viscous behavior of glass, due to Pernet (1876) and others, but more from the elimination of these errors by the invention of the Jena glass.

It is significant to note that the broad question of thermal expansion has yet no adequate equation, though much has been done experimentally for fluids by the magnificent work of Amagat (1869, 1873, *et seq.*).

Heat Conduction

The subject of heat conduction from a theoretical point of view was virtually created by the great memoir of Fourier (1822), which shed its first light here, but subsequently illumined almost the whole of physics. The treatment passed successively through the hands of many of the foremost thinkers, notably of Poisson (1835, 1837), Lamé (1836, 1839, 1843), Kelvin (1841–44), and others. With the latter (1856) the ingenious method of sources and sinks originated. The character of the conduction is now well known for continuous media, isotropic or not, bounded by the more simple geometrical forms, in particular for the sphere under all reasonable initial and surface conditions. Much attention has been given to the heat conduction of the earth, following Fourier, by Kelvin (1862, 1878), King (1893), and others.

Experimentally, Wiedemann and Franz (1853) determined the relative heat conduction of metals and showed that for simple bodies a parallel gradation exists for the cases of heat and of electrical conductivity. Noteworthy absolute methods for measuring heat conduction were devised in particular by Forbes (1842), F. Neumann (1862), Ångström (1861–64), and a lamellar method applying to fluids by H. F. Weber (1880).

Calorimetry

Practical calorimetry was virtually completed by the researches of Black in 1763. A rich harvest of experimental results, therefore, has since accrued to the subjects of specific, latent, and chemical heats, due in particularly important cases to the indefatigable Regnault (1840, 1845, *et seq.*). Dulong and Petit (1819) discovered the remarkable fact of the approximate constancy of the atomic heats of the elements. The apparently exceptional cases were interpreted for carbon silicon and boron by H. F. Weber (1875), and for sulphur by Regnault (1840). F. Neumann (1831) extended the law to compound bodies, and Joule (1844) showed that in many cases specific heat could be treated as additively related to the component specific heats.

Among recent apparatus the invention of Bunsen's ice calorimeter (1870) deserves particular mention.

Thermodynamics

Thermodynamics, as has been stated, in a singularly fruitful way interpreted and broadened the old Leibnitzian principle of *vis viva* of 1686. Beginning with the incidental experiments of Rumford (1798) and of Davy (1799) just antedating the century, the new conception almost leaped into being when J. R. Mayer (1842, 1845) defined and computed the mechanical equivalent of heat, and when Joule (1843, 1845, *et seq.*) made that series of precise and judiciously varied measurements which mark an epoch. Shortly after Helmholtz (1847), transcending the mere bounds of heat, carried the doctrine of the conservation of energy throughout the whole of physics.

Earlier in the century Carnot (1824), stimulated by the growing importance of the steam engine of Watt (1763, *et seq.*), which Fulton (1806) had already applied to transportation by water and which Stephenson (1829) soon after applied to transportation by land, invented the reversible thermodynamic cycle. This cycle or sequence of states of equilibrium of two bodies in mutual action is, perhaps, without a parallel in the prolific fruitfulness of its contributions to modern physics. Its continued use in fifty years of research has but sharpened its logical edge. Carnot deduced the startling doctrine of a temperature criterion for the efficiency of engines. Clapeyron (1834) then gave the geometrical method of representation universally used in thermodynamic discussions to-day, though often made more flexible by new coördinates as suggested by Gibbs (1873).

To bring the ideas of Carnot into harmony with the first law of thermodynamics it is necessary to define the value of a transformation, and this was the great work of Clausius (1850), followed very closely by Kelvin (1851) and more hypothetically by Rankine (1851). The latter's broad treatment of energetics (1855) antedates many recent discussions. As early as 1858 Kirchhoff investigated the solution of solids and of gases thermodynamically, introducing at the same time an original method of treatment.

The second law was not generally accepted without grave misgiving. Clausius, indeed, succeeded in surmounting most of the objections, even those contained in theoretically delicate problems associated with radiation. Nevertheless, the confusion raised by the invocation of Maxwell's "demon" has never quite been calmed; and while Boltzmann (1877, 1878) refers to the second law as a case of probability, Helmholtz (1882) admits that the law is an expression of our inability to deal with the individual atom. Irreversible processes as yet lie quite beyond the pale of thermodynamics. For these the famous inequality of Clausius is the only refuge. The value of an uncompensated transformation is always positive.

The invention of mechanical systems which more or less fully conform to the second law has not been infrequent. Ideas of this nature have been put forward by Boltzmann (1866, 1872), by Clausius (1870, 1871), and more powerfully by Helmholtz (1884) in his theory of cyclic systems, which in a measure suggested the hidden mechanism at the root of Hertz's dynamics. Gibbs's (1902) elementary principles of statistical mechanics seem, however, to contain the nearest approach to a logical justification of the second law — an approach which is more than a dynamical illustration.

The applications of the first and second laws of thermodynamics are ubiquitous. As interesting instances we may mention the conception of an ideal gas and its properties; the departure of physical gases from ideality as shown in Kelvin and Joule's plug experiment (1854, 1862); the corrected temperature scale resulting on the one hand, and the possibility of the modern liquid air refrigerator of Linde and Hampson (1895) on the other. Difficulties encountered in the liquefaction of incoercible gases by Cailletet and Pictet (1877) have vanished even from the hydrogen coercions of Olezewski (1895) and of Dewar and Travers.

Again, the broad treatment of fusion and evaporation, beginning with James Thomson's (1849) computation of the melting point of ice under pressure, Kirchhoff's (1858) treatment of sublimation, the extensive chapter of thermo-elastics set on foot by Kelvin's (1883) equation, are further examples.

To these must be added Andrews's (1869) discovery of the continuity of the liquid and the gaseous states foreshadowed by Cagniard de la Tour (1822, 1823); the deep insight into the laws of physical gases furnished by the experimental prowess of Amagat (1881, 1893, 1896), and the remarkably close approximation amounting almost to a prediction of the facts observed which is given by the great work of van der Waals (1873).

The further development of thermodynamics, remarkable for the breadth, not to say audacity, of its generalizations, was to take place in connection with chemical systems. The analytical power of the conception of a thermodynamic potential was recognized nearly at the same time by many thinkers:[1] by Gibbs (1876), who discovered both the isothermal and the adiabatic potential; by Massieu (1877), independently in his *Fonctions characteristiques;* by Helmholtz (1882), in his *Freie Energie;* by Duhem (1886) and by Planck (1887, 1891), in their respective thermodynamic potentials. The transformation of Lagrange's doctrine of virtual displacements of infinitely more complicated systems than those originally contemplated, in other words the introduction of a virtual thermodynamic modification in complete analogy with the virtual displacement of the *mécanique analytique,* marked a new possibility of research of

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[1] Maxwell's *available energy* is accidentally overlooked in the text.

which Gibbs made the profoundest use. Unaware of this marshaling of powerful mathematical forces, van 't Hoff (1886, 1888) consummated his marvelously simple application of the second law; and from interpretations of the experiments of Pfeffer (1877) and of Raoult (1883, 1887) propounded a new theory of solution, indeed, a basis for chemical physics, in a form at once available for experimental investigation.

The highly generalized treatment of chemical statics by Gibbs bore early fruit in its application to Deville's phenomenon of dissociation (1857), and in succession Gibbs (1878, 1879), Duhem (1886), Planck (1887), have deduced adequate equations, while the latter in case of dilute solutions gave a theoretical basis for Guldberg and Waage's law of mass action (1879). An earlier independent treatment of dissociation is due to Horstmann (1869, 1873).

In comparison with the brilliant advance of chemical statics which followed Gibbs, the progress of chemical dynamics has been less obvious; but the outlines of the subject have, nevertheless, been succinctly drawn in a profound paper by Helmholtz (1886), followed with much skill by Duhem (1894, 1896) and Natanson (1896).

Kinetic Theory of Gases

The kinetic theory of gases at the outset, and as suggested by Herapath (1821), Joule (1851, 1857), Krönig (1856), virtually reaffirmed the classic treatise of Bernoulli (1738). Clausius in 1857–62 gave to the theory a modern aspect in his derivation of Boyle's law in its thermal relations, of molecular velocity and of the ratio of translational to total energy. He also introduced the mean free path (1858). Closely after followed Maxwell (1860), adducing the law for the distribution of velocity among molecules, later critically and elaborately examined by Boltzmann (1868–81). Nevertheless, the difficulties relating to the partition of energy have not yet been surmounted. The subject is still under vigorous discussion, as the papers of Burbury (1899) and others testify.

To Maxwell (1860, 1868) is due the specifically kinetic interpretation of viscosity, of diffusion, of heat conduction, subjects which also engaged the attention of Boltzmann (1872–87). Rigorous data for molecular velocity and mean free path have thus become available, and van der Waals (1873) added a final allowance for the size of the molecules. Less satisfactory has been the exploration of the character of molecular force for which Maxwell, Boltzmann (1872, *et seq.*), Sutherland (1886, 1893), and others have put forward tentative investigations.

The intrinsic equation of fluids discovered and treated in the great paper of van der Waals (1873), though partaking of the character of a first approximation, has greatly promoted the coördination of most of the known facts. Corresponding states, the thermal coefficients, the vapor pressure relation, the minimum of pressure-volume products, and even molecular diameters, are reasonably inferred by van der Waals from very simple premises. Many of the results have been tested by Amagat (1896).

The data for molecular diameter furnished by the kinetic theory as a whole, viz., the original values of Loschmidt (1865), of van der Waals (1873), and others, are of the same order of values as Kelvin's estimates (1883) from capillarity and contact electricity. Many converging lines of evidence show that an approximation to the truth has surely been reached.

Radiation

Our knowledge of the radiation of heat, diathermacy, thermocrosis, was promoted by the perfection which the thermopyle reached in the hands of Melloni (1835–53). These and other researches set at rest forever all questions relating to the identity of heat and light. The subject was, however, destined to attain a much higher order of precision with the invention of Langley's bolometer (1881). The survey of heat spectra, beginning with the laborious attempts of Herschel (1840), of E. Becquerel (1843, 1870), H. Becquerel (1883), and others, has thus culminated in the magnificent development shown in Langley's charts (1883, 1884, *et seq.*).

Kirchhoff's law (1860), to some extent anticipated by Stewart (1857, 1858), pervades the whole subject. The radiation of the black body, tentatively formulated in relation to temperature by Stefan (1879) and more rigorously by Boltzmann (1884), has furnished the savants of the Reichsanstalt with means for the development of a new pyrometry whose upper limit is not in sight.

Among curious inventions Crooke's radiometer (1874) and Bell's photophone may be cited. The adaptation of the former in case of high exhaustion to the actual measurement of Maxwell's (1873) light pressure by Lebedew (1901) and Nichols and Hull (1903) is of quite recent history.

The first estimate of the important constant of solar radiation at the earth was made by Pouillet (1838); but other pyrheliometric methods have since been devised by Langley (1884) and more recently by Ångström (1886, *et seq.*).

Velocity of light

Data for the velocity of light, verified by independent astronomical observations, were well known prior to the century; for Römer had worked as long ago as 1675, and Bradley in 1727. It remained to actually measure this enormous velocity in the laboratory, apparently an extraordinary feat, but accomplished simultaneously by Fizeau (1849) and by the aid of Wheatstone's revolving mirror (1834) by Foucault (1849, 1850, 1862). Since that time precision has been given to this important constant by Cornu (1871, 1873, 1874), Forbes and Young (1882), Michelson (1878, *et seq.*), and Newcomb (1885). Foucault (1850), and more accurately Michelson (1884), determined the variation of velocity with the medium and wave-length, thus assuring to the undulatory theory its ultimate triumph. Grave concern, however, still exists, inasmuch as Michelson and Morley (1886) by the most refined measurement, and differing from the older observations of Fizeau (1851, 1859), were unable to detect the optical effect of the relative motion of the atmosphere and the luminiferous ether predicted by theory.

Römer's observation may in some degree be considered as an anticipation of the principle first clearly stated by Döppler (1842), which has since become invaluable in spectroscopy. Estimates of the density of the luminiferous ether have been published, in particular by Kelvin (1854).

Geometric optics

Prior to the nineteenth century geometric optics, having been mustered before Huyghens (1690), Newton (1704), Malus (1808), Lagrange (1778, 1803), and others, had naturally attained a high order of development. It was, nevertheless, remodeled by the great paper of Gauss (1841), and was thereafter generalized step by step by Listing, Möbius (1855), and particularly by Abbe (1872), postulating that in character, the cardinal elements are independent of the physical reasons by which one region is imaged in another.

So many able thinkers, like Airy (1827), Maxwell (1856, *et seq.*), Bessel (1840, 1841), Helmholtz (1856, 1867), Ferraris (1877, 1880), and others have contributed to the furtherance of geometric optics, that definite mention is impossible. In other cases, again, profound methods like those of Hamilton (1828, *et seq.*), Kummer (1859), do not seem to have borne correspondingly obvious fruit. The fundamental bearing of diffraction on geometric optics was first pointed out by Airy (1838), but developed by Abbe (1873), and after him by Rayleigh (1879). An adequate theory of the rainbow, due to Airy and others, is one of its picturesque accomplishments (1838).

The so-called astronomical refraction of a medium of continuously varying index, successively treated by Bouguer (1739, 1749), Simpson (1743), Bradley (1750, 1762), owes its recent refined development to Bessel (1823, 1826, 1842), Ivory (1822, 1823, *et seq.*), Radau (1884), and others. Tait (1883) gave much attention to the allied treatment of mirage.

In relation to instruments the conditions of aplantism were examined by Clausius (1864), by Helmholtz (1874), by Abbe (1873, *et seq.*), by Hockin (1884), and others, and the apochromatic lens was introduced by Abbe (1879). The microscope is still well subserved by either the Huyghens or the Ramsden (1873) eye-piece, but the objective has undergone successive stages of improvement, beginning with Lister's discovery in 1830. Amici (1840) introduced the principle of immersion; Stephenson (1878) and Abbe (1879), homogeneous immersion; and the Abbe-Zeiss apochromatic objective (1886), the outcome of the Jena-glass experiments, marks, perhaps, the high-water mark of the art for the microscope. Steinheil (1865, 1866) introduced the guiding principle for photographic objectives. Alvan Clark carried the difficult technique of telescope lens construction to a degree of astonishing excellence.

Spectrum — Dispersion

Curiously, the acumen of Newton (1666, 1704) stopped short of the ultimate conditions of purity of spectrum. It was left to Wollaston (1802), about one hundred years later, to introduce the slit and observe the dark lines of the solar spectrum. Fraunhofer (1814, 1815, 1823) mapped them out carefully and insisted on their solar origin. Brewster (1833, 1834), who afterwards (1860) published a map of 3000 lines, was the first to lay stress on the occurrence of absorption, believing it to be atmospheric. Forbes (1836) gave even greater definiteness to absorption by referring it to solar origin. Foucault (1849) pointed out the coincidence of the sodium lines with the D group of Fraunhofer, and discovered the reversing effect of sodium vapor. A statement of the parallelism of emission and absorption came from Ångström (1855) and with greater definiteness and ingenious experiments from Stewart (1860). Nevertheless, it was reserved to Kirchhoff and Bunsen (1860, 1861) to give the clear-cut distinctions between the continuous spectra and the characteristically fixed bright-line or dark-line spectra upon which spectrum analysis depends. Kirchhoff's law was announced in 1861, and the same year brought his map of the solar spectrum and a discussion of the chemical composition of the sun. Huggins (1864, *et seq.*), Ångström (1868), Thalén (1875), followed with improved observations on the distribution and wave-length of the solar lines; but the work of these and other observers was suddenly overshadowed by the marvelous possibilities of the Rowland concave grating (1882, *et seq.*). Rowland's maps and tables of the solar spectrum as they appeared in 1887, 1889, *et seq.*, his summary of the elements contained in the sun (1891), each marked a definite stage of advance of the subject. Mitscherlich (1862, 1863) probably was the first to recognize the banded or channeled spectra of compound bodies. Balmer (1885) constructed a valuable equation for recognizing the distribution of single types of lines. Kayser and Runge (1887, *et seq.*) successfully analyzed the structure of the spectra of alkaline and other elements.

The modernized theory of the grating had been given by Rayleigh in 1874 and was extended to the concave grating by Rowland (1892, 1893) and others. A general theory of the resolving power of prismatic systems is also due to Rayleigh (1879, 1880), and another to Thollon (1881).

The work of Rowland for the visible spectrum was ably paralleled by Langley's investigations (1883 *et seq.*) of the infra-red, dating from the invention of the bolometer (1881). Superseding the work of earlier investigators like Fizeau and Foucault (1878) and others, Langley extended the spectrum with detailed accuracy to over eight times its visible length. The solar and the lunar spectrum, the radiations of incandescent and of hot bodies, were all specified absolutely and with precision. With artificial spectra Rubens (1892, 1899) has since gone further, reaching the longest heat-waves known.

A similarly remarkable extension was added for the ultra-violet by Schumann (1890, 1892), contending successfully with the gradually increasing opacity of all known media.

Experimentally the suggestion of the spectroheliograph by Lockyer (1868) and by Janssen (1868) and its brilliant achievement by Hale (1892) promise notable additions to our knowledge of solar activity.

Finally, the refractions of absorbing media have been of great importance in their bearing on theory. The peculiarities of metallic reflection were announced from his earlier experiments (1811) by Arago in 1817 and more fully investigated by Brewster (1815, 1830, 1831). F. Neumann (1832) and MacCullagh (1837) gave sharper statements to these phenomena. Equations were advanced by Cauchy (1836, *et seq.*) for isotropic bodies, and later with greater detail by Rayleigh (1872), Ketteler (1875, *et seq.*), Drude (1887, *et seq.*), and others. Jamin (1847, 1848) devised the first experiments of requisite precision and found them in close agreement with Cauchy's theory. Kundt (1888) more recently investigated the refraction of metallic prisms.

Anomalous dispersion was discovered by Christiansen in 1870, and studied by Kundt (1871, *et seq.*). Sellmeyer's (1872) powerful and flexible theory of dispersion was extended to include absorption effects by Helmholtz (1874), with greater detail by Ketteler (1879, *et seq.*), and from a different point of view by Kelvin (1885).

The electromagnetic theory lends itself particularly well to the same phenomena, and Kolázek (1887, 1888), Goldhammer (1892), Helmholtz (1892), Drude (1893), and others instanced its adaptation with success.

Photometry, Fluorescence, Photochemistry

The cosine law of Lambert (1760) has since been interpreted in a way satisfying modern requirements by Fourier (1817, 1824) and by Lommel (1880). Among new resources for the experimentalist the spectrophotometer, the Lummer-Brodhun photometer (1889), and Rood's flicker photometer (1893, 1899), should be mentioned.

Fluorescence, though ingeniously treated by Herschel (1845, 1853) and Brewster (1846, *et seq.*), was virtually created in its philosophical aspects by Stokes in his great papers (1852, *et seq.*) on the subject. In recent years Lommel (1877) made noteworthy contributions. Phosphorescence has engaged the attention of E. Becquerel (1859), among others.

The laws of photochemistry are in large measure due to Bunsen and Roscoe (1857, 1862). The practical development of photography from its beginnings with Daguerre (1829, 1838) and Niépce and Fox-Talbot (1839), to its final improvement by Maddox (1871) with the introduction of the dry plate, is familiar to all. Vogel's (1873) discovery of appropriate sensitizers for different colors has added new resources to the already invaluable application of photography to spectroscopy.

Interference

The colors of thin plates treated successively by Boyle (1663), Hooke (1665), and more particularly by Newton (1672, *Optiks*, 1704), became in the hands of Young (1802) the means of framing an adequate theory of light. Young also discovered the colors of mixed plates and was cognizant of loss of half a wave-length on reflection from the denser medium. Fresnel (1815) gave an independent explanation of Newton's colors in terms of interference, devising for further evidence his double mirrors (1816), his biprism (1819), and eventually the triple mirror (1820). Billet's plates and split lens (1858) belong to the same classical order, as do also Lloyd's (1837) and Haidinger's (1849) interferences. Brewster's (1817) observation of interference in case of thick plates culminated in the hands of Jamin (1856, 1857) in the useful interferometer. The scope of this apparatus was immensely advanced by the famous device of Michelson (1881, 1882), which has now become a fundamental instrument of research. Michelson's determination of the length of the meter in terms of the wave-length of light with astounding accuracy is a mere example of its accomplishments.

Wiener (1890) in his discovery of the stationary light-wave introduced an entirely new interference phenomenon. The method was successfully applied to color photography by Lippmann (1891, 1892), showing that the electric and not the magnetic vector is photographically active.

The theory of interferences from a broader point of view, and including the occurrence of multiple reflections, was successively perfected by Poisson (1823), Fresnel (1823), Airy (1831). It has recently been further advanced by Feussner (1880, *et seq.*), Sohncke and Wangerin (1881, 1883), Rayleigh (1889), and others. The interferences along a caustic were treated by Airy (1836), but the endeavor to reconstruct geometric optics on a diffraction basis has as yet only succeeded in certain important instances, as already mentioned.

Diffraction

Though diffraction dates back to Grimaldi (1665) and was well known to Newton (1704), the first correct though crude interpretation of the phenomenon is due to Young (1802, 1804). Independently Fresnel (1815) in his original work devised similar explanations, but later (1818, 1819, 1826) gave a more rational theory in terms of Huyghens's principle, which he was the first adequately to interpret. Fresnel showed that all points of a wave-front are concerned in producing diffraction, though the ultimate critical analysis was left to Stokes (1849).

In 1822 Fraunhofer published his remarkable paper, in which, among other inventions, he introduced the grating into science. Zone plates were studied by Cornu (1875) and by Soret (1875). Rowland's concave grating appeared in 1881; Michelson's echelon spectrometer in 1899.

The theory of gratings and other diffraction phenomena was exhaustively treated by Schwerd (1837). Babinet established the principle bearing his name in 1837. Subsequent developments were in part concerned with the improvement of Fresnel's method of computation, in part with a more rigorous treatment of the theory of diffraction. Stokes (1850, 1852) gave the first account of the polarization accompanying diffraction, and thereafter Rayleigh (1871) and many others, including Kirchhoff (1882, 1883), profoundly modified the classic treatment. Airy (1834, 1838) and others elaborately examined the diffraction due to a point source in view of its important bearing on the efficiency of optical instruments.

A unique development of diffraction is the phenomenon of scattering propounded by Rayleigh (1871) in his dynamics of the blue sky. This great theory which Rayleigh has repeatedly improved (1881, *et seq.*) has since superseded all other relevant explanations.

Polarization

An infinite variety of polarization phenomena grew out of Bartholinus's (1670) discovery. Sound beginnings of a theory were laid by Huyghens (*Traité*, 1690), whose wavelet principle and elementary wave-front have persisted as an invaluable acquisition, to be generalized by Fresnel in 1821.

Fresh foundations in this department of optics were laid by Malus (1810) in his discovery of the cosine law and the further discovery of the polarization of reflected light. Later (1815) Brewster adduced the conditions of maximum polarization for this case.

In 1811 Arago announced the occurrence of interferences in connection with parallel plane-polarized light, phenomena which under the observations of Arago and Fresnel (1816, 1819), Biot (1816), Brewster (1813, 1814, 1818), and others grew immensely in variety, and in the importance of their bearing on the undulatory theory. It is on the basis of these phenomena that Fresnel in 1819 insisted on the transversality of light-waves, offering proof which was subsequently made rigorous by Verdet (1850). Though a tentative explanation was here again given by Young (1814), the first adequate theory of the behavior of thin plates of æolotropic media with polarized light came from Fresnel (1821).

Airy (1833) elucidated a special case of the gorgeously complicated interferences obtained with convergent pencils; Neumann in 1834 gave the general theory. The forbidding equations resulting were geometrically interpreted by Bertin (1861, 1884), and Lommel (1883) and Neumann (1841) added a theory for stressed media, afterwards improved by Pockels (1889).

The peculiarly undulatory character of natural light owes its explanation largely to Stokes (1852), and his views were verified by many physicists, notably by Fizeau (1862) showing interferences for path differences of 50,000 wave-lengths, and by Michelson for much larger path differences.

The occurrence of double refraction in all non-regular crystals was recognized by Haüy (1788) and studied by Brewster (1818). In 1821, largely by a feat of intuition, Fresnel introduced his generalized elementary wave-surface, and the correctness of his explanation has since been substantiated by a host of observers. Stokes (1862, *et seq.*) was unremittingly active in pointing out the theoretical bearing of the results obtained. Hamilton (1832) supplied a remarkable criterion of the truth of Fresnel's theory deductively, in the prediction of both types of conic refraction. The phenomena were detected experimentally by Lloyd (1833).

The domain of natural rotary polarization, discovered by Arago (1811) and enlarged by Biot (1815), has recently been placed in close relation to non-symmetrical chemical structure by LeBel (1874) and van 't Hoff (1875), and a tentative molecular theory was advanced by Sohncke (1876).

Boussinesq (1868) adapted Cauchy's theory (1842) to these phenomena. Independent elastic theories were propounded by MacCullagh (1837), Briot, Sarrau (1868); but there is naturally no difficulty in accounting for rotary polarization by the electromagnetic theory of light, as was shown by Drude (1892).

Among investigational apparatus of great importance the Soleil (1846, 1847) saccharimeter may be mentioned.

Theories

In conclusion, a brief summary may be given of the chief mechanisms proposed to account for the undulations of light. Fresnel suggested the first adequate optical theory in 1821, which, though singularly correct in its bearing on reflection and refraction in the widest sense, was merely tentative in construction. Cauchy (1829) proposed a specifically elastic theory for the motion of relatively long waves of light in continuous media, based on a reasonable hypothesis of molecular force, and deduced therefrom Fresnel's reflection and refraction equations. Green (1838), ignoring molecular forces and proceeding in accordance with his own method in elastics, published a different theory, which did not, however, lead to Fresnel's equations. Kelvin (1888) found the conditions implied in Cauchy's theory compatible with stability if the ether were considered as bound by a rigid medium. The ether implied throughout is to have the same elasticity everywhere, but to vary in density from medium to medium, and vibration to be normal to the plane of polarization.

Neumann (1835), whose work has been reconstructed by Kirchhoff (1876), and MacCullagh (1837), with the counter-hypothesis of an ether of fixed density but varying in elasticity from medium to medium, also deduced Fresnel's equations, obtaining at the same time better surface conditions in the case of æolotropic media. The vibrations are in the plane of polarization.

All the elastic theories essentially predict a longitudinal light-wave. It was not until Kelvin in 1889–90 proposed his remarkable gyrostatic theory of light, in which force and displacement become torque and twist, that these objections to the elastic theory were wholly removed. MacCullagh, without recognizing their bearing, seems actually to have anticipated Kelvin's equation.

With the purpose of accounting for dispersion, Cauchy in 1835 gave greater breadth to his theory by postulating a sphere of action of ether particles commensurate with wave-length, and in this direction he was followed by F. Neumann (1841), Briot (1864), Rayleigh (1871), and others, treating an ether variously loaded with material particles. Among theories beginning with the phenomena observed, that of Boussinesq (1867, *et seq.*) has received the most extensive development.

The difficult surface conditions met with when light passes from one medium to another, including such subjects as ellipticity, total reflection, etc., have been critically discussed, among others, by Neumann (1835) and Rayleigh (1888); but the discrimination between the Fresnel and the Neumann vector was not accomplished without misgiving before the advent of the work of Hertz.

It appears, therefore, that the elastic theories of light, if Kelvin's gyrostatic adynamic ether be admitted, have not been wholly routed. Nevertheless, the great electromagnetic theory of light propounded by Maxwell (1864, *Treatise,* 1873) has been singularly apt not only in explaining all the phenomena reached by the older theories and in predicting entirely novel results, but in harmoniously uniting, as parts of a unique doctrine, both the electric or photographic light vector of Fresnel and Cauchy and the magnetic vector of Neumann and MacCullagh. Its predictions have, moreover, been astonishingly verified by the work of Hertz (1890), and it is to-day acquiring added power in the convection theories of Lorentz (1895) and others.

Electrostatics

Coulomb's (1785) law antedates the century; indeed, it was known to Cavendish (1771, 1781). Problems of electric distribution were not seriously approached, however, until Poisson (1811) solved the case for spheres in contact. Afterwards Clausius (1852), Helmholtz (1868), and Kirchhoff (1877) examined the conditions for discs, the last giving the first rigorous theory of the experimentally important plate-condenser. In 1845–48 the investigation of electric distribution received new incentive as an application of Kelvin's beautiful method of images. Maxwell (*Treatise,* 1873) systematized the treatment of capacity and induction coefficients.

Riess (1837), in a classic series of experiments on the heat produced by electrostatic discharge, virtually deduced the potential energy of a conductor and in a measure anticipated Joule's law (1841). In 1860 appeared Kelvin's great paper on the electromotive force needed to produce a spark. As early as 1855, however, he had shown that the spark discharge is liable to be of the character of a damped vibration and the theory of electric oscillation was subsequently extended by Kirchhoff (1867). The first adequate experimental verification was due to Feddersen (1858, 1861).

The specific inductive capacity of a medium with its fundamental bearing on the character of electric force was discovered by Faraday in 1837. Of the theories propounded to account for this property the most far-reaching is Maxwell's (1865), which culminates in the unique result showing that the refraction index of a medium is the square root of its specific inductive capacity. With regard to Maxwell's theory of the Faraday stress in the ether as compared with the subsequent development of electrostriction in other media by many authors, notably by Boltzmann (1880) and by Kirchhoff (1885), it is observable that the tendency of the former to assign concrete physical properties to the tube of force is growing, particularly in connection with radioactivity. Duhem (1892, 1895) insists, however, on the greater trustworthiness of the thermodynamic potential.

The seemingly trivial subject of pyroelectricity interpreted by Æpinus (1756) and studied by Brewster (1825), has none the less elicited much discussion and curiosity, a vast number of data by Hankel (1839–93) and others, and a succinct explanation by Kelvin (1860, 1878). Similarly piezoelectricity, discovered by the brothers Curie (1880), has been made the subject of a searching investigation by Voigt (1890). Finally Kerr (1875, *et seq.*) observed the occurrence of double refraction in an electrically polarized medium. Recent researches, among which those of Lemoine (1896) are most accurate, have determined the phase difference corresponding to the Kerr effect under normal conditions, while Voigt (1899) has adduced an adequate theory.

Certain electrostatic inventions have had a marked bearing on the development of electricity. We may mention in particular Kelvin's quadrant electrometer (1867) and Lippmann's capillary electrometer (1873). Moreover, among apparatus originating in Nicholson's duplicator (1788) and Volta's electrophorus, the Töpler-Holtz machine (1865–67), with the recent improvement due to Wimshurst, has replaced all others. Atmospheric electricity, after the memorable experiment of Franklin (1751), made little progress until Kelvin (1860) organized a systematic attack. More recently a revival of interest began with Exner (1886), but more particularly with Linss (1887), who insisted on the fundamental importance of a detailed knowledge of atmospheric conduction. It is in this direction that the recent vigorous treatment of the atmosphere as an ionized medium has progressed, owing chiefly to the indefatigable devotion of Elster and Geitel (1899, *et seq.*) and of C. T. R. Wilson (1897, *et seq.*). Qualitatively the main phenomena of atmospheric electricity are now plausibly accounted for; quantitatively there is as yet very little specific information.

Volta Contacts

Volta's epoch-making experiment of 1797 may well be added to the century which made such prolific use of it; indeed, the Voltaic pile (1800–02) and Volta's law of series (1802) come just within it. Among the innumerable relevant experiments Kelvin's dropping electrodes (1859) and his funnel experiment (1867) are among the more interesting, while the *Spannungsreihe* of R. Kohlrausch (1851, 1853) is the first adequate investigation. Nevertheless, the phenomenon has remained without a universally acceptable explanation until the present day, when it is reluctantly yielding to electronic theory, although ingenious suggestions like Helmholtz's *Doppelschicht* (1879), the interpretations of physical chemistry and the discovery of the concentration cell (Helmholtz; Nernst, 1888, 1889; Planck, 1890) have thrown light upon it.

Among the earliest theories of the galvanic cell is Kelvin's (1851, 1860), which, like Helmholtz's, is incomplete. The most satisfactory theory is Nernst's (1889). Gibbs (1878) and Helmholtz (1882) have made searching critical contributions, chiefly in relation to the thermal phenomena.

Volta's invention was made practically efficient in certain famous galvanic cells, among which Daniell's (1836), Grove's (1839), Clarke's (1878), deserve mention, and the purposes of measurement have been subserved by the potentiometers of Poggendorff (1841), Bosscha (1855), Clarke (1873).

Seebeck Contacts

Thermoelectricity, destined to advance many departments of physics, was discovered by Seebeck in 1821. The Peltier effect followed in 1834, subsequently to be interpreted by Icilius (1853). A thermodynamic theory of the phenomena came from Clausius (1853) and with greater elaboration, together with the discovery of the Thomson effect, from Kelvin (1854, 1856), to whom the thermoelectric diagram is due. This was subsequently developed by Tait (1872, *et seq.*) and his pupils. Avenarius (1863), however, first observed the thermoelectric parabola.

The modern platinum-iridium or platinum-rhodium thermoelectric pyrometer dates from about 1885 and has recently been perfected at the Reichsanstalt. Melloni (1835, *et seq.*) made the most efficient use of the thermopyle in detecting minute temperature differences.

Electrolysis

Though recognized by Nichols and Carlisle (1800) early in the century, the laws of electrolysis awaited the discovery of Faraday

(1834). Again, it was not till 1853 that further marked advances were made by Hittorf's (1853–59) strikingly original researches on the motions of the ions. Later Clausius (1857) suggested an adequate theory of electrolysis, which was subsequently to be specialized in the dissociation hypothesis of Arrhenius (1881, 1884). To the elaborate investigations of F. Kohlrausch (1879, *et seq.*), however, science owes the fundamental law of the independent velocities of migration of the ions.

Polarization discovered by Ritter in 1803 became in the hands of Planté (1859–1879) an invaluable means for the storage of energy, an application which was further improved by Faure (1880).

Steady Flow

The fundamental law of the steady flow of electricity, in spite of its simplicity, proved to be peculiarly elusive. True, Cavendish (1771–81) had definite notions of electrostatic resistance as dependent on length section and potential, but his intuitions were lost to the world. Davy (1820), from his experiments on the resistances of conductors, seems to have arrived at the law of sections, though he obscured it in a misleading statement. Barlow (1825) and Becquerel (1825–26), the latter operating with the ingenious differential galvanometer of his own invention, were not more definite. Surface effects were frequently suspected. Ohm himself, in his first paper (1825), confused resistance with the polarization of his battery, and it was not till the next year (1826) that he discovered the true law, eventually promulgated in his epoch-making *Die galvanische Kette* (1827).

It is well known that Ohm's mathematical deductions were unfortunate, and would have left a gap between electrostatics and voltaic electricity. But after Ohm's law had been further experimentally established by Fechner (1830), the correct theory was given by Kirchhoff (1849) in a way to bridge over the gap specified. Kirchhoff approached the question gradually, considering first the distribution of current in a plane conductor (1845–46), from which he passed to the laws of distribution in branched conductors (1847–48) — laws which now find such universal application. In his great paper, moreover, Kirchhoff gives the general equation for the activity of the circuit and from this Clausius (1852) soon after deduced the Joule effect theoretically. The law, though virtually implied in Riess's results (1837), was experimentally discovered by Joule (1841).

As bearing critically or otherwise on Ohm's law we may mention the researches of Helmholtz (1852), of Maxwell (1876), the solution of difficult problems in regard to terminals or of the resistance of special forms of conductors, by Rayleigh (1871, 1879), Hicks (1883), and others, the discussion of the refraction of lines of flow by Kirchhoff (1845), and many researches on the limits of accuracy of the law.

Finally, in regard to the evolution of the modern galvanometer from its invention by Schweigger (1820), we may enumerate in succession Nobili's astatic system (1834), Poggendorff's (1826) and Gauss's (1833) mirror device, the aperiodic systems, Weber's (1862) and Kelvin's critical study of the best condition for galvanometry, so cleverly applied in the instruments of the latter. Kelvin's siphon recorder (1867), reproduced in the Depretz-D'Arsonval system (1882), has adapted the galvanometer to modern conditions in cities. For absolute measurement Pouillet's tangent galvanometer (1837), treated for absolute measurement by Weber (1840), and Weber's dynamometer (1846) have lost little of their original importance.

Magnetism

Magnetism, definitely founded by Gilbert (1600) and put on a quantitative basis by Coulomb (1785), was first made the subject of recondite theoretical treatment by Poisson (1824–27). The interpretation thus given to the mechanism of two conditionally separable magnetic fluids facilitated discussion and was very generally used in argument, as for instance by Gauss (1833) and others, although Ampère had suggested the permanent molecular current as early as 1820. Weber (1852) introduced the revolvable molecular magnet, a theory which Ewing (1890) afterwards generalized in a way to include magnetic hysteresis. The phenomenon itself was independently discovered by Warburg (1881) and by Ewing (1882), and has since become of special practical importance.

Faraday in 1852 introduced his invaluable conception of lines of magnetic force, a geometric embodiment of Gauss's (1813, 1839) theorem of force flux, and Maxwell (1855, 1862, *et seq.*) thereafter gave the rigorous scientific meaning to this conception which pervades the whole of contemporaneous electromagnetics.

The phenomenon of magnetic induction, treated hypothetically by Poisson (1824–27) and even by Barlow (1820), has since been attacked by many great thinkers, like F. Neumann (1848), Kirchhoff (1854); but the predominating and most highly elaborated theory is due to Kelvin (1849, *et seq.*). This theory is broad enough to be applicable to æolotropic media and to it the greater part of the notation in current use throughout the world is due. A new method of attack of great promise has, however, been introduced by Duhem (1888, 1895, *et seq.*) in his application of the thermodynamic potential to magnetic phenomena.

Magneticians have succeeded in expressing the magnetic distribution induced in certain simple geometrical figures like the sphere, the spherical shell, the ellipsoid, the infinite cylinder, the ring. Green in 1828 gave an original but untrustworthy treatment for the finite cylinder. Lamellar and solenoidal distributions are defined by Kelvin (1850), to whom the similarity theorems (1856) are also due. Kirchhoff's results for the ring were practically utilized in the absolute measurements of Stoletow (1872) and of Rowland (1878).

Diamagnetism, though known since Brugmans (1778), first challenged the permanent interest of science in the researches of Becquerel (1827) and of Faraday (1845). It is naturally included harmoniously in Kelvin's great theory (1847, *et seq.*). Independent explanations of diamagnetism, however, have by no means abandoned the field; one may instance Weber's (1852) ingenious generalization of Ampère's molecular currents (1820) and the broad critical deductions of Duhem (1889) from the thermodynamic potential. For the treatment of æolotropic magnetic media, Kelvin's (1850, 1851) theory seems to be peculiarly applicable. Weber's theory would seem to lend itself well to electronic treatment.

The extremely complicated subject of magnetostriction, originally observed by Matteuci (1847) and by Joule (1849) in different cases, and elaborately studied by Wiedemann (1858, *et seq.*), has been repeatedly attacked by theoretical physicists, among whom Helmholtz (1881), Kirchhoff (1885), Boltzmann (1879), and Duhem (1891) may be mentioned. None of the carefully elaborated theories accounts in detail for the facts observed.

The relations of magnetism to light have increased in importance since the fundamental discoveries of Faraday (1845) and of Verdet (1854), and they have been specially enriched by the magneto-optic discoveries of Kerr (1876, *et seq.*), of Kundt (1884, *et seq.*), and more recently by the Zeemann effect (1897, *et seq.*). Among the theories put forth for the latter, the electronic explanation of Lorentz (1898 1899) and that of Voigt (1899) are supplementary or at least not contradictory. The treatment of the Kerr effect has been systematized by Drude (1892, 1893). The instantaneity of the rotational effect was first shown by Bichat and Blondlot (1882), and this result has since been found useful in chronography. Sheldon demonstrated the possibility of reversing the Faraday effect. Finally terrestrial magnetism was revolutionized and made accessible to absolute measurement by Gauss (1833), and his method served Weber (1840, *et seq.*) and his successors as a model for the definition of absolute units throughout physics. Another equally important contribution from the same great thinker (1840) is the elaborate treatment of the distribution of terrestrial magnetism, the computations of which have been twice modernized, in the last instance by Neumeyer[1] (1880). Magnetometric methods have advanced but little since the time of Gauss (1833), and Weber's (1853) earth inductor remains a standard instrument of research. Observationally, the development of cycles of variation in the earth's constants is looked forward to with eagerness, and will probably bear on an adequate theory of terrestrial magnetism, yet to be framed. Arrhenius (1903) accentuates the importance of the solar cathode torrent in its bearing on the earth's magnetic phenomena.

Electromagnetism

Electromagnetism, considered either in theory or in its applications, is, perhaps, the most conspicuous creation of the nineteenth century. Beginning with Oersted's great discovery of 1820, the quantitative measurements of Biot and Savart (1820) and Laplace's (1821) law followed in quick succession. Ampère (1820) without delay propounded his famous theory of magnetism. For many years the science was conveniently subserved by Ampère's swimmer (1820), though his functions have since advantageously yielded to Fleming's hand rule for moving current elements. The induction produced by ellipsoidal coils or the derivative cases is fully understood. In practice the rule for the magnetic circuit devised by the Hopkinsons (1886) is in general use. It may be regarded as a terse summary of the theories of Euler (1780), Faraday, Maxwell, and particularly Kelvin (1872), who already made explicit use of it. Nevertheless, the clear-cut practical interpretation of the present day had to be gradually worked out by Rowland (1873, 1884), Bosanquet (1883–85), Kapp (1885), and Pisati (1890).

The construction of elementary motors was taken up by Faraday (1821), Ampère (1822), Barlow (1822), and others, and they were treated rather as laboratory curiosities; for it was not until 1857 that Siemens devised his shuttle-wound armature, and the development of the motor thereafter went *pari passu* with the dynamo, to be presently considered. It culminated in a new principle in 1888, when Ferraris, and somewhat later Tesla (1888) and Borel (1888), introduced polyphase transmission and the more practical realization of Arago's rotating magnetic field (1824).

Theoretical electromagnetics, after a period of quiescence, was again enriched by the discovery of the Hall effect (1879, *et seq.*), which at once elicited wide and vigorous discussion, and for which Rowland (1880), Lorentz (1883), Boltzmann (1886), and others put forward theories of continually increasing finish. Nernst and v. Ettingshausen (1886, 1887) afterwards added the thermomagnetic effect.

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[1] Dr. L. A. Bauer kindly called my attention to the more recent work of A. Schmidt summarized in Dr. Bauer's own admirable paper.

Electrodynamics

The discovery and interpretation of electrodynamic phenomena were the burden of the unique researches of Ampère (1820, *et seq.*, *Memoir*, 1826). Not until 1846, however, were Ampère's results critically tested. This examination came with great originality from Weber using the bifilar dynamometer of his own invention. Grassmann (1845), Maxwell (1873), and others have invented elementary laws differing from Ampère's; but as Stefan (1869) showed that an indefinite number of such laws might be constructed to meet the given integral conditions, the original law is naturally preferred.

Induction

Faraday (1831, 1832) did not put forward the epoch-making discovery of electrokinetic induction in quantitative form, as the great physicist was insufficiently familiar with Ohm's law. Lentz, however, soon supplied the requisite interpretation in a series of papers (1833, 1835) which contain his well-known law both for the mutual inductions of circuits and of magnets and circuits. Lentz clearly announced that the induced quantity is an electromotive force, independent of the diameter and metal and varying, *caeteris paribus*, with the number of spires. The mutual induction of circuits was first carefully studied by Weber (1846), later by Filici (1852), using a zero method, and Faraday's self-induction by Edlund (1849), while Matteuci (1854) attested the independence of induction of the interposed non-magnetic medium. Henry (1842) demonstrated the successive induction of induced currents.

Curiously enough the occurrence of eddy currents in massive conductors moving in the magnetic field was announced from a different point of view by Arago (1824–26) long before Faraday's great discovery. They were but vaguely understood, however, until Foucault (1855) made his investigation. The general problem of the induction to be anticipated in massive conductor is one of great interest, and Helmholtz (1870), Kirchhoff (1891), Maxwell (1873), Hertz (1880), and others have treated it for different geometrical figures.

The rigorous expression of the law of induction was first obtained by F. Neumann (1845, 1847) on the basis of Lentz's law, both for circuits and for magnets. W. Weber (1846) deduced the law of induction from his generalized law of attraction. More acceptably, however, Helmholtz (1847), and shortly after him Kelvin (1848), showed the law of induction to be a necessary consequence of the law of the conservation of energy, of Ohm's and Joule's law. In 1851 Helmholtz treated the induction in branched circuits. Finally

Faraday's "electrotonic state" was mathematically interpreted thirty years later, by Maxwell, and to-day, under the name of electromagnetic momentum, it is being translated into the notation of the electronic theory.

Many physicists, following the fundamental equation of Neumann (1845, 1847), have developed the treatment of mutual and self induction with special reference to experimental measurement.

On the practical side the magneto-inductor may be traced back to d'al Negro (1832) and to Pixii (1832). The tremendous development of induction electric machinery which followed the introduction of Siemens's (1857) armature can only be instanced. In 1867 Siemens, improving upon Wilde (1866), designed electric generators without permanent magnets. Pacinotti (1860) and later Gramme (1871) invented the ring armature, while von Hefner-Alteneck (1872) and others improved the drum armature. Thereafter further progress was rapid.

It took a different direction in connection with the Ferraris (1888) motor by the development of the induction coil of the laboratory (Faraday, 1831; Neef, 1839; Ruhmkoff, 1853) into the transformer (Gaulard and Gibbs, 1882–84) of the arts. Among special apparatus Hughes (1879) contributed the induction balance, and Tesla (1891) the high frequency transformer. The Elihu Thompson effect (1887) has also been variously used.

In 1860 Reiss devised a telephone, in a form, however, not at once capable of practical development. Bell in 1875 invented a different instrument which needed only the microphone (1878) of Hughes and others to introduce it permanently into the arts. Of particular importance in its bearing on telegraphy, long associated with the names of Gauss and Weber (1833) or practically with Morse and Vail (1837), is the theory of conduction with distributed capacity and inductance established by Kelvin (1856) and extended by Kirchhoff (1857). The working success of the Atlantic cable demonstrated the acumen of the guiding physicist.

Electric Oscillation

The subject of electric oscillation announced in a remarkable paper of Henry in 1842 and threshed out in its main features by Kelvin in 1856, followed by Kirchhoff's treatment of the transmission of oscillations along a wire (1857), has become of discriminating importance between Maxwell's theory of the electric field and the other equally profound theories of an earlier date. These crucial experiments contributed by Hertz (1887, *et seq.*) showed that electromagnetic waves move with the velocity of light, and like it are capable of being reflected, refracted, brought to interference, and polarized. A year later Hertz (1888) worked out the distribution of the vectors in the space surrounding the oscillatory source. Lecher (1890) using an ingenious device of parallel wires, Blondlot (1891) with a special oscillator, and with greater accuracy Trowbridge and Duane (1895) and Saunders (1896), further identified the velocity of the electric wave with that of the wave of light. Simultaneously the reasons for the discrepancies in the strikingly original method for the velocity of electricity due to Wheatstone (1834), and the American and other longitude observations (Walker, 1894; Mitchell, 1850; Gould, 1851), became apparent, though the nature of the difficulties had already appeared in the work of Fizeau and Gounelle (1850).

Some doubt was thrown on the details of Hertz's results by Sarasin and de la Rive's phenomenon of multiple resonance (1890), but this was soon explained away as the necessary result of the occurrence of damped oscillations by Poincaré (1891), by Bjerknes (1891), and others. J. J. Thomson (1891) contributed interesting results for electrodeless discharges, and on the value of the dielectric constant for slow oscillations (1889); Boltzmann (1893) examined the interferences due to thin plates; but it is hardly practicable to summarize the voluminous history of the subject. On the practical side, we are to-day witnessing the astoundingly rapid growth of Hertzian wave wireless telegraphy, due to the successive inventions of Branly (1890, 1891), Popoff, Braun (1899), and the engineering prowess of Marconi. In 1901 these efforts were crowned by the incredible feat of Marconi's first message from Poldhu to Cape Breton, placing the Old World within electric earshot of the New.

Maxwell's equations of the electromagnetic field were put forward as early as 1864, but the whole subject is presented in its broadest relations in his famous treatise of 1873. The fundamental feature of Maxwell's work is the recognition of the displacement current, a conception by which Maxwell was able to annex the phenomena of light to electricity. The methods by which Maxwell arrived at his great discoveries are not generally admitted as logically binding. Most physicists prefer to regard them as an invaluable possession as yet unliquidated in logical coin; but of the truth of his equations there is no doubt. Maxwell's theory has been frequently expounded by other great thinkers, by Rayleigh (1881), by Poincaré (1890), by Boltzmann (1890), by Heaviside (1889), by Hertz (1890), by Lorentz, and others. Hertz and Heaviside, in particular, have condensed the equations into the symmetrical form now commonly used. Poynting (1884) contributed his remarkable theorem on the energy path.

Prior to 1870 the famous law of Weber (1846) had gained wide recognition, containing as it did Coulomb's law, Ampère's law, Laplace's law, Neumann's law of induction, the conditions of electric oscillation and of electric convection. Every phenomenon in electricity was deducible from it compatibly with the doctrine of the conservation of energy. Clausius (1878), moreover, by a logical effort of extraordinary vigor, established a similar law. Moreover, the early confirmation of Maxwell's theory in terms of the dielectric constant and refractive index of the medium was complex and partial. Rowland's (1876, 1889) famous experiment of electric convection, which has recently been repeatedly verified by Pender and Cremieu and others, though deduced from Maxwell's theory, is not incompatible with Weber's view. Again the ratio between the electrostatic and the electromagnetic system of units, repeatedly determined from the early measurement of Maxwell (1868) to the recent elaborate determinations of Abraham (1892) and Margaret Maltby (1897), with an ever closer approach to the velocity of light, was at its inception one of the great original feats of measurement of Weber himself associated with Kohlrausch (1856). The older theories, however, are based on the so-called action at a distance or on the instantaneous transmission of electromagnetic force. Maxwell's equations, while equally universal with the preceding, predicate not merely a finite time of transmission, but transmission at the rate of the velocity of light. The triumph of this prediction in the work of Hertz has left no further room for reasonable discrimination.

As a consequence of the resulting enthusiasm, perhaps, there has been but little reference in recent years to the great investigation of Helmholtz (1870, 1874), which includes Maxwell's equations as a special case; nor to his later deduction (1886, 1893) of Hertz's equations from the principle of least action. Nevertheless, Helmholtz's electromagnetic potential is deduced rigorously from fundamental principles, and contains, as Duhem (1901) showed, the electromagnetic theory of light.

Maxwell's own vortex theory of physical lines of force (1861, 1862) probably suggested his equations. In recent years, however, the efforts to deduce them directly from apparently simpler properties of a continuous medium, as for instance from its ideal elastics, or again from a specialized ether, have not been infrequent. Kelvin (1890), with his quasi-rigid ether, Boltzmann (1893), Sommerfeld (1892), and others have worked efficiently in this direction. On the other hand, J. J. Thomson (1891, *et seq.*), with remarkable intuition, affirms the concrete physical existence of Faraday tubes of force, and from this hypothesis reaches many of his brilliant predictions on the nature of matter.

As a final commentary on all these divers interpretations, the important dictum of Poincaré should not be forgotten: If, says Poincaré, compatibly with the principle of the conservation of energy and of least action, any single ether mechanism is possible, there must at the same time be an infinity of others.

The Electronic Theory

The splendid triumph of the electronic theory is of quite recent date, although Davy discovered the electric arc in 1821, and although many experiments were made on the conduction of gases by Faraday (1838), Reiss, Gassiot (1858, *et seq.*), and others. The marvelous progress which the subject has made begins with the observations of the properties of the cathode ray by Plücker and Hittorf (1868), brilliantly substantiated and extended later by Crookes (1879). Hertz (1892) and more specifically Lenard (1894) observed the passage of the cathode rays into the atmosphere. Perrin (1895) showed them to be negatively charged. Röntgen (1895) shattered them against a solid obstacle, generating the X-ray. Goldstein (1886) discovered the anodal rays.

Schuster's (1890) original determination of the charge carried by the ion per gram was soon followed by others utilizing both the electrostatic and the magnetic deviation of the cathode torrent, and by Lorentz (1895) using the Zeeman effect. J. J. Thomson (1898) succeeded in measuring the charge per corpuscle and its mass, and the velocities following Thomson (1897) and Wiechert (1899), are known under most varied conditions.

But all this rapid advance, remarkable in itself, became startlingly so when viewed correlatively with the new phenomena of radioactivity, discovered by Becquerel (1896), wonderfully developed by M. and Madame Curie (1898, *et seq.*), by J. J. Thomson and his pupils, particularly by Rutherford (1899, *et seq.*). From the Curies came radium (1898) and the thermal effect of radioactivity (1903), from Thomson much of the philosophical prevision which revealed the lines of simplicity and order in a bewildering chaos of facts, and from Rutherford the brilliant demonstration of atomic disintegration (1903) which has become the immediate trust of the twentieth century. Even if the ultimate significance of such profound researches as Larmor's (1891) *Ether and Matter* cannot yet be discerned, the evidences of the transmutation of matter are assured, and it is with these that the century will immediately have to reckon.

The physical manifestations accompanying the breakdown of atomic structure, astoundingly varied as these prove to be, assume fundamental importance when it appears that the ultimate issue involved is nothing less than a complete reconstruction of dynamics on an electromagnetic basis. It is now confidently affirmed that the mass of the electron is wholly of the nature of electromagnetic inertia, and hence, as Abraham (1902), utilizing Kaufmann's data

(1902) on the increase of electromagnetic mass with the velocity of the corpuscle, has shown, the Lagrangian equations of motion may be recast in an electromagnetic form. This profound question has been approached independently by two lines of argument, one beginning with Heaviside (1889), who seems to have been the first to compute the magnetic energy of the electron, J. J. Thomson (1891, 1893), Morton (1896), Searle (1896), Sutherland (1899); the other with H. A. Lorentz (1895), Wiechert (1898, 1899), Des Coudres (1900), Drude (1900), Poincaré (1900), Kaufmann (1901), Abraham (1902). Not only does this new electronic tendency in physics give an acceptable account of heat, light, the X-ray, etc., but of the Lagrangian function and of Newton's laws.

Thus it appears, even in the present necessarily superficial summary of the progress of physics within one hundred years, that, curiously enough, just as the nineteenth century began with dynamics and closed with electricity, so the twentieth century begins anew with dynamics, to reach a goal the magnitude of which the human mind can only await with awe. If no Lagrange stands toweringly at the threshold of the era now fully begun, superior workmen abound in continually increasing numbers, endowed with insight, adroitness, audacity, and resources, in a way far transcending the early visions of the wonderful century which has just closed.

SECTION A—PHYSICS OF MATTER

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(*Hall* 11, *September* 23, 10 *a. m.*)

CHAIRMAN: PROFESSOR SAMUEL W. STRATTON, Director of the National Bureau of Standards, Washington.
SPEAKERS: PROFESSOR ARTHUR L. KIMBALL, Amherst College.
PROFESSOR FRANCIS E. NIPHER, Washington University.
SECRETARY: PROFESSOR R. A. MILLIKAN, University of Chicago.

THE RELATIONS OF THE SCIENCE OF PHYSICS OF MATTER TO OTHER BRANCHES OF LEARNING

BY ARTHUR LALANNE KIMBALL

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It is evident at the outset that it is quite out of the question, in the time at our disposal, to discuss adequately the relation of the physics of matter to the other sciences, even if the speaker were endowed with the requisite omniscience.

For *matter* is the very stuff in which the phenomena of all the natural sciences are manifested, the chemist finds himself confronted at every turn with physical relations which must be taken into account, the astronomer finds his greatest triumph in exhibiting the universe that he explores with the telescope as an harmonious illustration of physical principles, the geologist also hardly faces a single question that does not demand the aid of physics or chemistry in its solution, and even in the biological sciences the laws of matter still condition the phenomena of life.

Perhaps a brief consideration of the interrelations of these sciences may aid us in a clearer perception of their dependence on the physics of matter.

There are *three* sciences that may be said to be especially fundamental, in that they deal with the elements of the universe of phenomena. These are *physics,* which, if we define it somewhat narrowly, deals with all the phenomena that can be exhibited *by* and *through the means of* any one kind of matter, as well as all interactions between different kinds of matter in which each preserves its separate identity; *chemistry,* which has for its province those special phenomena in which one kind of matter is broken up into two or more kinds, or in which the interactions between different kinds of matter result in the formation of a substance different from either of the constituents; and that phase of *biology* which is concerned with the study of the living cell and of the simplest conditions under which matter exhibits the phenomena of life.

It might have been said that *physics* deals with those phenomena exhibited by and through matter when molecular groupings of atoms are not disturbed, while *chemistry* deals with the phenomena of the formation and breaking-up of the molecules. But such a statement is based upon a theory of the structure of matter which in itself calls for explanation, and therefore the previous statement is preferred as being more general and avoiding the theoretical assumptions that are involved in those just given.

If it is asked what constitutes a particular kind of matter, why, for instance, water-vapor is said to be the same substance as water in the liquid form, it may be said that it is because one can be wholly transformed into the other, each is homogeneous, and remains unchanged in its properties during the transforming, and the transformation is unique.

Professor Ostwald has recently given a most interesting statement of the criterion by which a substance or chemical individual may be recognized without the need of any atomic hypothesis. We may summarize his presentation thus: Where two substances are combined as in solution, there will be one and only one proportion between the quantities of the substances for which, on change of state, such as evaporation or crystallization, the vapor or crystals will have the same composition as the remaining substance, while with a greater or less proportion of either ingredient, there will be a change of concentration with change of state. When such a combination retains this property under widely different conditions of temperature and pressure, it is known as a chemical individual or definite compound. If under *no* circumstances it can be broken up into two phases which differ in constitution, it is called an element.

Ostwald remarks, "The possibility of being changed from one phase into another without variation of the properties of the residue and of the new phase is indeed the most characteristic property of a substance or chemical individual, and all our methods of testing the purity of a substance, or of preparing a pure one, can be reduced to this one property."

But returning to our classification, it is seen that physics, chemistry, and biology are the three fundamental natural sciences, each having as its primary object not the mere arrangement and classification of phenomena, but the formation of such a concept of matter in those relations with which it deals, that the varied facts of observation appear as natural and inevitable consequences.

The other sciences are in a certain sense secondary to the three that have been mentioned. Each is concerned with the investigation of some system that is built up out of matter, and involves the same fundamental relations which are the objects of study for the primary sciences, but the secondary science finds its interest not in the materials of which the structure is made, but in the study of the resulting structure itself.

Thus astronomy seeks to describe and make out the past history and future development of the universe of sun and star and planet. The sciences of the earth are concerned with the history of the development of our planet, with the present phenomena of its interior, of its crust, of its surface, and of its atmosphere, while the secondary biological sciences have as their aim to trace the relations of the various forms of life and to follow out the developments of each.

But while each secondary science thus has an aim of its own quite distinct from that of the primary sciences, nevertheless it must be controlled and to some extent guided by the sciences of matter. Thus in almost every science chemical phenomena play a part which must be reckoned with, while physics, dealing as it does with the most universal phenomena of matter, underlies and conditions all the sciences without exception. Therefore it is to be expected that with the development of physics both in discovery and theory there should be a greater or less reaction on the other sciences, for in so far as they depend for their development on the laws of matter they are dependent on the labors of the physicist.

We might therefore expect to find in every science, if we only knew it well enough, a response to every considerable advance in physics. For the advances in a science result not from discovery alone, but from new points of view taken by those who are thinking on its problems; and the ideas of physics, bearing as they may be said to do on the raw material of the other sciences, must in a preëminent degree influence the thinking of workers in all fields.

It deserves to be emphasized that every science is an intellectual structure. Only as this is conceded will science be yielded the lofty and dignified position which is its due. Experiments may be multiplied, facts and data may be accumulated in bewildering numbers, but there is no science without the clear intellectual vision that sees the parts in their dependencies and relations one to another and catches glimpses of the larger unities that run through all.

They are mistaken who think the true scientist less an idealist than is the artist or student of literature, or who think the path of experiment mere drudgery in the accumulation of insignificant facts. The investigator lives in a world of ideas, and in every step of a difficult inquiry he has the buoyant consciousness that he is getting a deeper, truer insight into his science.

This intellectual character of scientific research is well illustrated in the enthusiasm which marked the news of Hertz's discovery of electromagnetic waves. The facts observed might easily have been thought to be in themselves insignificant: a slight spark observed between the ends of a bent wire near a discharging electrified system. There was no thought of a practical application, and yet a wave of almost unprecedented excitement spread among physicists the world over. Nor was it alone admiration for the skill, the insight and grasp of the great experimenter that won the victory, though this had its effect. It was mainly an exultant enthusiasm over the triumph of an idea, the unification of science in the confirmation of Maxwell's great theory.

It is clear, then, that physics may react on the other sciences in a variety of ways, in its *methods* and *appliances*, in its *discoveries*, and in its *ideas and generalizations;* and it is evident, therefore, that we must limit ourselves to a brief consideration of certain phases of the subject. I have, therefore, chosen to present very briefly some considerations relative to theories of matter, for here physics and chemistry come into the closest contact; also to touch upon some other relations of chemistry and geology to physics, that are of particular interest at this present time.

The fundamental problem in the physics of matter is the nature of matter itself. Of course we recognize at the outset the limitations that bound our attempts at a solution. We may hope to reach eventually some conclusion as to the structure of matter, whether homogeneous or molecular or grained, also as to the relative motions of the parts of the molecule and the law of variation of force between them with the distance. But if we seek to go farther and explain the forces acting in and between molecules in terms of what appear to be more simple and general laws, it seems inevitable that a medium must be assumed, the properties of which will depend on what is assumed as a primary postulate. If we accept, as is usually done, the postulate that forces in their last analysis can only be explained when referred to pressures exerted between contiguous portions of some underlying medium, it seems probable that a theory must be adopted something like the vortex atom theory of Lord Kelvin, with its continuous, incompressible, perfectly fluid medium in which vortically moving portions constitute the atoms, or Osborne Reynolds's theory of space as filled with fine hard spherical grains, in which, regions with nonconformity in arrangement, are the atoms of ordinary matter. Though it must be said that the assumed hardness of the ultimate spherules in the latter theory is a property which in itself needs explanation.

Perhaps, however, in laying down the postulate mentioned above we are pushing too far inferences from our superficial experience.

The idea that force must be a pressure between contiguous portions of substance is derived directly from the notion of the impenetrability of matter. This is why the incompressible medium of Lord Kelvin's theory seems so simple a conception; it is the naked embodiment of the idea of impenetrability associated with inertia.

It is entirely natural that such ideas as impenetrability and inertia, borne in upon us as they are by our experience of matter in bulk, should affect our theorizing, but it should never be forgotten that as fundamental postulates they have no more authority than any others that might be assumed that will coördinate the same facts of observation.

But passing from this more speculative region we find a pretty general agreement on the rough outlines of the structure of matter. With one notable exception most physicists and chemists agree in the idea that matter is atomic or molecular in structure, and that these molecules are in a state of more or less energetic translatory motion, bounding and rebounding from each other. This seems to be the mechanical hypothesis which coördinates the largest number of facts.

A portion of matter is conceived as in a condition of equilibrium under three pressures: the cohesive pressure due to mutual attraction between all molecules which are not farther apart than 50 to 100 millionths of a millimeter; the external pressure, which also acts to cause contraction; and the internal pressure, which balances the two former, and is due to a repulsive force called the force of impact, which is usually supposed to be exerted only between contiguous molecules.

In the solid and liquid states the cohesive pressure is usually very great compared with the external pressure. In case of gases it nearly vanishes. The force between molecules is thus conceived as an attraction which increases rapidly as they approach, until at a certain distance it is balanced by a repulsive force which, increasing still more rapidly, is the controlling force at all less distances.

Lord Kelvin has recently followed out a study of equilibrium conditions in a group of atoms which are assumed to have no mutual influence until within a certain distance, then to attract each other with a force that increases as they approach still nearer, rising to a maximum and then diminishing, and finally becoming a repulsion when the atoms are very near. He remarks, "It is wonderful how much toward explaining the crystallography and elasticity of solids, and the thermo-elastic properties of solids, liquids, and gases, we find without assuming in the Boscovitchian law of force more than one transition from attraction to repulsion."

The fundamental soundness of the conception of matter as having a grained structure of some sort seems to be established by the remarkable degree of agreement in the estimates by various physicists of the size of these ultimate particles, meaning by that the smallest distance between their centres as they rebound from each other, especially when it is considered that these results have been reached from so many different points of view, and are based on such a variety of physical data.

As to the structure of the atom itself a most remarkable theory has been recently developed. J. J. Thomson has marshaled the evidence in favor of the theory proposed by Larmor that matter has an electrical basis, and the theory has already been considerably developed by Lorentz and others. There appears to be reason for believing that the corpuscles of the Kathode rays are simply moving charges of negative electricity, their whole apparent mass being due to their relation to the ether, in consequence of which there is a magnetic field around the moving charge having energy dependent on the square of its velocity. The corpuscle, therefore, effectively has mass in consequence of this reaction between it and the ether.

The corpuscles are found always to carry the same charge, whatever the nature of the gas in which the Kathode rays are formed, and whatever the nature of the electrodes — the charge being the same as that given up by the hydrogen atom in electrolysis, while the mass of the corpuscle is about one one-thousandth that of the hydrogen atom.

The energy in the ether associated with the moving corpuscle depends on the size of the corpuscle as well as upon its charge, and it is found that to account for its apparent mass it must be of extremely small size relative to ordinary atomic dimensions.

Professor Thomson suggests that the primordial element of matter is such a negative electron combined with an equal positive charge, the latter being of nearly atomic dimension. An atom of hydrogen may be thought of as made up of nearly a thousand such pairs, the positive charge being distributed throughout a spherical region giving rise to a field of force within it in which the force on a negative corpuscle will be towards the centre and proportional to its distance from the centre. In this field of force the corpuscles are conceived as describing closed orbits with great velocities.

The internal energy of such an atom is conceived as enormous. In case of the atoms contained in a gram of hydrogen Thomson reckons about 10^{19} ergs as the energy received from mutual attractions in the formation of the atoms, an amount of work that would lift a hundred million kilograms, one thousand meters.

The whole mass of the atom is supposed to be due to the *negative* electrons or corpuscles which it contains. As to the *positive* charge, although it determines the apparent *size* of the atom, it appears to make no contribution to its mass.

When such an atom impacts against another, the corpuscles in each will be disturbed by the jar in their orbital motion, and there will be superposed oscillations which will cause radiation of energy.

If a corpuscle escapes from such an atom, the latter will be left with a positive charge, while if an additional free corpuscle is entrapped, the atom will have a negative charge. The conditions of stability of motion of the corpuscles in the atom would thus determine whether in case of electrolysis the substance would appear electro-positive or electro-negative.

J. J. Thomson, Drude, and others have discussed the electric conduction of metals from the standpoint of this theory. Drude states that in non-conductors only bound electrons are present, that is, positive and negative in combination; and that it is these that determine the dielectric constant of the medium and consequently its index of refraction and optical dispersion; while Langevin explains magnetism and diamagnetism.

Thus we have a theory already surprisingly developed which appears to be applicable to explain many of the properties of matter, though it is not clear that it can give an explanation of cohesion and gravitation. A theory of matter, to be accepted as final, must offer some explanation of the relation between the various elements. Many thinkers have been led to look for some primordial element from which the others are derived, influenced on the one hand by the present evolutionary ideas of biology, and on the other by comparison of spectra and by the remarkable tendency towards whole numbers observed in the atomic weights of the elements which Strutt has discussed from the standpoint of the theory of probabilities. Professor Thomson has accordingly shown how atoms of matter containing great numbers of corpuscles may have been evolved from a simpler primordial form containing fewer corpuscles. But though he has made clear how the hydrogen atom with its thousand corpuscles might be the surviving atom having the *least* number of corpuscles, it is not so clear why there might not be atoms having any number of corpuscles greater than that of hydrogen, within certain limits; why none should be found between hydrogen and helium for example. Some kind of natural selection seems to be needed to explain why some atoms having special numbers of corpuscles survive while intermediate ones are eliminated, though probably the answer is to be sought in the conditions of stability of the motions of the corpuscles.

It is an interesting question what would be the effect of change of temperature of the substance on the motions of the corpuscles in this theory. If the corpuscles in the atom were very numerous, all moving in the same orbit at equal distances apart, they would produce almost the effect of a circular current of electricity, — a steady magnetic field and no radiation; and it seems probable that in the actual case the radiation of internal energy is extremely small, and the total internal energy may be supposed to be so enormous compared with the energy of translation of the atom due to temperature that we may expect no appreciable change in the radiation of internal energy of the atom, whatever the temperature may be.

That component of the vibration of a corpuscle which is radial within the atom, and is set up by the impact of one atom against another, seems to furnish the great mass of radiated energy. This radiation must also react on the motion of the atom as a whole, taking away from the translatory energy of the atom.

The question how the Boltzmann law of partition of energy between the various degrees of freedom will apply to molecules made up of such atoms as are here conceived is an interesting and important one. Is it possible that the *cloud,* as Lord Kelvin calls it, resting on the kinetic theory of gases may be dissipated by the new theory?

This theory of the atom seems also to explain the possibility of the production of spectra of great complexity. It is to be hoped that Balmer's formula and Rydberg's laws of the grouping of lines in spectra may be shown to be the natural outcome of the system of vibration possible in such an atom.

We are startled at first by the very audacity of this theory, seeming as it does to upset the old point of view, and seek the explanation of matter and its laws in terms of the properties of ether and electricity, instead of trying to unravel the secrets of electricity and ether in terms of matter and motion.

Only a few years ago it was thought that the electromagnetic theory of light must be rationalized by giving a mechanical explanation of the various phenomena of the ether, or by showing at least that such an explanation was possible. Witness Maxwell's wonderfully ingenious mechanical model illustrating the phenomena of magnetism, induced currents, and the propagation of electromagnetic waves.

But is it necessary to regard the mechanical explanation as the only sound one? If electricity and ether are fundamental entities underlying all matter and material phenomena, is it not more logical to find a basis for the mechanical laws in some more fundamental laws of ether and electricity which must be accepted as the primary postulates?

In all this development of the atomic view of matter, chemistry and physics have gone hand in hand. The atomic theory of Dalton has been the basis on which both sciences have worked. Avogadro's law for gases has been reached not only by chemical evidence, but has been raised to the rank of a mechanical deduction from the kinetic theory. The significance of the arrangement of atoms in the molecule in determining chemical reaction was emphasized and developed by Kekulé, but it was not until 1874 that the space diagrams of molecules of van't Hoff and Le Bel marked a full appreciation of the possibilities of structure in explaining the differences of isomeric forms.

All of these physical and chemical developments of the atomic theory have been in accordance with a general method of scientific procedure which may be called the method of mechanical models. According to this method, an attempt is made to conceive a certain mechanism by which the various phenomena sought to be explained may be imagined to be brought about.

Such a theory of atoms, for example, if perfect, would exhibit all the properties of atoms as direct consequences of the assumed structure. This cannot, however, be taken as proof that the assumption is real, though for the purpose of our thinking such a theory would have all *the value* of reality, since all consequences deduced from it would conform to the facts of observation. And this suggests wherein the great value of such a theory lies, not alone in the large number of observations which it correlates and brings under a few general principles, but in that it suggests the application of experiments and tests of its sufficiency, thereby enlarging and making more precise our knowledge.

Perhaps the most remarkable instance of the application of this method was Maxwell's development of a mechanical model to illustrate the reactions in the electromagnetic field. Working from this model he developed the equations of the field, which later he deduced in a more general way. And Hertz speaking of them says, "We cannot study this wonderful theory without at times feeling as if an independent life and a reason of its own dwelt in these mathematical formulæ; as if they were wiser than we were, wiser even than their discoverer; as if they gave out more than had been put into them." On which Boltzmann's comment is, "I should like to add to these words of Hertz only this, that Maxwell's formulæ are simple consequences from his mechanical models; and Hertz's enthusiastic praise is due in the first place, not to Maxwell's analysis, but to his acute penetration in the discovery of mechanical analogies." Such an example well illustrates the importance of the method.

But of recent years, the influence of quite a different method has been strongly marked in chemical research. A method in which certain general laws are established and then applied to particular cases by a process of mathematical reasoning, deducing conclusions quite independently of the particular details of the operation by which they are brought about. This method is well illustrated in Professor J. J. Thomson's work on the application of dynamics to problems in physics and chemistry, and in the deductions based on the laws of thermodynamics that have marked the development of the new physical chemistry.

It is under the influence of this method that Professor Ostwald has been led to propose a theory of matter which does not recognize the necessity of any atomic structure whatever. In a recent address, he says, "It is possible to deduce from the principles of chemical dynamics all the stoichiometrical laws; the law of constant proportion, the law of multiple proportion, and the law of combining weights." And he continues, "You all know that up to this time it has only been possible to deduce these laws by the help of the atomic hypothesis. Chemical dynamics has, therefore, made the atomic hypothesis unnecessary for this purpose and has put the theory of the stoichiometrical laws on more secure ground than that furnished by a mere hypothesis." And then farther on he continues, "*What we call matter is only a complex of energies which we find together in the same place.* We are still perfectly free if we like to suppose either that the energy fills the space homogeneously, or in a periodic or grained way; the latter assumption would be a substitute for the atomic hypothesis." And then he adds, "Evidently there exists a great number of facts — and I count the chemical facts among them — which can be completely described by a homogeneous or non-periodic distribution of energy in space. Whether there exist facts which cannot be described without the periodic assumption, I dare not decide for want of knowledge; only I am bound to say that I know of none."

It is interesting and remarkable that this challenge to the atomic theories of matter should come from the side of chemistry, the very science for which the atomic theory of Dalton was conceived. Especially is it remarkable, in view of the measure of success that has attended the explanation of the differences between such forms as right and left rotating tartaric acids on the basis of molecular structure. And it is difficult to see how it is possible to give any satisfactory explanation of these differences, simply on the basis of the laws of energetics applied to a conception of matter as homogeneous.

With reference to the view that "*What we call matter is only a complex of energies which we find together in the same place,*" it may be said that we recognize different forms of energy only in association with matter or ether; as heat, light, chemical energy, kinetical energy, etc. Hence the term, "a complex of energies," can only mean the total energy in a given region, unless we recognize some vehicle, as matter or ether, in which the special manifestations of energy may exist. This seems to be admitted tacitly by Ostwald himself, for a little farther on he says, "The reason why it is possible to isolate a substance from a solution is that the available energy of the substance is at a minimum." He thus distinguishes between the available and the total energy of a portion of matter. But this discrimination can have no meaning unless it is granted that a portion of the energy of a substance is not available. If we ask why it is not available, the answer may be that when a substance passes from one state to another at constant temperature the work that it can do is less than its total intrinsic energy as a consequence of the laws of thermodynamics. The case must therefore be one to which the second law of thermodynamics can apply. That is, it must involve flow of energy by some such process as heat conduction.

It might perhaps be successfully argued that the very existence of such a process implies grained structure of some sort to which a statistical law may apply. However this may be, it is certainly difficult to conceive of energy as existing apart from some vehicle, matter or ether or both as you will; but to conceive of this sublimated energy as in part available and in part non-available is surely quite beyond attainment.

It is with great diffidence that we dissent from the expressed views of one who has done so much for the advance of physical chemistry, and our excuse for entering on the discussion must be that as the latest utterance with regard to matter, and coming from one who has won the right to have his views given a respectful consideration, it seemed more fitting to present this brief and imperfect discussion than to pass them by without comment.

One of the most important reactions of physics upon the other sciences has resulted from the extension of the *thermodynamic* laws to chemical problems which has marked the new physical chemistry, a science which has sprung into being within the last seventeen years and has already, under the leadership of van 't Hoff, Ostwald, Arrhenius, and Nernst, attained a surprising development, and is making itself felt in many other lines of scientific activity, notably in electrochemistry, geology, and biology. The starting-point in this development was the idea conceived by van 't Hoff that Avogadro's law might be so extended as to apply to the case of substances in solution. Just as a gas expands and fills the containing vessel exerting a pressure against its walls, so a salt dissolved in a liquid diffuses uniformly throughout the liquid and exerts a pressure within the liquid tending to expand it. This osmotic pressure, so called, had been measured in certain cases by Pfeffer and de Vries, but it remained for van 't Hoff to show that, as in case of a gas, the pressure was proportional to the absolute temperature and to the number of molecules of the dissolved substance contained in unit volume.

As has so often happened before, the study of the apparent exceptions to the rule led to a second great advance, the theory of electrolytic dissociation proposed by Arrhenius, to account for the observation that in solutions of electrolytes the osmotic pressure was greater than that reckoned on the basis of the number of molecules present, but was to be explained by their dissociation into ions; thus reaching the same conclusion which Clausius had announced in 1857, but affording a method by which the precise amount of the dissociation might be measured. Additional evidence in favor of this theory was afforded by the studies of the electrical conductivity of dilute solutions of electrolytes made by Kohlrausch.

All this was accompanied by an increasing realization of the important relations that might be established by an application of the laws of thermodynamics to chemical problems. Thus van 't Hoff showed in his paper of 1887 that the depression of the freezing-point of a liquid due to a substance in solution depended directly on the osmotic pressure and could be used to measure it; a result which had already been experimentally reached by Raoul.

In this field, Professor J. Willard Gibbs, in whose recent death the world of science has lost a most profound thinker, was a pioneer. His most important contributions to the subject were in two extraordinary papers, *On the Equilibrium of Heterogeneous Substances.* The first of these related to chemical phenomena, while the second was concerned especially with capillarity and electricity.

To quote from a recent writer, "The most essential feature of Gibbs's discoveries consisted in the extension of the notion of thermodynamical potential to mixtures consisting of a number of components, and the establishment of the properties that the potential is a linear function of certain quantities which Gibbs has called the potentials of the components, and that where the same component is present in different phases, which remain in equilibrium with each other, its potential is the same in all the phases, besides which the temperatures and pressures are equal. The importance of these results was not realized for a considerable time. It was difficult for the experimentalist to appreciate a memoir in which the treatment is highly mathematical and theoretical, and in which but little attempt is made to reduce conclusions to the language of the chemist; moreover it is not unnatural to find the pioneer dwelling at considerable length on comparatively infertile regions of the newly explored territory, while fields that were to prove the most productive were dismissed very briefly."

"It was largely due to Professor van der Waals that two new and important fundamental laws were discovered in Gibbs's paper, namely, the phase rule and the law of critical states."

The phase rule has been the guiding principle in some most important studies of chemical equilibrium. It furnishes a clue by which the polymorphism of such substances as sulphur and tin may be scientifically investigated and the conditions of equilibrium between the different polymorphic forms determined. The studies of the case of ferric chloride by Roozeboom, and of the crystallization out of sea-water of the contained salts by van 't Hoff and Meyerhoffer indicates the great value of the phase rule in bringing scientific order out of the complicated relations of the various components and phases involved.

Speaking of this department of physical chemistry, van 't Hoff remarked, "Since the study of chemical equilibrium has been related to thermodynamics, and so has steadily gained a broader and safer foundation, it has come into the foreground of the chemical system, and seems more and more to belong there." And Ostwald says in answer to the question, "What are the most important achievements of the chemistry of our day? I do not hesitate to answer: chemical dynamics, or the theory of the progress of chemical reaction, and the theory of chemical equilibrium."

These statements, coming from two masters in the field, are most significant of the importance of the introduction of these ideas into chemistry.

The conceptions and methods of physical chemistry have also been most strongly felt in the field of electrochemical theory. To the question what is the nature of electrolysis, Faraday and Hittorf and Clausius had each contributed important elements of the final answer, then came Arrhenius with the theory of electrolytic dissociation, which has proved so fruitful of consequences, not only in the domain of chemistry, but also in biology and in physics.

One of the most interesting scientific questions connected with electrochemistry is the relation between electromotive force and electrolytic separation, and the development of the theory of the voltaic cell. The question of the seat of electromotive force in the cell was for many years the very storm-centre of physical discussion; but from the standpoint of electrolytic dissociation Nernst has supplemented the work of Helmholtz and Gibbs, and out of all has come a theory which, while not perfect, seems to be in its main features on the solid foundation of the conservation of energy and the laws of thermodynamics.

Another important service for which the world of science is indebted to physics is the determination of the absolute zero of temperature in terms of degrees of the ordinary centigrade scale. About a century ago, Dalton, in his new chemical philosophy, adopts −3000° C. as the probable zero of temperature. While Lavoisier and Laplace make various estimates of the zero ranging from 1500 to 3000 degrees below the freezing-point of water. But when the doctrine of energy became firmly established together with the kinetic theory of gases, it was natural that the condition of a gas in which the particles had no energy of motion, and hence no pressure, should have been taken as indicating the absolute zero. But it was Clausius and Lord Kelvin who based firmly on the laws of thermodynamics the absolute scale of temperature, as we know it to-day.

The absolute zero of temperature has to the physicist all the fascination that the North Pole has to Arctic explorers, and is probably even more difficult to attain. Yet steady progress has been made in conquering the difficult territory that lies toward this goal. The experimental efforts to liquefy the more refractory gases showed that far lower temperatures than had previously been reached must be employed; and step by step, following the suggestions of thermodynamics, the means of attaining low temperatures have been improved, at first cooling by adiabatic expansion of more compressible gases, then aided by the sudden expansion of the gas itself which had been compressed and cooled, and then by a continuous self-intensive action, in which the cold produced by the expansion of one portion of the compressed gas was made use of to cool the still unexpanded gas as it approached the point of expansion.

The mere record of the temperatures reached marks a series of triumphs of ingenuity and perseverance. Thus Faraday, in 1845, reached a temperature of -110 by the use of solid carbon dioxide and ether evaporated at low pressure. Pictet in 1877 reached -140, and liquefied oxygen under pressure. Olszewski in 1885 obtained a temperature of -225 by the evaporation of a mass of solid nitrogen. In 1898 Dewar obtained liquid hydrogen boiling at -252, or only 20.5 above the absolute zero, and later by boiling at reduced pressures he was able to obtain -259.5 or 13.5 degrees absolute scale, at which point hydrogen is frozen solid.

The attainment of these low temperatures has not alone made possible investigations of the greatest interest to the physicist, such as studies of the magnetic and electric properties of bodies as they approach the absolute zero, but has enabled the effect of extreme cold on chemical actions to be determined, and has led to the interesting conclusion that "The great majority of chemical interactions are entirely suspended." Though it has been shown by Dewar and Moissan that in case of solid hydrogen and liquid fluorine, violent reaction still takes place even at that small remove from the absolute zero.

A very interesting field has also been opened to biological research, in the effect of extreme cold on the vitality of seeds and micro-organisms. It was found, for example, that barley, pea, and mustard seeds steeped for six hours in liquid hydrogen and thus kept at a temperature of minus 252 degrees, showed no loss of vitality. So, also, certain micro-organisms, among others the bacilli of typhoid fever, Asiatic cholera, and diphtheria, were kept by MacFadyen for seven days at the temperature of liquid air without appreciable loss of vitality. It has been suggested by Professor Travers that, "It is quite possible that if a living organism were cooled only to temperatures at which physical changes, such as crystallization, take place with reasonable velocity, the process would be fatal, whereas, if they were cooled to the temperature of liquid air no such change would take place within finite time, and the organism would survive."

Also the study of the various combinations of carbon and iron that may exist in steel, and the conditions of equilibrium that exist between them has proved a most important investigation in the field of what van 't Hoff calls solid solutions.

Geology, dealing as it does with the greatest variety of physical processes, such as changes of state, fusion, crystallization, solution, conduction of heat, radiation, with complications depending on variations of pressure and temperature, presents many problems for the solution of which the resources of modern physics must be taxed. The fusing-points of the different chief minerals of the earth's crust, the effect of great pressure on their fusing-points and modes of crystallization, the crystallization of the various elementary minerals out of a fused magma also studied at different pressures, the effect of pressure not only on fusing-points, but on the viscosity and rigidity of minerals at high temperature, the heat conductivities of the various substances making the bulk of the earth's crust, all these are questions that must be thoroughly studied to enable the geologist to determine the probable condition both of temperature and pressure which prevailed during the formation of a given rock mass, and to throw light on the great problem of geology, the age of the earth.

To this latter question, physics has already given a tentative answer. Lord Kelvin's discussion, based on the assumption of the earth as a mass cooling from a uniform high temperature, points to a period of between twenty and one hundred million years, within which geologic changes in the crust of the earth must have occurred; while Helmholtz and Kelvin's deduction of the time during which solar radiation can have been of such an intensity that life conditions on the earth were possible gives about twenty million years as the limit.

But later investigations giving new data as to the properties of the materials of the earth's crust, as to the laws of variation of radiation with temperature, and as to absorption and radiation by the solar and earth's atmospheres, will all contribute to modify and make more precise these methods. Already some progress in this direction has been made. A few years ago, Clarence King gave a most interesting and ingenious rediscussion of Kelvin's cooling of the earth method, making use of the determinations made by Barus of the fusing-points of diabase at different pressures, and gives as the most probable result of the method the period of twenty-four million years, a period in close agreement with that found by Helmholtz and Kelvin from the radiation of the sun.

It should be remarked, however, that in discussing the state of things in the earth's interior, where the pressures so far transcend anything that can be approached in the laboratory, such constants as melting-points should be looked on with great suspicion.

Assuming Laplace's law of distribution of density in the earth, the pressure at a depth of one two-hundredth of the earth's radius is 8600 atmospheres, while at the centre of the earth it becomes more than three million atmospheres. Now the largest pressures that have been used in high temperature experiments are less than three thousand atmospheres. It is evident, then, that any conclusion as to melting-points from laboratory data must be violent exterpolations, if deduced for the enormous pressures at depths greater than one one-hundredth of a radius within the earth, where the pressure will be over 17,000 atmospheres.

But not only is there necessarily great uncertainty as to the fusing-points at these great pressures, but it seems probable that such a process as fusion marked by sudden increase in liquidity can hardly take place at all. In the phenomenon of fusion, the equilibrium of a substance may be regarded as conditioned by the external pressure, the cohesive pressure, and the internal pressure due to the translatory kinetic energy of the molecules, which may be called the kinetic pressure. In a state of equilibrium, the external pressure plus the cohesive pressure must equal the kinetic pressure, the last tending to produce expansion, while the two former act to cause contraction. At ordinary atmospheric pressures in the liquid and solid state, the cohesive pressure is enormously greater than the external pressure. In water at ordinary temperatures it is estimated about 6500 atmospheres, while in a solid such as steel it may have a value of perhaps 18,000 atmospheres. And not only is this cohesive force great relatively to the external pressure, but it decreases with great rapidity as the substance expands. Under these conditions it is easy to see that a slight rise in temperature with consequent expansion and weakening of the cohesive pressure while the kinetic pressure is increased may bring the substance to a point of transition, a melting-point or boiling-point where great changes occur within narrow limits of temperature.

But if we conceive the external pressure to be so great that the cohesive pressure is relatively insignificant, then we should not expect to find any sharply marked changes of state for small changes of temperature or pressure.

To make the case definite assume a temperature of 1000 degrees absolute scale, and a pressure of 1,000,000 atmospheres, and suppose the cohesive pressure is 10,000 atmospheres. Under these circumstances a rise in temperature of ten degrees or a one per cent increase in temperature may be expected to produce a one per cent increase in the kinetic pressure at the original volume; but as the external pressure is constant and the cohesion is insignificant, we may expect a one per cent increase in the volume in which the molecular motions take place or an increase in the mean distance between molecules of one third of one per cent. Such an expansion will be accompanied by slightly lessened cohesive force, less rigidity, and less viscosity, probably; but nothing like a sudden change of state is suggested. The fact that at pressures greater than the critical pressures there can be observed no sharp transition from the liquid to the gaseous state with rise of temperature is quite in accord with the above considerations, and it seems probable that in case of solids under great pressure nothing like melting will be observed, but rather a gradual loss of rigidity or transition to great viscosity, and that the viscosity will decrease steadily with rise in temperature.

But a new aspect is now given to the problem of the age of the earth by the discovery of radioactivity and its attendant phenomena. The earth, instead of being thought of as a cooling body, is now conceived as having within itself a source of almost unlimited energy. Locked up in each atom is believed to be a store of energy so vast that the breaking down of comparatively few of them in the radioactive process will supply the known outflow of heat from the earth.

Rutherford has shown that the observed dissemination of radioactive substances in the earth's crust is probably sufficient to account for the outflow of energy from its surface. Thus the method of estimating the age of the earth from the consideration of it as a cooling body, a method which until lately seemed to physicists to be based on essentially sound premises, and deserving of confidence because of its greater simplicity as compared with the methods by which geological and biological estimates are obtained, is now by the very progress of physics itself abandoned as unreliable.

So also has the study of radioactivity thrown new light on the question of the maintenance of the sun's heat. It is now seen that possible atomic transformations accompanied by the liberation of the vast stores of energy locked up within the atoms of matter may permit an enormous extension of the time during which the sun may have been radiating with something like its present intensity.

In conclusion it may be remarked that a new world is opened to the investigator by the discovery of radioactivity. The atoms of matter are no longer thought of as necessarily fixed and unchangeable. Besides the older problems of matter questions now arise as to evidences of atomic disintegration and change from more complex to less complex forms, and also the possible development of more complex atoms from simpler ones.

Already we begin to see the effect of these recent discoveries and ideas on other departments of science. The clue at last seems to have been found to those long-standing enigmas of nature, thunderstorms, the Aurora Borealis, the zodiacal light, and the tails of comets. But these achievements belong perhaps rather to the realm of the physics of the ether and of the electron, than to that of the physics of matter.

PRESENT PROBLEMS IN THE PHYSICS OF MATTER

BY FRANCIS EUGENE NIPHER

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In dealing with the subject allotted to me by the officers of the Congress, I must say that I have not presumed to solve the problems which present themselves at this time, nor do I feel competent even to state many of them. But it is instructive, in a time like this, to attempt a general survey of some of the great questions of the day, with a view of noting their bearing upon the knowledge of the past. We are continually made to feel that all of our inquiries and results must be reëxamined, and our conclusions broadened and modified by new phenomena.

Charles Babbage, whose last published work was, if I mistake not, a review of the London Exposition of 1851, in the Ninth Bridgewater Treatise, gave incidentally, by way of enforcing his thoughts, a review of his earlier work on calculating-machines. His work covered the simple case of a machine composed of wheels and levers, capable of computing the successive terms of any series. The simplest case is an arithmetical series, the differences between the successive terms being unity. This is the device which we now use in the street-cars for counting fares. He asserted the possibility of making a machine, capable of computing the terms of such a series, or of any other, continuing the operation for thousands of years; and pointed out that the machine may be so designed that it will then compute one single arbitrary term, having no relation to the series which had preceded. It may then resume the former series, or it may begin computing a geometrical series, or a series of squares or cubes of the natural numbers. A scientific investigator, who is not permitted to see the mechanism, begins to observe and record the series of numbers which are being disclosed on the dials. He soon learns the mathematical law of the series. He observes the time-sequence of the successive terms, and computes the date when this order of things began. He then makes use of his knowledge of other machinery, and makes a working drawing of the hidden mechanism which produces these results. He verifies his work by years of subsequent observations. With what amazement does he finally behold that single arbitrary term! With what amazement does he then see the machine begin to compute the squares or the cubes of the numbers it had previously disclosed! The date when that machine was created and set to work has been rudely called in question by the new and seemingly lawless behavior of which it appears to be capable. And yet the observer still feels that the principles of mechanism have not been shaken by this unlooked-for disclosure. He again begins his work, with broader conceptions of the plan of this machine. And his subsequent work is along precisely the same lines, and by the same methods as his previous work.

It is in exactly this way that all scientific work has proceeded, and I wish to point out a few interesting cases of this kind. I find it impossible to do this without presenting the present aspect of these problems in connection with the work of the past. This plan gives a perspective which not only adds to the interest but to the clearness of the presentation.

The nebular hypothesis was an attempt by Kant, Laplace, and Herschel to trace the evolution of the solar system from a glowing mass of incandescent vapor or gas. As the theory was considered and developed, an immense number of correlated phenomena were found to be in harmony with this hypothesis, and a few discordant phenomena were also found. The operation was, moreover, based on a few fundamental and well-established laws, governing the present condition of the system; such as gravitation, radiation of heat, etc. The case became more and more convincing, as the knowledge of the last century was applied. All of this caused the astronomers and physicists to find it very easy to give to the hypothesis their tacit assent.

Later, Sir William Thomson, now Lord Kelvin, took up the question of underground temperature, and determined the limit in time since which the earth must have begun to solidify. He also assumed that the present order of things had come down to us from the past, and that the present order of things consisted in the radiation of heat from a cooling earth.

The time-interval which Kelvin thus determined was in entire harmony with the nebular hypothesis, but the results were received with something like consternation by geologists, and those who had followed Darwin in the study of the evolution of organic life upon the earth. Afterwards Kelvin sought to show that the process of solidification might have required but a short interval of time, and the evolutionists have found that evolution goes on by steps or sudden changes rather than by a continuous succession of imperceptible increments.

The geologists have never been reconciled to Kelvin's results, and their protests have of late seemed to be on the increase. Of late the situation has changed in various ways. The discovery of radioactive matter in wide diffusion in the earth's crust has reopened the whole question of underground temperature as related to the age of the earth and its past history. Nevertheless, if the nebular theory in any form, or any similar theory, represents the process of evolution of the solar system, a large amount of heat due to gravitational contraction must have resulted, and must have been disposed of by radiation.

During several years I have been giving attention to the conditions of evolution of a gaseous nebula. The equations of equilibrium for such a mass have been developed.[1] A cosmical mass of gas was assumed, satisfying everywhere the Boyle-Gay-Lussac law, capable therefore of expanding, of being compressed, and of transmitting pressure, and having a centre towards which it gravitates.

Such a mass of gas is a simple heat-engine. The piston face is any spherical concentric surface. The load on the piston is the weight of superposed layers, external to the piston face. The radially inwardly directed pressure is exactly that required to balance the outward pressure of the inclosed mass. As radiation and contraction proceed, the load on the piston increases, in a perfectly definite way, due to increase in weight of each element of mass as it approaches the gravitating centre. Whatever may be the nature of the gas, as determined by the numerical value of the Boyle-Gay-Lussac constant, at some time in its history contraction will have proceeded until some fixed or definite mass shall have been compressed within a fixed volume of definite radius. The equations show that the pressure at the surface of this mass, that is to say, the load on the piston, will then be entirely independent of the nature of the gas.

The difference between gases will only be shown in the time required for them to reach this assumed stage in their gravitational history. A gas which permits the heat of compression within the piston face to escape most quickly into the refrigerator external to the nebula will reach this stage most quickly. When this has been done, pressures and densities at the piston face are wholly independent of the nature of the gas. The total work of compression done on the mass within the piston face up to this time is also independent of the nature of the gas. But the temperatures at the piston face will be inversely as the numerical value of the Boyle-Gay-Lussac constant.

It is evident, therefore, that the law of contraction cannot be indeterminate as in the case where the load is imposed by the hand of man. There is, therefore, in addition to the Boyle-Gay-Lussac law, another definite relation between any two of the three variables involved in that law. The application of well-known equations of

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[1] *Transactions*, Academy of Science of St. Louis, XIII, no. 3; XIV, no. 4.

thermodynamics led to the result that the density at any such piston face was directly proportional to the *n*th power of the pressure. The value of *n* is found to be 0.908 for all gases like oxygen, hydrogen, nitrogen, and air. The operation is, therefore, one lying between isothermal and isentropic compression, and near to the former. The specific heat of gravitational compression is therefore negative. The unit mass of gas at any point rises in temperature during compression, and for a rise of temperature of 1°C., it gives off by radiation a definite amount of heat.

If, now, such a nebula be supposed to extend to an infinite distance from the gravitating centre, the mass of the nebula will be infinite. Pressure, density, and temperature then all become zero at an infinite distance. Suppose such a nebula to have reached such a stage in its contraction that the mass of our solar system, 1.99×10^{33} grammes, is internal to Neptune's orbit, then it turns out that the pressure there will be about what it is in Crookes tube, 1.74×10^{-7} atmospheres. The density will be far less than in a Crookes tube, viz.: 1.40×10^{-12} C. G. S. The temperature for a hydrogen nebula will be 3000°C., and for other gases it will be higher in inverse ratio as the value of the Boyle-Gay-Lussac constant.

If the mass of the nebula be made finite, the conditions become still more interesting. Let the condition be imposed that the mass of the nebula is that of our solar system, and that it has so contracted that Neptune's mass only is external to Neptune's orbit. Then the temperature at Neptune's place drops to about 1900°C., for hydrogen,[1] and both pressure and temperature become very much less than before. P 1.49×10^{-10}; d 1.93×10^{-15}. The thickness of the spherical shell which would contain Neptune's mass is about a million miles (1.65×10^{-11} cm.). At the external surface of this nebula, the condition imposed makes P, d, and T zero, as the equations show. Nevertheless, a large fraction of Neptune's mass would be gaseous and far above its critical temperature. It seems to me impossible to think of a nebula having such properties generating by any reasonable rotation a system of planetary bodies. With Neptune's mass on the surface of such a nebula consisting of matter having a density and pressure less than a thousandth of these values in a Crookes tube vacuum, how could we conceive of this matter being gathered into a single planet?

A much more reasonable hypothesis is one discussed by G. H. Darwin in 1889, in the Philosophical Transactions of the Royal Society.[2] Darwin discussed the properties of a swarm of solid meteoric masses, and gives very strong proof of the proposition that

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[1] In a nebula of mixed gases, each gas will, of course, have its own temperature, as is well understood.

[2] On the "Mechanical Conditions of a Swarm of Meteorites," and on "Theories of Cosmogony," *Phil. Trans.* 1889.

a system of planetary bodies may originate in this way, although he is very cautious and conservative in stating conclusions. The great importance of this theory of planetary origin from the standpoint of planetary geology and the evolution theory seems to demand that it should receive more attention than it has yet received. The temperature of the great mass of such a swarm will be very much lower than in the case of the gaseous nebula. The larger part of such a mass will approach absolute zero in temperature. According to this hypothesis, even Mercury may have been solid when it separated from the parent mass, although in its later stages a large mass might become a gaseous nebula, as the sun now is. But in case of a body like our earth, of such relatively small size, and so far removed from the heated core, there does not seem to be any necessity for the assumption that it was ever in a fused condition.

In view of these new developments, it seems peculiarly important that a discussion of the limits of maximum temperature which the mass of our earth has reached in the past should now be taken in hand again. Suppose a swarm of meteorites to fill the space internal to the moon's orbit, having a total mass equal to that of our earth. Assume that the mass is in rotation, so that the moon is about to separate from the parent mass. It would probably be too radical to assume that each element of mass has either the same actual velocity or the same angular velocity. Various hypotheses, more or less probable, are possible. Assume an initial temperature approaching zero absolute. It seems clear that the highest temperature reached in passing to the present condition of things may be far below the temperature of fusion.

A body falling directly from the moon's distance to the earth will develop 59/60 of the kinetic energy it would acquire in falling from an infinite distance. The earth is yet being bombarded by meteoric matter having such velocities. But the operation is taking place so slowly that the heat has time to become dissipated by radiation, so that no appreciable rise in temperature of the earth results. To what extent may this condition have held in the past? Darwin discussed the tendency of the larger masses in such a swarm to accumulate towards the centre. It is a kind of sorting process. These larger masses would be in general of a metallic character. The more brittle rocks of smaller density would therefore form the outer layers of our earth. May not the heterogeneous character of our so-called igneous rocks be explained in this way? And the shrinking of the earth would then perhaps be in part the flowing of this porous mass into continuity. And it may incidentally be pointed out that the existence of the belt of meteorites known as the asteroids is a most significant indication of the conditions which must have existed at a certain stage in the history of our solar system.

The problems of the present which have aroused general interest are those which pertain to the physical constitution of matter. And here we are at once confronted with the question, What do we mean by matter? How is matter to be recognized? Of late we have been hearing such phrases as "the electrical theory of matter." There seems to be a marked tendency towards the idea that matter and its properties are alike electrical phenomena. Some even intimate that the molecular theory of gases, and the atomic theory of the chemist are tottering to a fall. We have long known that matter in motion is a form of energy. This energy of moving matter is continually being converted into molecular or atomic vibration, and then escapes from us, apparently, forever, in the form of ether waves. We have also long known that electricity in motion is a form of energy, and that the energy so manifesting itself is also all finally converted into heat, and then into ether waves.

Now this parallel certainty suggests an electrical theory of matter, but it also suggests, equally, a material theory of electricity. And so far from being antagonistic, these two theories are identical. There is nothing whatever to show that electricity has ever been separated from something which has what we have been accustomed to call mass. Rowland[1] found that when the charged sectors on his rotating disk were rotated, a magnetic field was produced, corresponding to that produced by a current of electricity. If the motion of the matter which carries the positive electric charge is in a positive direction, the field is the same as that produced when a negative charge is moved in a negative direction.

Rutherford has recently found phenomena of radioactive matter which have a most vital interest in connection with Rowland's work. The a and β particles which are shot off from such matter are moving in the same direction, and they are oppositely deflected in a magnetic field. They behave like superposed or perhaps juxtaposed electric currents of opposite sign flowing in the same direction. If in these radiations the a and β particles were moving in opposite directions, then in a magnetic field they would be deflected in the same direction. This at once raises a question concerning the nature of an electric current in a conducting wire. Let us assume that we start with the positive and negative charges on the terminals of the Holtz machine. What is it that is taking place when the terminals are joined by wires leading to a galvanometer? We get a current which we are wont to say is due either to a positive current flowing in a positive direction, or to a negative current flowing in an opposite direction. If we cease to apply work to the rotating wheel, it comes to rest, and the potential of the conducting wire becomes uniform throughout. Its extremities which terminate in front of the charged

[1] *American Journal of Science,* [3] **xv**, 30–38, 1878.

inductors are therefore so charged as to produce this uniform potential in the presence of these charged inductors, and the polarized glass of the rotor. The ends of the conductor are therefore oppositely charged. There is on its surface a neutral line of no charge. During the motion of the rotor these opposite charges are oppositely directed in the conductor. They are continually being added together. Equal quantities of unlike signs are continually being added together. Are we to assume that equal currents of unlike signs are superposed? Is a positive current in a positive direction identical with a negative current in a negative direction? Mathematically we should say yes. The resulting current, moreover, is uniform throughout the circuit, when measured by its external electromagnetic effects. We may loop in calibrated galvanometers at any point in the circuit, and they tell the same story. But what do the results of Rowland and Rutherford teach us? The β particles carry the negative charge. The negative charge is part and parcel of something which has a positive mass. The a particles are perhaps a combination of more β particles in combination with other particles having (or being) a positive charge of greater numerical value. We have found long ago that the products of an explosion are not necessarily composed of matter in its most elementary form. But these a particles are also part and parcel of something which has a positive mass.

Are we to think of this conductor as being the seat of some action by which positive masses are being urged in a positive direction and positive masses are also being urged in an opposite direction? Are we to think that the mass of such a conductor, carrying a direct current, is slowly increasing, and that after many thousands of years this increase will become appreciable, resulting, perhaps, in a clogging of the conductor, and a decrease in its conduction? In that case a current of positive electricity moving in a positive direction is not a current of negative electricity moving in a negative direction. In that case the nature of positive and negative currents of electricity flowing in opposite directions is fundamentally different from that of the flow of heat and cold in opposite directions, for it involves the motion of masses in opposite directions. It would be interesting to examine whether the long-continued use of a conductor carrying a continuous current may not result in conferring upon it radioactive properties. The results of J. J. Thomson [1] on the phenomena shown by a Geissler tube 15 meters in length are very significant in this connection. He finds the positive luminescence to travel in a direction opposite to that of the cathode stream in the Crookes tube, with a velocity somewhat more than half that of light. The older results of Wheatstone [2] also show that the current from a Leyden jar travels in

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[1] *Recent Researches in Electricity and Magnetism*, p. 116.

[2] *Phil. Trans.*, Royal Society, London, 1834.

opposite directions within the conductor which joins its coatings. The middle point of the conductor is last reached by the discharge. If the discharge is maintained and a steady current is finally produced, this current must apparently consist of positive and negative electricity flowing in opposite directions.

If air be pumped out of one boiler and into another, two kinds of pressure are thus generated. If these pressures are added together, by connecting the boilers by means of a conductor, these pressures are added together, and both disappear. If we tap these charged boilers, the discharge from one will attract, and from the other will repel, an uncharged testing sphere. If the testing sphere be itself charged, we shall find that like charges repel, if both are positive, and attract, if both are negative.

It is unnecessary here to enlarge upon the well-known differences between the positive and negative terminals of an exhausted tube. All of these phenomena will finally be helpful in arriving at the nature of the difference between positive and negative electricity. But I will refer to certain phenomena which do not seem to be so well known. Every one is familiar with the small points of light which may often be seen dancing in a crazy fashion over the cathode knob of the Holtz machine. A similar appearance can be seen on the negative carbon of a direct current arc, and in the negative bulb of the mercury vapor-lamp. These points of light may be made to pass from the cathode knob of the Holtz machine to the surface of a photographic dry-plate, exposed in open daylight.[1] Separate the knobs so that no spark will pass. Place the plate near or between them. Connect the knobs with two small metal disks, each armed with a pin-point, so bent that it makes contact with the film. The point of the pin may rest upon the short mark of a lead pencil, drawn upon the film, the pins pointing towards each other on the plate. Points of light, like the so-called ball-lightning discharges, will come from the cathode terminal and successively travel slowly over the plate, leaving a blackened trail of reduced silver behind. By means of a lead pencil held in the hand with the point near the cathode pin-point, these discharges may be induced to make their appearance on the film, and may be deflected into various directions after they have appeared. When left to themselves these minute specimens, of what may perhaps be called ball-lightning, tend to follow the lines of the field, but their paths are somewhat affected by the paths of prior discharges. If one of these points of light is seen on the pin which arms the cathode terminal, there will usually be none upon the film of the dry-plate. It may be brought upon the plate by holding a pencil-point near it.

These ball discharges come from the cathode and travel to or towards the anode. They cannot be induced to come from the anode,

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[1] *Transactions* of the Academy of Science of St. Louis, x, no. 6.

or to travel against the negative current. The anode terminal has a visible discharge which appears to pass from it, and the photographic plate at the anode looks somewhat like a picture of a relief map of the delta formation at the mouth of a river.

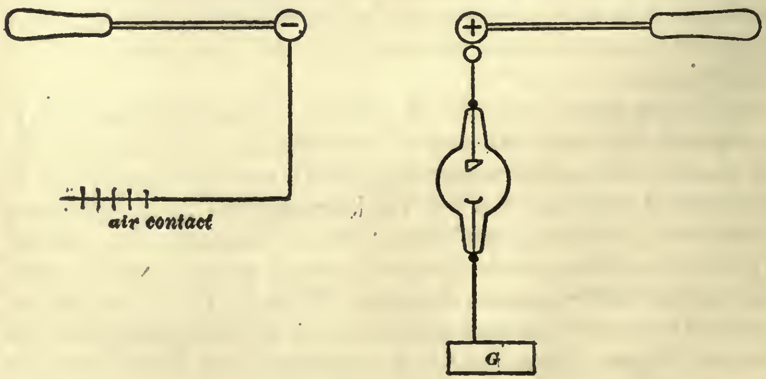
If a conductor be laid upon the plate between the two pin-points, there are then two gaps in the circuit. Each has an anode and a cathode. This conductor may be a metal disk armed with pins 180 degrees apart, which face the discharge points. It may be a pencil-mark upon the film or even a spot of reduced silver on the film. The same discharge will start from the cathode terminal of this intermediate conductor and will travel slowly in the negative direction.

With an induction coil giving an eight-inch spark, these ball discharges can be formed on the surface of wood. In all cases it is evident that chemical work is being done by the slowly advancing ball or point of light, and it is interesting to observe that it is the cathode discharge only which seems to be active. The reason for this may be partly electrical and partly chemical. The anode terminal of the machine may be grounded on a gas-pipe, and the cathode terminal only armed with a point, and the plate may be placed far away from the machine, connection being made between its cathode terminal and the pin-point on the film, with the same results. It may be added that these plates may be of the most sensitive character, and may be freely exposed to daylight for days before they are used. They may also be developed in the light in a bath not very strongly alkaline. The plate will develop clear, with the discharge tracks dark. The picture will not reverse photographically. It probably would do so if the plate were exposed to direct sunlight while the electrical exposure is made.

With an induction coil having an alternating potential on its terminals, these ball discharges may be obtained from both terminals. They will travel towards each other if on the same plate, but they will not unite.

In a closed circuit, one part of which is moved across the lines of a magnetic field, as in the case of a dynamo, we must suppose that the positive and negative currents, if both exist, are superposed in that part of the wire in which the electromotive force originates. The currents are superposed at their origin. The same ether machinery which urges the positive current in one direction urges the negative current in the opposite direction. With the Holtz machine, we have one half of the machine positively and the other half negatively charged. If the knobs are widely separated, and conductors each armed with the pin-point be led off in opposite directions, each terminating on the film of a photographic plate, the cathode will deliver a ball discharge upon its film, while the anode will not. The machine terminal which is not being used may, if desired, be grounded on a gas-pipe. If a pencil-mark be made upon the plate near the anode it will be acted upon inductively, and a ball discharge will pass from it to the anode pin-point. The positive discharge will go in the opposite direction from the pencil-mark, but it leaves no trace. It appears that this ball discharge upon the surface, which results in a destruction of the insulation of the surface, is a characteristic of the negative current.

What would be the result if a suspended Maxwell coil were to be looped into either of these unipolar circuits? Would this case necessarily give the same result that Maxwell obtained?[1] Of course we know that the result which Maxwell sought to detect is very small. We are more particularly concerned with the nature of the action than with the magnitude of the result. If the *a* particles are so large that they can contribute little or nothing to the current through a metallic conductor, then the positive current may practically be left out of consideration. But it seems doubtful whether the *a* particles are ultimate in their character, and here is where experimental work is yet needed. It would be exceedingly interesting to study these ball discharges upon a photographic plate under diminishing pressures, as they gradually become a cathode discharge, in a Crookes tube. A Crookes tube may be connected by only one of its terminals to the Holtz machine. The free terminals of the machine and tube may be connected to wires hung on silk fibres and making contact with many pointed ground plates hung on long silk fibres in air. The terminals are then in fact grounded on the dust particles in the air. Either one of these air contacts may be replaced by a ground on the gas-pipe. In all of the possible arrangements covered in this description the tube will give excellent X-ray pictures.



One of these arrangements is represented in the annexed figure, where the cathode terminal of the tube is grounded on the gas-pipe,

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[1] *Electricity and Magnetism*, II, p. 201.

and is therefore at zero potential. The ground contact of the tube may be replaced by an air contact, and the negative terminal of the machine may then be grounded on the gas-pipe if desired. In none of these cases are the positive and negative currents delivered by the machine superposed in the X-ray tube. In all these cases X-ray effects are obtained, but in some respects the tube behaves very differently when in the positive current from what it does in the negative. In the negative unipolar circuit, the cathode terminal of the tube is in direct communication with the negative terminal of the machine. When in the positive circuit, the anti-cathode terminal of the tube is in direct communication with the positive terminal of the machine, and the cathode terminal is acted upon inductively across the Crookes tube vacuum. In the negative current the luminous appearances are normal and stable. When in the positive current, the discharge may be made to cease by holding the hands near the bulb, and the luminous glow is affected by the motion of neighboring bodies. The discharge is much more unstable. If the observer approaches the suspended grounding device the face and the hands are covered by luminous points of light, which characterize the cathode terminal. This phenomenon is very striking under these conditions. Ball discharges may be drawn from such point discharges on a metal point to a photographic plate, moving on the plate towards the anode wire or contact plate suspended in air. It is apparent that the wire, when considerably removed from other bodies, is discharging upon the dust particles in the air.

In 1879 Spottiswoode and Moulton[1] published a paper containing a great array of experiments upon the spark discharge through gases. They there dealt with unipolar discharge, and their conclusions are well worthy of notice in this connection. They conclude that "the independence of the discharge from each terminal of the tube is so complete that we can at will cause the discharges from the two terminals to be equal in intensity but opposite in sign (as in the case of the coil) or of any required degree of inequality (as in the case of the coil with a small condenser). Or we can cause the discharge to be from one terminal only, the other terminal acting merely receptively (as in the case of the air-spark discharge with the Holtz machine); or we can cause the discharge to pass from one terminal only, and return to it, the other terminal not taking any part in the discharge; or finally, we can make the two terminals pour forth independent discharges of the same sign, each of which passes back through the terminal from whence it came." This work was done before the Crookes tube had appeared. It is certainly interesting to observe that when a high degree of rarefaction has been reached, the activity within the tube is represented by the cathode stream,

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[1] *Phil. Trans.*, 1879.

even when the terminal from which it comes is acted upon only inductively. The remarkable thing is that the X-ray effects and the luminosity of the tube should then be so great. The unipolar positive discharge in the positive direction and the unipolar negative discharge in the negative direction give, in the same time, an X-ray picture of the same intensity, when developed in the same bath, although in the latter case the cathode is only acted on inductively.

Unquestionably the great problem of to-day is the determination of the nature of positive electricity and its relation to what is left when the β particles have been removed. When the cathode particles have left the induced cathode terminal it is positively charged, and communicates that charge to the dust in the air, or to neighboring bodies. It does this, however, by a similar inductive action, and the ball discharge traveling over the photographic plate suggests that here also the negative particles are the active ones.

The few who have search-lights have of late been throwing them upon the great mass of experimental work on the discharge through gases, published during the last generation. It is most instructive to remember that the Crookes tube was known for seventeen years before Roentgen discovered that something was going on outside of it. A repetition of some of the work done on spark discharge, and in particular the work of Wheatstone, in the light of what is now known, would be likely to yield results of the greatest value. It would be of particular value to study by the Wheatstone method the unipolar discharges of the Holtz machine.

A few words only may be added respecting radioactive phenomena.

We have long been familiar with the changes in matter, of a character such as may perhaps be described as spontaneous. Many crystals slowly lose their water of crystallization. They give off emanations. They explode very slowly. Now emanations, like all other matters and things, have individual peculiarities which enable us to recognize them. The emanation from crystallized sodium carbonate is also given off by all animals and plants, and is evidently a very useful and widely diffused substance. There are many substances which go to pieces and give off energy. They explode. Many of them give off more energy per gram per second than any radioactive body, while radium gives off more energy per gram than any other body. The radium explosion also goes on at a lower temperature than that of any other body. It hardly seems to be warranted, to say that the action is the same at the temperature of freezing hydrogen as at ordinary temperatures, for it does not seem that any high degree of precision has been attained in such a measurement. And certainly it can hardly be claimed that we know what these radioactive bodies would do at a temperature below 16 degrees absolute.

Seven years ago, an attempt was made in my laboratory to obtain

X-ray effects from explosions. High-grade gunpowder was loaded by strong compression into rifle-shells designed for a 40-grain charge. This powder was discharged from a heavy rifle, against an oak target six inches from the muzzle of the gun. The target was faced with thin plates of aluminum, which required frequent renewal. The concussion was sufficient to extinguish a gas-flame seven feet from the line of discharge. The plate used was one which would yield distinct X-ray effects from an exposure of one second to a Crookes tube, operated by an eight-plate Holtz machine. The dry plate was placed behind the target, and was subjected to the discharge of twenty-five pounds of powder, the operation requiring the spare time of the experimenter for forty days. The result was negative. No fluorescent effects could be detected by an observer behind the target. A rapid-fire gun might yield different results.

The same experiment was made with a thousand copper shells loaded with mercury fulminate. They were exploded in twos, one being fired electrically, the other being exploded by the concussion. The first shell was laid upon a wooden block resting on a two-inch plank. The second shell, to be exploded by it, was laid upon it with a heavy iron bolt-head just above. No metal was interposed between the explosive and the photographic film beneath the plank, and it was necessary to replace the block by a fresh one at each explosion. These explosions were so violent that a photographic plate of glass was shattered by the shock at almost every shot, and the windows thirty feet distant were perforated by bits of copper which occasionally escaped through the surrounding screens. A sensitive film of gelatine was used, on which the shadow picture was expected, but none was obtained. There is yet some reason to expect positive results from experiments of this kind. It may well be that explosives differ in this respect as in others. An investigation of the products of such explosions by the electrical means now used in the study of radioactive bodies is a wide and most inviting field, which is likely to aid in the explanation of radioactive phenomena.

Some of the products of explosion in the case of radium and uranium are more nearly elementary in character than other bodies yield, and some of the products are more elementary than others.

Now there is nothing unusual in finding here and there a substance which has some property to a very exalted degree. The diamond is such a case. Iron is vastly more magnetic than any other substance. All substances are magnetic. A group consisting of iron, cobalt, nickel, etc., are more magnetic than the great body of substances, and iron heads the list. There is nothing more remarkable in finding a group of radioactive substances with one which enormously surpasses all others than there is in finding an Academy of Science with some member surpassing all the others in some particular direction.

The relations which have been found to exist between atoms and molecules are no more disturbed by the behavior of radioactive substances than by the explosion of nitroglycerine. We have learned that what we have provisionally called atoms are, at least in some cases, as has long been believed, very complex in their structure. We should hardly expect an architect to lose confidence in houses, if he finally learns that the bricks with which he is familiar are not the final elements in their structure. That the bricks are made up of molecules, and the molecules of atoms, and the atoms of electrons, and that some houses have been observed to fall into pieces and give off energy, would hardly affect the usefulness of houses which do not fall to pieces, even if inertia is shown to be an electromagnetic phenomenon. And I think we should all remember that the proposition that matter has mass is fundamentally different from the proposition that a mass of matter has inertia. If inertia can be explained to be an electromagnetic quantity, and if it can be measured in new units, we have not changed the properties of matter. It is still matter, and it still has both mass and inertia. If inertia is an electromagnetic phenomenon, it may be measured in terms of the fundamental units in which all electromagnetic quantities are measured, — the units of length, time, and mass.

Formerly a force was measured in terms of the unit of mass only. People talked about a force of one pound. Later it was discovered that a force could also be measured in terms of the pound, the foot, and the second. At this time we did not hear any intimation that matter had had its day and was about to be abolished.

In physics we now think we have reached the domain of small things. But the electron may also be a very complex structure. If we accept Poynting's view of the nature of electromagnetic induction, the electron in a conductor is acted upon by a distant and moving electron, through a medium external to the conductor. The experimental verification of this is very convincing. In addition to this complex machinery we have to deal with machinery of gravitation.

We may always assume that nature is everywhere complex and ingenious. A visitor to our solar system, who should begin to study it from our earth, might begin with physical astronomy. He finally comes to chemistry, to zoölogy, and the phenomena of life, to governmental organization, to the moral and religious influences which dominate the lives and actions of men, to the simultaneous jurisdiction of state and federal courts within the same territory. By the time he had come to know this world as we know it, he would conclude that this universe of ours, which he first perceived as a faint and distant speck of light in the blazing firmament of stars, is, after all, very wonderful, and very much more complex than was at first believed. In arriving at our present ideas of the mechanism through which matter reacts on matter, we have not reached them by finding that the old ideas must be renounced, in order to explain some new phenomenon which is apparently out of harmony with the explanation previously made. It is rather that each new development has confirmed what had gone before, has made it seem more reasonable, and has filled in some gap in the knowledge of the past. The ether, which only a few years since was assumed to exist because it seemed to be necessary, has become more and more centrally important, and has finally come to monopolize most of the attention of those who would seek to understand matter. It is no reproach to modern ideas concerning the physics of matter, that they are complex. The fact that they are also harmonious and beautiful, and that they furnish an explanation of why a mass of matter has inertia, and promise the explanation of other long-standing puzzles, converts the accusation of complexity into a crowning glory.

SECTION B — PHYSICS OF ETHER

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(*Hall* 11, *September* 23, 3 *p. m.*)

Chairman: Professor Henry Crew, Northwestern University.
Speaker: Professor Dewitt B. Brace, University of Nebraska.
Secretary: Professor Augustus Trowbridge, University of Wisconsin.

THE ETHER AND MOVING MATTER

BY DEWITT BRISTOL BRACE

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The question whether the luminiferous ether passes freely through matter or participates in the translation of the same, considered as a moving system, stands to-day without positive answer, notwithstanding the numerous experimental attempts and the varied hypotheses which have been made since the discovery of aberration by Bradley in 1726. The simple explanation of this phenomenon on the corpuscular theory may have caused the century of delay in the closer examination of the question until it became necessary to consider it from the standpoint of undulations in an ether. As compared with the many efforts to examine the question in the second or ether period we have perhaps but two belonging to the first or corpuscular period. Boscovich, in 1742, reasoning from this theory, on the ground of a difference of velocity in air and water, proposed to examine the aberration of a star with a telescope whose tube was filled with water. This experiment was not carried out till long after by Airy in 1872, who found that the variation in the aberration was absolutely insensible. Arago, in the second instance, reasoning on the same theory, concluded that the deviation produced by a prism would vary with the direction of the earth's motion; but he was unable to detect any such change, a result verified later by more delicate means in the hands of Maxwell, Mascart, and others. This experiment, which demonstrated the absence of any effect of the earth's movement on refraction is of great historical interest. This negative result, which to Arago was inconsistent with the corpuscular theory, suggested to Fresnel the important hypothesis of a quiescent ether penetrating the earth freely but undergoing a change of density within the medium proportional to the square of its index and being convected in proportion to this excess of density, which would give an apparent velocity to the ether of $(1-\mu^{-2})\nu$, instead of the velocity of the earth. Stokes suggested, as a simpler idea, that we suppose the ether is not convected but passes freely through the earth, being condensed as it passes into a body in the ratio of 1 to μ^2, so that its velocity within the refracting medium becomes $(1-\mu^{-2})\nu$, from the law of continuity.[1]

Babinet in the second-century period attempted to test Fresnel's theory by examining the interference of two rays traversing a piece of glass, the one in the direction of the earth's motion and the other in the opposite direction. Stokes showed that a negative result was not contrary to the theory of aberration, since the retardation would be the same as if the earth were at rest.

He showed further, what Fresnel had not proven to be true in general, that on Fresnel's theory the laws of reflection and refraction for single refracting media are uninfluenced by the motion of the earth. In fact, Rayleigh has shown that, in using terrestrial sources, no optical effect can be produced by any system of reflecting or refracting optical surfaces moving as a rigidly connected system relatively to the ether, if we take into account the Döppler "effect," and neglect quantities of the second order of the aberration. Since, as Stokes says, the theory of a quiescent ether may be dispensed with, and as there is no good evidence that the ether moves quite freely through the solid mass of the earth, he proposes to explain the phenomenon of aberration on the undulation theory of light, upon the supposition that the earth and the planets carry a portion of the ether along with them, so that the ether close to their surfaces is at rest relatively to those surfaces and diminishes in velocity till at no great distance in space there is no motion. Cauchy had previously discussed the theory of a mobile ether, and had proposed to explain aberration by a shearing of the wave-fronts due to the translatory motion of the medium, but he did not develop his method sufficiently to explain how much the aberration would be.

On the other hand Stokes has specifically indicated his assumptions and formulated his conclusions. He examines the displacements of a wave-front in its passage from the ether at rest, across the region of transition to the ether in the neighborhood of the observer, which is at rest relatively to him. Adopting the same method which is used in the case of an ether at rest in determining the wave-front at any future time from that of a given one at any instant, he shows,

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[1] If x is the velocity of the ether relative to the moving matter, and the density of ether within it is μ^2, the density of free ether being unity, we have from the law of continuity $\nu=(\nu-x)\mu^2$ and hence,

$$x \quad \frac{\nu\mu^2-\nu}{\mu^2}=(1-\mu^{-2})\nu$$

on the one condition, viz. that the motion of the ether is differentially irrotational, that if we neglect the square of the aberration and of the time, the change in direction of the ray as it travels along is *nil*, and therefore the course of a ray is a straight line, notwithstanding the motion of the ether. Following out the analysis on this supposition, a body, a star for example, will appear displaced toward the direction in which the earth is moving through an angle equal to the ratio of the velocity of the earth to that of light, when moving normal to the star's direction. This rectilinearity of propagation of a ray, which would likely seem to be interfered with in the motion of the ether, is the tacit assumption made in explaining aberration. If the physical causes, in consequence of which the motion of the ether becomes irrotational, could be adduced, the theory of Stokes would satisfy completely aberration and the negative results of the many and various experimental investigations which have thus far been made and whose validity is unquestioned, whether in refraction, interference, diffraction, rotary polarization, double refraction, induction, electric convection, etc. In an ordinary fluid, tangential forces proportional to the relative velocities destroy the irrotational condition in a steady state of motion. If we suppose these forces to be diminished indefinitely we obtain now a motion totally different from that for the steady state when these forces are assumed to be absent initially; and hence such a motion would be unstable. When, however, tangential forces depending on relative displacements in the ether are considered, it becomes possible to explain the irrotational condition. Any deviation from this state, for example at a surface of *slip*, would be dissipated away into space with the velocity of light by means of transverse vibrations. He illustrates such apparent incompatibilities in physical states by successive dilutions of gelatine. Such a medium shows elastic tangential forces for small constraints, and yet apparent fluidity for motions through it, mending itself as soon as dislocated. He regards these qualities as consistent and self-sufficient to explain the phenomena in question. Against the view of Stokes, Lorentz raises objection to his assumptions concerning the ether motions in the neighborhood of the earth, which he considers inconsistent, a difficulty which he is unable to set aside. Larmor demurs against an appeal to a highly complex medium, such as pitch, for studying the behavior of a simple one like the ether. A time-rate much shorter than the time of relaxation will of course provide approximate rigidity, while a time-rate much longer will provide approximate fluidity, but this requires inevitable dissipation. This objection would be valid for a viscous solid, but such Stokes apparently did not have in mind, since he specifically proves such a case unstable. A solid like pitch is a very different type of solid from that of a vesicular solid like jelly. An ether after the model of a viscous solid would always contain the viscous terms, so that even for the high time-rates of light-waves there would be dissipation however small. Such a condition, it can be proven, would give coloration to the remote members of the stellar system; a fact inconsistent with observation. On the other hand, a soft vesicular solid like gelatine may not necessarily contain the time-factor, and yet be so soft that dislocation may occur even with constraints of the order of aberration, but not of the square of that order. Such an ether without a *time of relaxation* factor would fulfill completely the conditions of a luminiferous ether, if, as Stokes tried to show, it could be reconciled with the phenomena of aberration and the motions of the heavenly bodies. The method of double refraction shows that a solution of gelatine of one part in a thousand is rigid, while at the same time it appears as mobile as water, and its rate of flow through small tubes does not vary largely from the same. This experiment illustrates very markedly Stokes's example. When such a solution is continuously dislocated between two surfaces in relative motion, the same double refraction is present, indicating that the stress is still active during dislocation. Also a metal, like copper, shows a similar stress while being strained beyond its elastic limit. If this takes place by *slip* or dislocation throughout the mass which, though irregular, may give a mean uniformity for sensible dimensions, such a medium might serve as our model. Any deviation from perfect regularity in molecular distribution and activity we might anticipate would give such minute irregular dislocations at the limit of elasticity. Such a medium would thus transmit completely any disturbance within this strain limit.

It is difficult, however, to conceive of the transmissions of a disturbance across a surface of dislocation. For many ordinary media, we should expect at such a surface total reflection. If we suppose such a transmission of disturbance, its mode is not apparent, even if we suppose a thin lamina in rotational motion which would diffuse at least a portion, if not all, of the incident disturbance. Similar difficulties would arise if we assume the ether a solid which becomes fluid under stress and thus allows bodies to pass through it (as, for example, through a block of ice, as Fitzgerald suggested). While such solutions may seem highly artificial and do violence to our convictions, the consequences of a quiescent ether may, when fully developed and tested, demonstrate its impossibility and command a more extended examination into the structural qualities of an all-sufficient medium than the single case of an essentially vesicular medium like jelly brought forward by Stokes and in a different form as a contractile ether by Kelvin. The theory of Fresnel of a quiescent ether in space presupposes a change of its density proportional to μ^2 within a ponderable medium, and a convection coefficient

$(1-\mu^2)\nu$. This hypothesis satisfies the phenomena of aberration and the uniformity of the laws of reflection and refraction of a body, whether in motion or at rest, and, as already mentioned, does not affect interference, as Stokes showed, so far as the earth's motion is concerned. That the ether apparently is carried along within moving matter not with its full velocity, but diminished to the extent indicated by Fresnel's coefficient of convection, Fizeau demonstrated in his famous interference experiment with streaming water, repeated later with greater refinement by Michelson and Morley. The significance of this experiment in its bearings on the question of the drift of the ether has perhaps been overestimated. In fact, neglecting the square of the aberration, it is exactly what we should expect from the dynamical reaction of a moving material system on a periodic disturbance, propagated through it without reference to the motion of translation of the interpenetrating medium, but simply to the frequency of the vibration impressed upon the system by this ether. Thus if we transform the ordinary differential equations of motion of the material system from fixed to moving axes, the form of the solution contains Fresnel's convection coefficient as a factor exactly, neglecting quantities of the second order of the aberration. This experiment cannot then be adduced as a positive result in favor of a quiescent ether. On account of its physical consequences, however, it should be extended to the case of gases and to absorbing substances, using light corresponding to the natural frequences of the latter if possible. Although negative results have heretofore been obtained with a gas, yet, with high pressures and greater dimensions and velocities, the test is within present experimental limitations. Results with solid bodies are still lacking, but a preliminary examination of the problem encourages us to expect successful results, at least with double-refracting substances. Reasoning in a similar manner as on the dynamical reaction of a moving system, we should look for the acceleration of a circularly polarized ray propagated coaxially within a rapidly rotating medium. This may possibly be brought within experimental limits. Again we have the important experiment of Lodge on the effect of moving masses upon the motion of the ether near them. This experiment, like that of the preceding one of Fizeau, is a first order test, *i. e.* the effect to be observed would arise from a change in the first power of the aberration factor. Two interfering beams were sent around several times in opposite directions between two rotating steel disks, and the effect on the bands noted from rest to motion or reversal. With a linear velocity not far from one two-hundredth that of the earth's orbital motion, and a distance of some ten meters or more, no influence on the interfering rays could be detected, thus making the effect, calculated from the aberration factor if the ether were carried around between the disks, something like twice the limit of observation. Lodge estimates from this experiment that the disks must have communicated less than the eight-hundredth part of their velocity to the ether. It is to be noted that the masses of these disks were not great, being only some two or three centimeters thick and about one meter in diameter. If we suppose the ether to be set in motion by means of reactions of a viscous nature, the experiment would be conclusive. To this extent, that the ether is not viscous, the test seems to be valid, but as there are other modes conceivable by which such movement might be brought about, it is not conclusive. If now we have to give up the notion of a quiescent ether, it will be necessary to suppose such motions are engendered in some way depending on the mass of the moving system, which we might imagine to be the fact in the case of the earth and the surrounding ether (possibly as, Des Coudres suggests, through gravitational action). It would be desirable to repeat this experiment, using great masses, and also testing to a much higher degree of sensibility (the third order would be possible) by means of double refraction. Michelson has recently attempted to determine directly whether the velocity of the ether diminished as we recede from the earth, but with negative results. He sent two interfering rays in opposite directions around the four sides of a rectangle of iron piping from which the air had been exhausted, the same being in a vertical east and west plane, the horizontal length of which was 200 feet and the height 50 feet. Assuming an exponential law for the variation in the velocity of the ether as we recede from the earth, he finds that if the earth carries the ether with it, this influence must extend to a distance comparable with the earth's diameter. The negative result in many of the experiments on refraction and interference which different investigators have obtained and which apparently follow on the assumption of a mobile ether have been usually experiments capable of giving only second order effects instead of the first order effects looked for, which, as mentioned above, are quite as consistent with a quiescent ether, as Stokes and Rayleigh have shown. Among these may be mentioned the experiments of Hoek, Ketteler, Mascart, and others on interference in ponderable media, over opposite paths relatively to the earth's motion; as also those of the two latter with double-refracting media. All of the experiments were first order tests, and hence should give negative results on either theory, since, with a terrestrial source of light, the phenomena are independent of the orientation of the apparatus neglecting second order effects.

The positive results of Fizeau and of Ångström have not been confirmed and should not be seriously considered. In the experiments of the latter, the variation of the position of the Frauenhofer lines, as obtained by a grating when observed in directions with and opposite to the earth's orbital motion, has never been noted since, beyond the anticipated displacement calculated from the purely kinetical principle of Döppler. The experiments of the former, as a first order test, on the rotation of the plane of polarization of a ray after passing through a pile of plates has perhaps offered the greatest difficulty to the exponents of both theories in reconciling the observations with the results which should follow from each theory. In this experiment, performed in 1859, the optical systems was mounted so as to be rotated about a vertical axis alternately from east to west, or *vice versa.* This system consisted of the usual polarizing nicol or sensitive tint-system and analyzing nicol between which were placed several piles of plates and compensating systems for producing the rotations and the magnifying of the same, and also for compensating for the rotary dispersion and elliptic polarization of the transmitted light which was polarized in an azimuth of 45°. In a series of observations extending over some time the mean of the rotations of the plane of polarization showed a maximum excess in the direction toward the west at noon and at the time of the solstice. It is to be noted that light from a heliostat was reflected into the system alternately by two fixed mirrors when the system was rotated. This required an interruption and readjustment of the heliostat during a single observation, *i. e.* from east to west and west to east, the difference in the setting of the analyzer in the two positions to give the same field of view being, of course, the effect sought for. Fizeau refers to the irregularities arising from successive settings of the heliostat. The calculated effect was much below that which could have been observed directly with the usual polarizing system. To magnify any such effect, a second system of plates was used which gave an amplification as high as eighty times. Thus any residual rotation from whatever cause would receive the corresponding amplifications. Now, in experiments with polarizing systems using sunlight as a source of illumination, it has frequently been noted that any shift in the direction of the light through the apparatus, either due to a change in the direction of the beam (arriving, say, from the heliostat) or to a shift in the optical system itself, produced a change in the field of view, whether with a half-shade system or otherwise. In the former the match was destroyed, the change being of an order much greater than that which Fizeau anticipated from calculation. Further, with such limited beams of light, a mere shift of the eye may produce an effect of similar magnitude. Hence, in all polariscopic experiments where sunlight is used, it is absolutely essential that, during any single observation, the ray of light pass through the system and into the eye over exactly the same path. This Fizeau failed to carry out, and this is entirely sufficient to explain the very great discrepancies in his various series of observations, and probably the apparent constant difference in the results of his settings in the two directions.

In fact, Fizeau himself has stated since that his observations were not absolutely decisive. While the test is now probably within experimental limits with the more highly refined half-shade systems, other modes of experimenting on different optical principles with greater sensibilities have given negative results, thus disproving the existence of a phenomenon which Fizeau's experiment apparently established, and making a repetition of this experiment, which is of doubtful execution, unnecessary.

The effect of the motion of a natural rotative substance through the ether on the rotation of the plane of polarization is of considerable importance in its bearings on certain controverted points in some of the recent theories of a quiescent ether. Mascart, who first studied the problem in the case of quartz, was unable to detect any difference in the rotation when a ray was propagated in and against the direction of motion of the earth. This variation in the total rotation, which he could detect, was one part in 20,000, or one part in 40,000 on reversal. This experiment as thus carried out corresponds to a first order effect. Rayleigh quite recently has repeated this experiment with a sensibility five times as great, and obtained negative results, likewise. The impossibility of obtaining quartz in sufficient quantity and purity, or natural rotary liquids of sufficient power, to attain the extreme limit of polariscopic possibilities seems to make even an approximation to a second order effect entirely improbable, although the higher frequencies might be used, where the power may be ten times as great. On the other hand, the effect of the mechanical rotation of such a medium on the circular components is, however, probably not beyond experimental possibilities in polariscopic work.

On the electrical side several first order experiments have been made which likewise have given negative results. Des Coudres has attempted to determine the difference in the induction on each of two coils placed symmetrically, with respect to a third coaxial coil between them. On compensating for the effects of each on the galvanometer when the axis of the system was in the direction of drift, and then reversing the direction of the system, no influence on the galvanometer could be observed. The effect which should be observed corresponds to the second order of the aberration. However, without compensating factors, the theory of induction phenomena shows that second order effects should be looked for in systems moving through the ether. The same may be said of other electrical experiments.

The difficulties in formulating a theory which will explain the results of all experiments involving tests to the first order of sensibility only on the assumption of either a quiescent or a convected ether, are much easier met than when second and higher orders have to be taken into consideration. Here we find what, at first sight, appear as rather startling assumptions; but it is only in this manner that present observational facts can be reconciled with a quiescent ether. With each advance in experimental refinement, theory has had to adapt itself by the adoption of new hypotheses. This has now been done up to second order phenomena for a quiescent ether. Thus far, however, no hypothesis has been brought forward to adapt specifically the theory of a quiescent ether to observations which have already been carried up to the third order of the aberration constant.

The first second order experiment was carried out by Michelson and Morley, and was an optical test in which the method of interference of two rays passing over paths mutually at right angles to one another was used. The apparent intent of the originators of this experiment was initially to look for a first order change in the aberration factor by means of a second order interference effect. The difficulty in reconciling the negative results of this test has, however, given rise to hypotheses involving second order dimensional factors, so that from this point of view it becomes a second order experiment. It could not, however, show a first order change in the velocity of the moving system, which latter, referred to the velocity of light, is taken as a magnitude of the first order, and hence the former change would count as a second order magnitude. In this experiment the entire system was mounted on a float so that the optical system could be rotated consecutively through all quadrants of the circle while the interference bands were being continuously observed. If now the difference in time of passage of one of the rays, say along the line of drift, and the other at right angles to it, is calculated on the basis of a moving ether, we find it to be equivalent to the time of passage over a length corresponding to a diminution of this length, in the direction of drift, proportional to the square of the aberration. Their results show that had there been an effect, it must have been probably sixteen times, certainly eight times, less than that calculated. It is understood that Morley and Miller will soon report as the result of a repetition, during the present year, of this experiment on a much larger scale, that, if there is any effect, it must be one hundred times less than the calculated value. This result is entirely consistent with a moving ether, but seemingly contradictory to a quiescent ether, as proposed by Fresnel. Apparently, then, either some condition in the fundamental hypothesis of such a medium has been overlooked, or a supplementary hypothesis must be imagined. Similar hypotheses were conceived of by both Lorentz and Fitzgerald independently, shortly after the publication of the experiments of Michelson and Morley in 1887. They assume that a contraction in the direction of motion takes place in a system moving through the ether, so that this dimension is reduced by a fraction of itself equal to one half the square of the constant of aberration. This of course, as an assumption, merely suggests a compensation to meet an apparent residual effect, and would be of no significance if it were impossible to incorporate such a condition into a consistent theory of ethereal action. This has been done by Lorentz and by Larmor in their theories of moving systems. Lorentz, who was the first to develop a satisfactory theory of a quiescent ether, assumes that, in all electrical and optical phenomena taking place in ponderable matter, we have to deal with charged particles, free to move in conductors, but confined in dielectrics to definite positions of equilibrium. These particles are perfectly permeable to the ether, so that they can move while the ether remains at rest.

If now we apply the ordinary electromagnetic equations of a system of bodies at rest to a system having a constant velocity of translation in addition to the velocities of its elements, the ether remaining at rest, the displacements of the electrons arising from the electric vibrations in the ether and the electric and magnetic forces are the same functions of the new system of parameters as for the case of rest, if we neglect quantities of the second order of the aberration. This theorem assumes that the distance of molecular action is confined to such excessively small distances that the difference in their local times would have no effect. An exception to this may be found in a rotary substance like quartz which, as mentioned above, has been examined by Mascart and Rayleigh to the first order with negative results, which seems to warrant the conclusion that the molecular forces are themselves altered by translation. This theory of Lorentz seems capable, then, of explaining the uniformly negative results of all the first order tests which have been described previously, without, however, necessarily establishing it finally, since we have not yet studied its adaptability to second and higher orders of the aberration.

The suggestion of a contraction, as stated above, lends itself in a similar manner and under like restrictions to that for the first order transformation. This requires the introduction of a second coefficient differing from unity by a quantity of the second order as did the coefficient used in the first transformation, but differing from the latter in that it is left indeterminate from the fact that there are no means as yet for giving it a definite value. Introducing these new parameters we again obtain a set of equations in which the velocity of translation does not explicitly appear. Such a moving system has therefore its correlate in a system at rest, the former having changed into the latter through the assumed contraction the moment motion begins. The occurrence of these coefficients as factors in the electric forces and the accelerations arising from the electric vibrations in the ether in the expression for the corresponding system at rest, necessitates that if the degree of similarity required is to exist in the two systems, the electrons must have different masses depending on whether their vibrations are parallel or perpendicular to the velocity of translation. This startling conclusion of Lorentz is borne out by what we now know of the dependence of the effective mass of an electron upon what is taking place in the ether. Such an hypothesis as this would require that Michelson and Morley's experiment should always give a negative result.

Of electrical experiments on the drift of the ether we have one second order test carried out very recently by Trouton at the suggestion of the late Professor Fitzgerald. The latter, reasoning on the condition of a magnetic field produced by a charged condenser moving edgewise to the drift of the ether, and the consequent additional supply of energy of such a system on charging, thought that this might produce a mechanical drag on charging and an opposite impulse on discharging, just as might occur if the mass of earth were to become suddenly greater. This experiment was carried out in the form of a condenser mounted upon an arm carried by a delicate suspension, with negative results. A second and more sensitive test was made later in a modified form by Trouton and Noble. Since. edge on to the drift, we have a magnetic field, while at right angles it vanishes, the energy will vary with the azimuth, and we shall have a maximum in an azimuth of 45°. A delicate suspension carrying the armature of a condenser showed no movement, although the calculated effect was ten times the limit of observation. The negative results of these experiments may be accounted for on like assumptions with that of the Michelson and Morley experiment, namely a contraction or change in the dimensions of the condenser producing corresponding changes in density and potential difference of the charge.

The assumption of a contraction suggests at once, from what we know of transparent media, the anisotropic state which such media are thrown into under dimensional strain. Rayleigh has examined this question in the case of water, carbon disulphide, and glass without result. In the case of glass his sensibility was several times the calculated second order effect, and much more in case of liquids.

The degree of refinement to which the polariscopic test lends itself is perhaps beyond that of any other instance in physical application. Here then is an opportunity to examine the question beyond what theory has anticipated, and the test has been carried so as to reach safely a third order effect, with negative results. The experiments as performed by the writer consisted in sending a beam of sunlight plane polarized at 45° to the horizon, through 28.56 meters of water in a horizontal direction and examining the same by a sensitive elliptic analyzer. On rotating the entire system from the meridian, where the one component of vibration to the drift was parallel and the other perpendicular, into a plane at right angles to the meridian where both components would be at right angles to the drift, and therefore where no differential effect would be produced, no change in the field of view could be detected. Had there been a total difference of 7.8×10^{-13} of the whole velocity between the components, the effect would have been manifest. We may, therefore, conclude that there is no third order effect. How well the various theories of a quiescent ether will lend themselves to this further adaptation remains to be seen, but undoubtedly by properly choosing the coefficients it may be done; however, any theory which does not contain explicitly the exact and complete adaptation to all orders of the aberration must certainly impress itself as highly artificial in its successive auxiliary hypotheses and approximations.

Larmor, in reference to his theory, says, "It is, in fact, found that the Maxwellian circuital equations of æthereal activity, in the ambient æther referred to axes moving along with the uniform velocity of convection, v, can be reduced to the same form as for axes at rest up to and including $\left(\frac{v}{V}\right)^2$ but not $\left(\frac{v}{V}\right)^3$ by adopting certain coefficients." "If, then, matter is for physical purposes a purely æthereal system, if it is constituted of simple polar singularities or electrons, positive and negative, in the Maxwellian æther, the nuclei of which may be either practically points or else small regions of æther with internal connections of pure constraint, the propositions above stated for the first order are extended to the second order of $\frac{v}{V}$ with the single addition of the Fitzgerald-Lorentz shrinkage in the scale of space and an equal one in the scale of time, which, being isotropic, is unrecognizable." "On such a theory as this the criticism presents itself, and was in fact at once made, that one hypothesis is needed to annul optical effects to the first order; that when these were found to be actually null to the second order, another hypothesis had to be added: and that another hypothesis would be required for the third order, while in fact there was no reason to believe that they were not exactly null to all orders. Such a train of remarks indicates that the nature of the hypothesis has been overlooked. And if indeed it could be proved that the optical effect is null up to the third order, that circumstance would not demolish the theory, but would rather point to some finer adjustment than it provides for; needless to say the attempt would indefinitely transcend existing experimental possibilities." And further, "up to the first order the electron hypothesis, that electricity is atomic, suffices by itself, as Lorentz was first to show." "Up to the second order, the hypothesis that matter is constituted electrically — of electrons — is required in addition."

The necessity in view of the present experimental data for leaving indeterminate the units of transformation is here illustrated in the theory of Larmor.

In the most recent discussion by Lorentz, the necessity of a general treatment is shown for not only the second but also the higher orders. In a consideration of transparent media, his theory attempts to show that translation would not alter interference, diffraction, or polarization. He would thus, by means of the assumption of so-called "Heaviside ellipsoids" as the shape of electrons, explain the negative results of optical experiments, as well as the observations of Kaufmann on Becquerel rays.

Attention should also be called to the recent theory of Abraham, who gives as the ratio of the axes of the moving electron $1-\frac{4}{5}\left(\frac{v}{V}\right)^3 : 1$, omitting fourth and higher orders. This would give a residual in double refraction of $\frac{1}{5}\left(\frac{v}{V}\right)^2 = 2 \times 10^{-9}$ for transparent media, which he acknowledges is difficult to reconcile with the experimental results which show no double refraction to the first order beyond this.

SECTION C — PHYSICS OF THE ELECTRON

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(*Hall* 5, *September* 22, 3 *p. m.*)

CHAIRMAN: PROFESSOR A. G. WEBSTER, Clark University.
SPEAKERS: PROFESSOR PAUL LANGEVIN, Collège de France.
PROFESSOR ERNEST RUTHERFORD, McGill University, Montreal.
SECRETARY: PROFESSOR W. J. HUMPHREYS, Mount Weather, Va.

THE RELATIONS OF PHYSICS OF ELECTRONS TO OTHER BRANCHES OF SCIENCE

BY PAUL LANGEVIN

(*Translated from the French by Bergen Davis, Ph.D., Columbia University*)

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THE remarkable fertility shown by the new idea, based on the experimental fact of the discontinuous corpuscular structure of electrical charges, appears to be the most striking characteristic of the recent progress in electricity.

The consequences extend through all parts of the old physics; especially in electromagnetism, in optics, in radiant heat; they throw a new light even on the fundamental ideas of the Newtonian mechanics, and have revived the old atomistic ideas and caused them to be lifted from the rank of hypotheses to that of principles, owing to the proper relation which the laws of electrolysis have established between the discontinuous structure of matter and that of electricity.

Without seeking here to run through the whole field of their applications, I hope to indicate upon what solid foundations, both experimental and theoretical, rests at present the notion of the electron so fundamental to the new physics; to indicate the points which seem to require more complete light, and to show how vast is the synthesis which we can hope to attain, a synthesis whose main lines only are fixed to-day.

Under actual and provisional form, this synthesis constitutes an admirable instrument of research, and owing to it the questions extend in all directions. There is there a kind of New America, full of wealth yet unknown, where one can breathe freely, which invites all our activities, and which can teach many things to the Old World.

I. *The Electromagnetic Ether*

(1) *Fields and Charges.* One can say that the combined efforts of Faraday, Maxwell, and Hertz have resulted in giving us a precise knowledge of the properties of the electromagnetic ether, and of light; of a medium, homogeneous and void of matter, whose state is completely defined, with the exception of gravitation, when we know at any point the direction and magnitude of the electric and magnetic fields.

I insist, for the present, on the possibility of arriving at a conception of fields of force, as well as the related idea of electric charges, independently of all dynamics; I wish by this to imply only a knowledge of the laws of motion and of matter.

The two fields possess this property, that their divergence is zero in all parts of the ether; that is to say, the flux of electric and magnetic force is rigorously zero across a closed surface which does not contain any matter in its interior. It is in fact always matter in the ordinary sense of the word which contains and can furnish the electric charges around which the divergence of field exists whose direction varies with the sign of the charges.

In extreme cases where the electric charges appear to be most completely separated from their material support, as in the case of the cathode rays for example, the experimental fact of the granular structure of these rays and the complete indestructibility of their charge, the fact finally that cathodic particles are charges possessing the fundamental property of matter, inertia, and experiencing acceleration in the electromagnetic field, these facts do not allow us to distinguish their charge from the so-called free charge of ordinary electrified matter.

Furthermore, we shall come to the idea not only that there can be no electric charge without matter, but that, in fact, there can be no matter without electricity, an aggregation of electrical centres of the two kinds. Electrons, analogous to the cathode particles, possess almost all the known properties of matter by the fact alone that these centres are electrified. We shall see within what limits this conception can be considered sufficiently known, and if it is necessary to superimpose other properties on those which result from electrically charged centres in order to obtain a satisfactory representation of matter; the ether alone, on the contrary, never contains any electricity.

If experiment obliges us to admit the existence of electric charges, positive and negative, from the flux of electric force different from zero across a closed surface drawn entirely in the ether and containing matter, it is otherwise for the magnetic field. Experiment has never furnished an instance where a closed surface drawn in the ether was traversed by a magnetic field different from zero. One interesting phenomenon observed recently by P. Villard in the effect of an intense magnetic field on the production of the cathode rays, appears to receive a simple explanation in the hypothesis of free magnetic charges; but it is not certain that this hypothesis is necessary.

(2) *The Equations of Hertz.* The two fields, electric and magnetic, of which the ether can be the seat, are related to one another in such a manner that one of them can exist only on the condition that the other varies; all variations of an electric field produce a magnetic field; it is the displacement current of Maxwell: and all variations of the magnetic field produce an electric field; this is the phenomenon of induction discovered by Faraday. These two relations are expressed by Hertz's equations; they sum up completely our knowledge of the electromagnetic medium, and from these it results that all disturbances of this medium are propagated with the velocity of light. Hertz had the glory of proving this fact experimentally.

(3) *Energy.* We can now say that the ether is the seat of two distinct forms of energy, the electric and the magnetic, capable of transformation from the one into the other, *but only through matter as an intermediary, that is to say, by means of the electrified centres which it contains.*

In the ether alone, in fact, in the free radiation which it propagates, the electric and magnetic fields, transverse with respect to the direction of propagation, represent always equal energies in each element of volume, without oscillation of the energy from one form to the other. In the presence of matter, on the other hand, the electric energy can exist alone, and it is the motion of electrified centres which allows the transformation into magnetic energy, and *vice versa. Matter only can be the source of radiation.*

It is necessary, to the two preceding forms of energy, to add gravitation, which corresponds probably to a third mode of activity of the ether, whose connection with the two others is still obscure.

I insist here on the point that the principle of equivalence of various forms of energy, as far as the process allows of measurement, can be attained independently of all dynamical notions, by the process of using solely material systems in equilibrium.

One can find some information on this subject in a recent exposition by M. Perrin.[1]

(4) *The Theory of Lorentz.* The ether being thus completely known to us from the electromagnetic and optical point of view, the problem which follows as a continuation of the work of Maxwell and of Hertz is that of the connection between ether and matter, inert matter, the source and recipient of the radiations which the ether

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[1] I. Perrin, *Traité de chimie Physique. Les Principes.* Gauthier-Villars, Paris.

transmits. The connection sought for is furnished us by the electron or corpuscle, an electrical centre movable with respect to the ether, and carrying with it its divergent electric field.

This was the fundamental idea which caused Lorentz to conceive of the possibility of a relative displacement of electrified centres of divergence of the electric field, and of the ether considered as immovable. This displacement takes place without any change in the amount of the charge, that is to say, that the surface which is displaced in the ether with the electron is crossed by an electric flux which is completely invariable. It is the fundamental principle of the conservation of electricity, which will perhaps absorb the principle of the conservation of matter, as we cannot have matter without electricity. It is, however, probable that electricity alone is not sufficient to constitute matter.

We have actually no very precise information of the relative displacement of charges and of the ether, of electrified centres in an immovable medium, no tangible form under which we can conceive it. The attempts which have thus far been made to obtain a concrete representation, in order to give a material structure to the ether, have all been sterile of results. Perhaps there is a difficulty which belongs to the actual constitution of our minds, habituated by our secular evolution to think through matter, unable to form a concrete representation which is not material; also it seems scarcely reasonable to seek to construct a simple medium such as the ether by considering it to spring from a complex and various medium like matter. I believe it will be necessary to think *ether*, to conceive of it independently of all material representations, by means of those electromagnetic properties which put us in contact with it. I will return to this point later in reference to the mechanical theories of the ether.

If the electric charge is assumed to have a volume distribution in a portion of the medium, the principle of the conservation of electricity, and also the possibility of relative displacement of electricity and ether, makes it necessary for us, in this portion of space, to modify the equations of Hertz relative to the displacement current by the addition of a convection current, a necessary consequence of the existence of a displacement current connected with a motion of charges, and implying the production of a magnetic field by the motion of electrified bodies across the medium. This consequence of Hertz's equations has now received complete experimental confirmation.

Moreover, the experimental facts impose on these movable charges a discontinuous, granular structure, and lead to the idea of the electron as a singular region of the ether, carrying a charge equal to that of the hydrogen atom in electrolysis, but of different sign, and distributed on the surface or in the volume of the electron according as the intensity of the electric field is supposed to present, or not, a discontinuity when it crosses the surface which limits the volume occupied by the electron. Inertia, of electromagnetic origin, which we are about to refer to a similar centre, is opposed also, under the difficulty of its becoming infinite, to the hypothesis of a finite electric charge condensed in a point without extension.

The various considerations, more and more precise, all converging toward this notion of the atomic structure of charges, form the starting-point of all recent works on electricity.

II. *The Atom of Electricity*

(6) *The Electron.* The remarkable laws of electrolysis discovered by Faraday establish an intimate and necessary connection between the atomic structure of matter and that of electricity. They were sufficient to lead Helmholtz to conceive the latter as constituted of distinct, indivisible portions, elements of charge, all identical from the point of view of the quantity of electricity which they carry, and differing only in the sign. This elementary charge is equal to that carried by a monovalent atom or radical in electrolysis; a polyvalent atom or radical carries an equivalent number of such charges.

It was Johnstone Stoney who first used the word electron to designate atoms of electricity as distinct from matter, with which they combine to furnish the electrolytic ions. The presence of similar electrons combined with material atoms allows us to represent certain peculiarities of the spectrum, the existence of doublets of like frequencies; the electron, in motion, is thus considered as the origin of the emission of all luminous rays.

(7) *Gaseous Conductors.* But there are the researches on the electrical conductivity of gases, which have presented to us in a forcible manner the idea of electrical atoms, which have made this notion more tangible by allowing us to count these electric centres, to lay hold of them individually, and to measure for the first time the charge of each of them in absolute value.

As early as 1882, Giese, in observing the peculiarities of the conductivity of gases escaping from flames, the departure from Ohm's law, the impossibility of drawing from the gas, whatever might be the electric field employed, more than a limited amount of electricity of each kind, the progressive recombination of the free charges in the gas, had expressed in a precise manner the idea, that as in electrolytes the free electric charges in a gas are carried by distinct positive and negative centres in limited numbers, capable of moving in opposite directions under the action of an external electric field in order to discharge the electrified body which produces the field.

It is difficult, in fact, to conceive how, on the hypothesis that the charges are distributed in a continuous manner in space, a mass of gas electrically neutral could furnish a limited quantity of electricity of each kind, decreasing with the time by progressive recombination if one delays the establishment of the electric field in the gas.

It is indeed necessary to admit, for the two electricities, a discontinuous structure in order to allow their coexistence without completely neutralizing one another. The progressive recombination of the charged particles or ions of two kinds would produce this neutralization at the moment of their mutual collisions.

The phenomena of the saturation current, of the limited quantity of free electricity in a gas, were obtained under conditions most favorable to experimental study, when, immediately after the discovery of Roentgen rays and like radiations, one had recognized their property of making the gas they traversed a conductor of electricity. The limited charge which we can extract from a gas thus modified, the velocity, finite and easily measured, with which they move under the action of an electric field, their progressive recombination, are interpreted in an admirable manner on the hypothesis that the radiations, as well as the intense heat agitations in a flame, dissociate a certain number of the molecules of the gas into electrified parts carrying charges of opposite kinds.

(8) *The Phenomena of Condensation.* We know how the phenomena of condensation of supersaturated water vapor in the presence of a conducting gas, already referred by R. von Helmholtz to the presence of ions, has given the preceding hypothesis a brilliant confirmation. As a result of the researches of J. J. Thomson, Townsend, C. T. R. Wilson, and H. A. Wilson, these droplets of visible water, each formed by condensation around an electrified centre, bring forward a tangible witness to the existence of these centres, and furnish a means of measuring the individual charge, present on each drop of water formed, and equal to about 3.4×10^{-10} electrostatic units of electricity according to the recent measurements of J. J. Thomson and H. A. Wilson.

The fundamental idea in these kinds of measurements, applied for the first time by Townsend to the charged drops which are produced in the presence of saturated water vapor in recently prepared gases, consists in deducing the mass of each drop from its velocity of fall under the action of gravity by means of Stokes's formula, which gives the frictional resistance of a sphere moving through a viscous medium, and which expresses the velocity of fall in terms of the radius of the drop and consequently of its mass. We can obtain from this the electric charge carried by each drop if we know the ratio of this charge to the mass.

This ratio can be obtained, as was done by Townsend and J. J. Thomson, by measuring or calculating the total mass of water carried by the droplets, considered as uniform, as well as the total quantity of electricity carried by the ions which have served as centres for the formation of the drops. The charge thus obtained by Townsend was found to be 3×10^{-10} electrostatic units for each centre in the case of gases of electrolysis, and to 6.5×10^{-10} by J. J. Thomson from the first series of measurement on gases ionized by Roentgen rays.

H. A. Wilson obtained the ratio of charge to the mass of a drop more simply by comparing the velocity of fall under the action of gravity alone with the velocity of fall in a vertical electric field. He obtained thus directly the ratio sought for. This method has the advantage of showing that the electric charges are really carried by the drops, and of separating those drops which carry a single elementary charge from those which, by diffusion of the ions toward one another, carry a double or triple charge.

Wilson gives as the mean result of his measurements 3.1×10^{-10}, a value very near to that of Townsend.

A second series of experiments by Professor J. J. Thomson, in which he used radioactive substances as sources of ionization more constant than the Crookes tube, and in which he took care to cause the drops to form on all the ions present in the gas, by producing a supersaturation of the water vapor by a rapid expansion of sufficient magnitude to cause the condensation on the ions of both kinds, gave as a mean result 3.4×10^{-10}, a value in complete agreement with the other two experimenters. The principles of thermodynamics account perfectly for the influence of electrified centres on the condensation of water vapor: the electric charge of a drop in fact diminishes the pressure of water vapor in equilibrium with it. Moreover, the least supersaturation found necessary, by C. T. R. Wilson, for the formation of drops of water on the ions, which are the same whatever may be the means of producing them (Roentgen rays, Becquerel rays, brush discharge, action of ultra-violet light on metal negatively charged), allows us by purely thermodynamical reasoning to calculate approximately the charge carried by each of the ions, and this calculation, entirely distinct from direct measurement, gives in the case of the positive centres a value of 4×10^{-10} E. S. units.

(9) *The Radiation Integral.* More surprising still is the result recently obtained by H. A. Lorentz, who succeeded in basing a precise measurement of the elementary charges carried by the electrified centres present in metals on the experimental study of the radiation integral or black body radiation.

We will see how the emission and absorption of heat- and light-waves by matter are dependent on the presence in it of electrons in motion. The ratio, for a radiation of given wave-length, between the emissive and absorptive power, a ratio independent of the nature of the substance, represents the emissive power of the radiation integral, which bolometric measurements give directly.

Now this ratio can be calculated, as Lorentz has shown, for wavelengths which are long in comparison with the mean path of free electrons in the metal, as a function of the charge carried by each of them. The comparison of these results with those of Kurlbaum furnishes an entirely new method of obtaining this charge, and gives 3.7×10^{-10} E. S. units.

(10) *The Kinetic Theory.* Finally, the last confirmation, which states more precisely still our knowledge of the electric atom, and our confidence in this fundamental idea, Townsend, through comparing by the simple reasoning of the kinetic theory the velocities of ions in a gas under the action of an electric field with their coefficient of diffusion through the interior of the gas, two quantities directly measurable by experiment, has been able to demonstrate the identity of the charge of one of these gaseous ions with the electric atom of Helmholtz, the charge of a monovalent atom in electrolysis.

From this comes directly a new confirmation of the values previously obtained, for it allows us to know, owing to Townsend's results, the charge on an atom in electrolysis, and from it to deduce immediately the constant of Avogadro, the number of molecules contained in a given volume of a gas. The results are well in agreement with the values of this constant (in general a little greater), which we can directly deduce from the kinetic theory of gases.

Here is an important group of concordant indications, all of absolutely distinct origin, which show without doubt the granular structure of electric charges, and consequently the atomic structure of matter itself. The measurements which I have just enumerated allow us to establish, in great security, the hypothesis of the existence of molecular masses.

I seek to point out here this extremely remarkable result, which belongs without doubt to some fundamental property of the ether and of the electrons, that all these electrified centres, whatever may be their origin, are now identical from the point of view of the charge which they carry.

It is necessary for us to penetrate further into their properties, into their relations with material atoms, to determine their relative sizes, in order to add among others to the more exact ideas which we possess in this field, that the electrons, or negative cathode corpuscles, are all identical not only from the point of view of their charge, but also from the point of view of their dynamic properties and of their masses. We are unhappily not so well informed in regard to the positive centres.

III. *Inertia and Radiation*

(11) *The Electromagnetic Wake.*[1] Before going farther it is important to point out what we can draw from the point of view to which we have now come. Electrified centres, whose existence is experimentally proven, whose charge we know in absolute units, are movable with respect to a fixed ether defined according to the equations of Hertz, without its having been necessary for us to have recourse to dynamic principles to arrive at this point of view.

To what extent can the known properties of matter be deduced from these two ideas of the electron and the ether, and is it necessary to add something to them in order to build up a synthesis? We are going to see rapidly and definitely from our idea of the electron, how it is sufficient to represent at the same time the inertia of matter, its dynamic properties, also how it can emit and absorb the radiations which the ether transmits.

The possibility of conceiving of inertia, mass, not as a fundamental idea, but as a consequence of the laws of electromagnetism, is a conception which owes its origin to an important memoir published in 1881 by Professor J. J. Thomson.[2] He studies there, basing his assumptions on the existence of the displacement currents of Maxwell, the electromagnetic field accompanying an electrified sphere in motion. This motion implies a change in the electric field at a point fixed with respect to the medium, and this displacement current immediately produces a magnetic field according to the ideas of Maxwell. The necessity of a convection current is pointed out later. The magnetic field thus produced, identical with that of an element of current parallel to the velocity of the moving charge, is proportional at each point to that velocity, at least, if it does not approach too nearly to that of light.

The creation of a magnetic field at the time of setting the charged centre in motion implies an expenditure of energy, energy of self-induction of the convection current, proportional to a first approximation to the square of the velocity, for those velocities which are small compared to the velocity of light. It is thus an expression of the same form as that of ordinary kinetic energy. A part, at least, of the inertia of an electrified body, of its capacity for kinetic energy, is thus a consequence of its electric charge.

Moreover, the magnetic field thus produced, and the electric field as well, modified by the velocity as it approaches more nearly to that of light, constitute around the electrified centre in translation a wake which accompanies it in its translation through the ether without change so long as the velocity remains constant. It is besides neces-

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[1] *Le Sillage Electro-magnétique.*

[2] J. J. Thomson, *Phil. Mag.* t. 11, p. 229. 1881.

sary that an external action should intervene in order to modify the energy of this wake and consequently to increase or diminish the velocity. This implies, in the absence of all other kinetic energy than this of electromagnetic origin, corresponding to the production of the wake, by the law of Galileo on the conservation of the velocity acquired, in the absence of action of all external fields of force, that an electrified centre possesses inertia by the fact alone that it is electrified.

It is the immovable ether, the electromagnetic medium, which serves as a fixed support for the axes with respect to which the principle of inertia is applicable, and of which the ordinary mechanics limits itself in affirming the existence by saying: there exists a system of axes, determined by a nearly uniform translation with respect to which the principle of Galileo is exactly verified.

(12) *The Absolute Motion.* If we are able, from the actual point of view, to conceive of the ether as supporting these Galilean axes, it does not necessarily follow that the electromagnetic phenomena enable us to arrive at this absolute motion. It seems, on the contrary, so far, that static experiments, carried on in a material system by an observer carried along with it with a uniform motion of translation, do not allow, whatever may be the degree of accuracy of observation, the detection of a relative motion of the ether with respect to matter.

Larmor, and more completely Lorentz, have shown that there exist in the system actions of electromagnetic origin; it is possible to establish in a complete manner a static correspondence (relating to the positions of equilibrium or to the black fringes in optics) between the system in motion and a system fixed with respect to the ether, by means of a change of variables which preserves for the equations of the medium for a moving system the exact form which they possess for a system at rest.

The two systems differ from one another in that the moving system is slightly contracted compared with the fixed system in the direction of the resultant motion by an amount always very small, proportional to the square of the ratio of the velocity of motion to the velocity of light. This contraction affects equally all the elements of the moving system, *i. e.* the electrons themselves, if we admit with Lorentz that the interior actions of these electrons are solely electromagnetic actions or are modified in the same manner by the translation, — with the result that observation cannot prove this contraction any more than it can prove the general dragging of the ether. These elements behave as though they belonged to a corresponding fixed system. Thus is found an explanation of the negative results of experiments undertaken to show the absolute motion of the earth, by Michelson and Morley, Lord Rayleigh, Brace, Trouton, and Noble, if one admits that all the internal forces of matter are of electromagnetic origin, and that the energy is entirely divided between the two fields, electric and magnetic.

We shall see, however, farther on that it is difficult to eliminate in this way all other forms of energy, all other forces, such as gravitation; and it would then be necessary to admit with Lorentz, in order that the correspondence between the two systems should actually subsist, that in the moved system the forces and masses of different origins are modified exactly as the electromagnetic forces and masses, an hypothesis too complicated and arbitrary in the actual state of the question.

But this does not seem to be a necessary consequence: it appears probable that these actions, foreign to electromagnetism, and necessary at the interior of the electron in order to give stability and in order to represent gravitation, and which are probably connected with one another, do not intervene in a sensible manner in the negative experiments referred to above, and that everything transpires as if the electromagnetic forces alone played a rôle, alone existed.

We shall see farther on that perhaps experiments of another kind than those referred to here, for example, some dynamic measurements bringing in a relative motion of the system moved, or some static experiments bringing in gravitation, would enable us to understand the absolute motion, the axes bound to the ether, instead of conceiving simply of their existence.

(13) *Electromagnetic Inertia.* The problem of the electromagnetic wake accompanying an electrified sphere or ellipsoid in the ether has been taken up since J. J. Thomson by Heaviside and Searle.

Max Abraham has shown their results to consist approximately of a numerical factor when, instead of supposing the body to be a conductor having a surface charge, we suppose its charge to have a uniform volume distribution.

Among the more important results contained in this solution of J. J. Thomson's problem, I will point out these: that in the case of a conducting sphere, the charge remains uniformly distributed on the surface whatever may be the velocity, and that in all cases the electric field at a distance tends to become more and more concentrated in the equatorial plane with respect to the direction of the velocity in proportion as this velocity approaches that of light.

Moreover the kinetic energy which it is necessary to expend at the moment of putting it in motion in order to create the electromagnetic wake ceases to be proportional to the square of the velocity, and increases indefinitely as the velocity approaches the velocity of light-waves; the law of the increase of this kinetic energy with the velocity, the energy of self-induction of the current to which the charged body in motion is equal, may be easily deduced by Searle's solution.

Without any other hypothesis than that of its electric charge, the electron is found to have inertia defined as capacity for kinetic energy, but with a particular law of variation of this as a function of the velocity, and this inertia appears to approach infinity as the velocity approaches that of light.

The behavior of this law depends very little on the hypothesis made as to the form of the electron and the distribution of the electric charge which it carries. In all cases it is found to be impossible to give the electron a velocity equal to that of light, at least permanently.

Instead of considering with Max Abraham the electron to be spherical at all velocities, Lorentz admits it to be spherical when at rest and to have a uniform distribution of charge; but if all internal forces are solely electromagnetic or act as such, we have the view that the electron is flattened in the direction of motion by a quantity proportional to the square of the ratio $\left(\beta=\frac{v}{V}\right)$ of its velocity to that of light, becoming an ellipsoid of revolution, the equatorial diameter remaining equal to that of the original. This leads, as we shall see, to a law of inertia different from that of an invariable sphere.

We shall likewise see that it does not appear to be necessary to assign to the electrons, the negative ones at least, any other inertia than this in order to account for the dynamic properties of the cathode rays; however, experiments are not yet sufficiently exact to allow us to infer the form of the electron itself, which depends on the law of the variation of the kinetic energy with the velocity.

(14) *Two Problems.* We have examined, so far, only the case of an electron in uniform motion in the absence of any external electromagnetic field capable of modifying the motion of the electron by giving it an acceleration.

The general problem of the connection between the ether and the electron, which probably represents the most important of the connections between ether and matter, is double.

In the first place, what is the electromagnetic disturbance in the ether accompanying any given motion of the electrons whatsoever?

In the second place, what motions would free electrons have if displaced in an external magnetic field superimposed on that which constitutes their wake?

(15) *The Velocity Wave — The Acceleration Wave.* We actually possess all the elements necessary for the solution of the first problem, in which the motion is uniform in a particular case. Lorentz has given in a very simple form the general solution by the use of a delayed potential.

Each element of the charge in motion is determined by its position, its velocity, and its acceleration at the time T, the electric and magnetic fields at the time $T+t$, on a sphere having for its centre the position at the time T and for radius the path passed over by light during the time t.

Lorentz has given in this way the expressions for the two electric and vector potentials from which the fields can be deduced by the well-known formula. The complete expressions for these fields have been given for the first time, I believe, by Lenard; I obtained them independently at the same time as Schwartzschild by putting them in the following form.

The expressions for the two fields consist of two parts: the first depends solely on the velocity of the element at the time T and contributes to form the wake (*sillage*) which accompanies the electron in its motion; I shall call this the *velocity wave.* This velocity wave, which exists only in the case of uniform motion, has its electric field always directed toward the position which the element of charge will occupy at the time $T+t$, if it had retained from the time T the velocity which it had at that moment. Schwartzschild calls this position the point of aberration. It coincides with the true position of the moving element at time T if the motion has been uniform. The other part of the two fields is proportional to the acceleration projected on the direction of propagation, and the directions of the two fields are there perpendicular to one another, and perpendicular to the radius, at the same time the two electric and magnetic fields represent equal energies per unit volume; they have all the characteristics of a *radiation* which is freely propagated in the ether. I shall call this part the *acceleration wave.* Moreover, the intensities of the fields in this case vary inversely as the distance from the centre of emission, the energy represented by this wave does not tend toward zero as the time T increases indefinitely; there is thus energy radiated to infinity by the acceleration wave.

The velocity wave, on the contrary, in which the fields vary inversely as the square of the radius Vt, does not carry any energy to infinity: the energy of the velocity wave accompanies the electron in its motion and corresponds to its kinetic energy.

(16) *Radiation implies Acceleration.* We can conclude from this that when an electrified centre experiences an acceleration, and only then, it radiates to infinity in the form of a transverse wave, electromagnetic radiation, a definite quantity of energy, proportional per unit of time to the square of the acceleration.

The origin of electromagnetic radiation, of all radiation, is, then, in the electron undergoing acceleration. It is through the electron that matter acts as the source of Hertzian or light waves. All acceleration, all change which takes place in the state of motion of electrons, result in the emission of waves. The character of the emitted waves changes naturally according as the acceleration is abrupt, discontinuous, or periodic.

In the first case, realized, for example, in the sudden stopping of the negative electrons, or corpuscles, by the anti-cathode, the radiation consists of an abrupt pulse whose thickness is equal to the product of the velocity of light into the time taken to stop them, and which gives us a good representation of the Roentgen rays or of the rays from radioactive substances.

If the acceleration is periodic, on the contrary, as in the case when the electron revolves around an electrified centre of opposite sign to itself, the acceleration is periodic, and the radiation emitted constitutes a light-wave whose length is determined by the period of revolution of the electron.

The solution of the first of the two fundamental problems thus appears complete and raises no difficulty.

IV. *Dynamics of the Electron*

(17) *Maxwell's Idea.* The inverse problem is less simple. It consists in finding the motion, the acceleration which a movable electron experiences in electric or magnetic fields of given intensities; it is, properly so to speak, the problem of the dynamics of the electron.

The equations which solve this problem ought to consist, like the equations of ordinary dynamics, of two kinds of terms: one of these dependent on the external fields, which produce their actions on the electron, and are analogous to the external forces in dynamics; the other, representing forces dependent on the motion itself, and producing a resistance to motion, similar to the forces of inertia.

The terms corresponding to external actions, the forces, have been obtained by Lorentz following a method which was the natural continuation of Maxwell's idea as to the possibility of a mechanical explanation, otherwise indeterminate, by the facts of electromagnetism. The analogy to the equations of electrodynamic induction, and to the equations of Lagrange, appeared to justify such an explanation, and it was natural to continue to look upon the ether-electron system as a mechanical system, and to apply to the motions of electrified centres Lagrange's equations, deducing thus the forces exerted on the electrons by its electric and magnetic energies considered as corresponding to the potential and kinetic energies of a mechanical system, substituted in the ether. We are thus led to apply to the medium, ether, in consideration of the fundamental notions of force and mass, which they imply, the equations of material dynamics, deduced from principles founded on observations of matter only, always taken in mass and without an appreciable amount of radiation.

(18) *Ether in Matter.* We extend thus, by a bold deduction, these principles to a region for which they have not been designed, and thus admit implicitly the possibility of a material representation of the ether. However, as I have already pointed out, an attempt at such a representation raises many difficulties, and the efforts so far made to extend these principles in a more precise manner have not been successful. The most profound attempt, that of Lord Kelvin, the gyrostatic ether, lends itself rigorously only to the representation of the propagation of periodic disturbances in the ether, but makes impossible the existence of a permanent deformation, necessary, however, for the representation of a constant electrostatic field. The gyrostats would turn back again at the end of a finite time, and the system would cease to react against a deformation which has been imposed. Moreover, it would appear impossible to include in this conception the permanent existence of electrons, centres of deformation in the medium.

To get around this difficulty, Larmor had occasion, in the material image which he proposed for the ether, to superimpose on the gyrostatic system of Lord Kelvin the properties of a perfect fluid, of which the displacements representing the magnetic field should be at each instant irrotational in order not to produce an electric field by the rotation of the gyrostats present in the medium. But a great difficulty is added to the preceding: if the motion of a fluid satisfies at every moment the condition of being irrotational for infinitely small displacements, it is not so for finite displacements, and a magnetic field could not continue to exist without giving rise to an electric field.

I believe it impossible to overcome these difficulties and to give a material image of the ether, whose properties are entirely distinct, and probably much more simple than those of matter.

(19) *Action and Reaction.* Let us, however, retain this view in order that we may meet new difficulties. By means of Lagrange's equations Lorentz obtains two external forces acting on each electron in motion, two terms representing the action of the electromagnetic field.

One force is parallel to the electrostatic field; it is the ordinary electric force, due to the superposition of the electric field produced by the electron on the external electric field: the other is perpendicular to the direction of the velocity of the electron and of the external magnetic field; it is the electromagnetic force analogous to the force of Laplace exerted by a magnetic field on an element of current, and due to the superposition on the external magnetic field of the magnetic field produced by the electron during its motion. This double result includes all the elementary laws of electromagnetism and of electrodynamics, if we consider the current in ordinary conductors as due to the displacement of electrified particles.

We easily see that the forces thus obtained, exerted on the electrons by the ether, *i. e.* on the matter which contains them, do not satisfy the principle of the equality of action and reaction, if we consider all the forces which act at the same moment on all the electrons constituting matter. In the case of a body which radiates in an unsymmetrical manner, a recoil, an acceleration, is produced which is not compensated at the same moment by an acceleration set up in another portion of the matter. Later, at the time that the emitted radiation meets an obstacle, the compensation is made (but only in a partial manner if all the radiation is not absorbed) by means of the pressure which the radiation exerts on the body which receives it; a pressure whose existence is shown by experiment.

The equality of action and reaction has never been verified in similar cases, and it adds no difficulty to this subject if we do not seek to extend the principle beyond the facts which suggested it.

(20) *Quantity of Electromagnetic Motion.* If we could nevertheless realize this extension of the principle, an extension somewhat arbitrary, we should be led not only to apply this principle to matter, but to suppose the ether to have a quantity of motion which would be that of a material system to which we compare it.

Poincaré has shown that this quantity of electromagnetic motion ought to be, at every point in the ether, in direction and in magnitude, proportional to Poynting's vector, which gives at the same time a definition of the energy transmitted through the medium.

By starting with this idea of the quantity of electromagnetic motion, Max Abraham has been able to calculate the terms, put to one side by Lorentz, which depend on the motion of the electron itself, its force of inertia, by the variation of the quantity of electromagnetic motion contained in its train. He was led for the first time, by the form of the terms which represent this force of inertia, to the notion of an unsymmetrical mass as a function of the velocity.

(21) *Quasi-Stationary Motion.* The calculation can be completely made only in the case, always realizable from the experimental point of view, where the acceleration of the electron is so small that its train can be considered at each instant as identical with that of an electron having the actual velocity, but whose motion has been uniform for a long time. This is what Abraham calls a quasi-stationary motion. In this case, the train is entirely determined at each moment by the actual velocity of the electron, also the quantity of electromagnetic motion which it contains, and consequently the variation of this quantity which represents the force of inertia. The condition of quasi-stationary motion is simply that in the neighborhood of the electron, where the quantity of electromagnetic motion is localized, the wave of acceleration may be neglected in comparison with the velocity wave.

(22) *Longitudinal Mass and Transverse Mass.* We find under these conditions that the force of inertia is proportional to the acceleration with a coefficient of proportionality analogous to mass, but which is here a function of the velocity, and increases indefinitely, like the kinetic energy, as the velocity tends to approach that of light. Moreover, this electromagnetic mass differs for the same velocity, according as the acceleration is parallel or perpendicular to the direction of the velocity. There is, corresponding to the direction, a longitudinal and a transverse mass. Mass is then no longer a scalar quantity, but has the symmetry of a tensor parallel to the velocity. No experimental fact yet allows us to verify this dissymmetry of the mass of the electrons, which becomes evident only when the velocity is of the same order as that of light, but the variation of the transverse mass with the velocity has been proven by Kaufmann for the β rays of radium, which consist of particles identical with the cathode rays. It is sufficient to compare the deviations of these rays in the electric and magnetic fields perpendicular to their direction in order to deduce, by application of the equations of the dynamics of the electron, their velocity and the ratio of the charge to the transverse mass of the particles which compose them. This ratio decreases as the velocity increases, and, if we consider as fundamental the principle of the conservation of electricity, we conclude from it an actual increase of the transverse mass according to a law easy to compare with that which the theory gives for the electromagnetic mass.

(23) *Matter of the Philosophers.* But, before discussing the result of this comparison, I wish to point out a logical difficulty raised by the course which we have followed: we are accustomed to consider as fundamental the ideas of mass and force, built up in order to represent the laws of motion of matter; we, *a priori*, conceive of mass as a perfectly invariable scalar quantity.

Now, let us suppose the possibility of a material representation of the ether: we apply to it the equations of material dynamics, and we are led to admit for the electrons, which form a part of matter, and consequently for matter itself, a dissymmetrical mass, tensorial and variable.

To what, then, should the equations of ordinary dynamics apply, and what are the ideas considered as fundamental which they imply? To an abstract matter, the matter of the philosophers, which could not be ordinary matter, since it is inseparable from electric charges, and which is probably made up of an agglomeration of electrons in periodic motion, stable under their mutual actions? Or to the ether? But we have no idea of what can be its mass or motion.

It is, indeed, rather the ether which it is necessary to consider as fundamental, and it is then natural to define it initially by those properties of it which we know, that is to say, by the electric and magnetic fields, which it is possible to arrive at, as I have already remarked, without admitting at any time the laws of dynamics, the ideas of mass and force under their ordinary form. We will find this last to be a derived and secondary idea.

V. *Electromagnetic Dynamics*

(24) *Change of Point of View.* It seems thus much more natural to reverse the conception of Maxwell and to consider the analogy which he has pointed out between the equations of electromagnetism and those of dynamics under Lagrange's form as justifying much more the possibility of an electromagnetic representation of the principles and ideas of ordinary, material mechanics, than the inverse possibility.

It is necessary then for us to solve our second problem, that of the dynamics of the electron, of its motion in a given external field, without having recourse to the principles of mechanics, by purely electromagnetic considerations.

Hertz's equations, which permit a solution of the first problem, are here not sufficient, and we have need of a more general principle, which assumes not the motion of the electrons given, but that determines it.

(25) *The Law of Stationary Energy.* We will use this principle under a form indicated by Larmor, and which we can look upon as a generalization of the known laws of electrostatics and of electrodynamics. We know that the distribution of electric charges and electric fields in a system of electrified bodies is always such that the electrostatic energy W_e, contained in the medium modified by the field, is a minimum. The analogous principle holds for the magnetic field produced by currents of given intensities. The energy W_m localized in the magnetic field is less for the real distribution of it than for all other distributions satisfying the condition that the integral around a closed line is equal to 4π times the intensities of the currents inclosed by the line.

If displacements are possible, the conductors maintained at constant potential are in stable equilibrium if the electrostatic energy is a maximum, and the currents of given intensities are likewise in stable equilibrium if the energy of their magnetic field is a maximum. In all cases of maxima and minima, an infinitely small modification of the system from the configuration of equilibrium produces a zero variation in the energy: it is stationary.

(26) *General Principle.* When, instead of remaining permanent, the state of the system is variable, and if there are represented necessarily at the same time the two kinds of fields, we seek to find how,

as in the permanent case, an expression which remains stationary, that is to say, the variation of which is zero when supposed slightly modified, can start from its real state. We are thus led to replace the energies W_e, W_m, which play this rôle in the permanent case, by an integral taken with respect to the time, and which represents not the sum of the energies, since this quantity, equal to the total energy, ought to remain constant if only electromagnetic action come in, but their difference:

$$\int_{t_0}^{t_1}(W_e - W_m)dt,$$

an integral which remains stationary for all virtual modifications of the system, such modifications being subject to the condition of disappearing at the limits t_0 and t_1 of the integral, exactly as in the analogous principle of Hamilton in mechanics. The principle of zero variation just announced, and which we will consider as the result of an induction based entirely on electromagnetic principles, allows us in fact to find three of Hertz's equations, if we admit the three others as an imposed interconnection of the system, and furnishes in the most simple manner the solution which we have obtained for the first problem by means of these equations. Moreover, the motion of the electrons supposed given only at the times t_0 t_1 comes into the integral, and the condition that this must be stationary allows us to find the law of the motion during the interval, by starting from a principle whose signification is purely electromagnetic. We obtain thus exactly the results of Max Abraham; the equations of motion contain terms which depend first on the motion of the electron, and are proportional, in the hypothesis of quasi-stationary motion, to its acceleration, having coefficients that are functions of the velocity which we will call the longitudinal and transverse masses of the electron; also some terms depending on the charge, and on the external fields, which we will call the forces, and we find that they coincide with those given by Lorentz. The external motion of the electron is thus determined by the actual electromagnetic state of the system.

(27) *The Process in the Electron.* In order to simplify the analysis and to avoid considering the motion of rotation of the electron, I will consider it as a cavity in the ether; the volume integrals which express the energies W_e, W_m of the electric and magnetic fields extend only over the space external to the surface which bounds the cavity. We can suppose as a special condition outside of the electric charge that the form of this surface is fixed, spherical for example, due to an unknown action of nature, and we find the equations of Abraham for the longitudinal and transverse masses of a spherical electron.

But we can suppose a more simple condition, implying only a fixed volume of the cavity on account of the incompressibility of the external ether; if we seek, then, what is, in the case of uniform translation, the form that the electron would spontaneously take in order to satisfy the condition of zero variation, we find precisely the oblate ellipsoidal form assumed by Lorentz, with this difference, that the equatorial diameter increases with the velocity instead of remaining constant, as Lorentz considers it; this constancy implies a diminution of the volume as the velocity increases. The equations which express in this case the variation of the longitudinal and transverse mass with the velocity are different from those of Abraham and Lorentz, although giving always an indefinite increase of the two masses as the velocity approaches that of light.

The equations thus obtained for the ratio $\frac{m}{m_0}$ of the transverse mass m, the only one so far accessible to experiment, to the mass m_0 for very small velocities, as a function of the ratio $\beta=\frac{v}{V}$ of the velocity of the electron to that of light are:

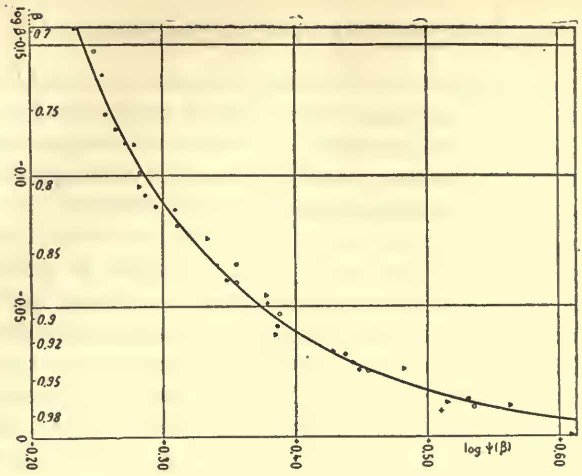
(1) Invariable spherical electron,

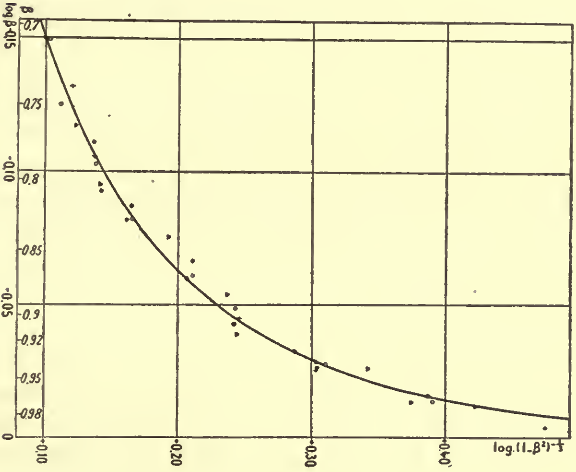
$$\frac{m}{m_0}=\frac{3}{4}\,\psi\ (\beta)=\frac{3}{2\,\beta^2}\left[\frac{1+\beta^2}{2\beta}L\frac{1+\beta}{1-\beta}-1\right]$$

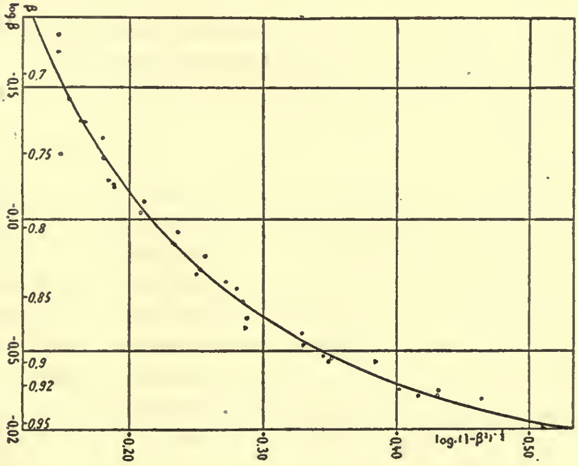
$$\text{(2) Variable Electron}\begin{cases}\text{Equatorial diameter constant} & \dfrac{m}{m_0}=(1-\beta^2)^{-1/2}\\[2ex] \text{Volume constant} & \dfrac{m}{m_0}=(1-\beta^2)^{-1/3}\end{cases}$$

(28) *Comparison.* The researches of Kaufmann are not yet exact enough to determine which of these equations represents most nearly the experimental variation of the ratio $\frac{e}{m}$ with the velocity. In order to make the comparison, I have used a process similar to that of Kaufmann, who eliminated the two electric and magnetic fields used to deviate the β rays, seeking to obtain the best concordance possible between the experimental variation of $\frac{e}{m}$ and the theoretical variation calculated on the hypothesis that the mass is entirely electromagnetic.

In order to make this elimination, I draw the two experimental and theoretical curves representing $\frac{e}{m}$ as a function of β, on logarithmic coördinates, and seek for what relative positions of the curves we obtain the best correspondence. The results are given for the three theoretical equations and the same series of experimental values. The experimental points corresponding to four different series are given by Kaufmann, and we see that they correspond equally well with the three theoretical curves.


β
log β
-0.15
0.7
0.75
-0.10
0.8
0.85
-0.05
0.9
0.92
0.95
0.98
0
0.20
0.30
0.40
0.50
0.60
log ψ(β)


β
log β
-0.15
0.7
0.75
-0.10
0.8
0.85
-0.05
0.9
0.92
0.95
0.98
0
0.10
0.20
0.30
0.40
log.(1-β²)^-½


β
log β
0.7
-0.15
0.75
-0.10
0.8
0.85
-0.05
0.9
0.92
0.95
-0.02
0.20
0.30
0.40
0.50
log.(1-β²)^-½

The more important values from the point of view of choice of equations are those corresponding to values of the velocity very near to that of light, and which amounted to ninety-five per cent of it in Kaufmann's experiments. But the β rays are then very little deviated, and exact measurements are extremely difficult.

It would be extremely important to determine the longitudinal mass by the use of an intense electric field parallel to the velocity of the electron, furnishing to it a known energy and producing a variation of the velocity, which if measured would give the longitudinal mass.

(29) *Matter and Electrons.* But if the accuracy of experiment is not sufficient to determine completely the law, the agreement with the equations, obtained by supposing the mass to be entirely electromagnetic, is so good that we can reasonably conclude that cathode particles constituting the β rays have no mass other than that due to their electric charges or the train which they carry with them in their motion through the ether.

It is interesting to extend the same result to ordinary matter by conceiving it as made up of an aggregation of electrons of both signs; it is unreasonable on the other hand to apply to two phenomena so nearly identical as inertia of ordinary matter and that of the cathode particles, two entirely distinct explanations, of which the one, the electromagnetic explanation, is definite and confirmed by experiment, while the other remains entirely unknown.

The inertia of a similar aggregation of electrons should be equal to the sum of the partial inertias because of the great distance of the electrified centres from one another compared to their radii, which one can calculate by supposing all their inertia electromagnetic.

In these conditions, the trains of the different electrons do not interfere appreciably, and we find thus the law of the conservation of inertia as a consequence of the conservation of the electrons in the transformations to which matter is subject. But the theory is not incompatible, on account of the interference of trains, with a slight disagreement between the inertia of an assemblage and the sum of the partial inertias.

The complexity of the atomic system to which we are led, each atom of the molecule containing probably a very great number of electrons, seems also to be a necessary consequence of the complexity of the luminous spectrum sent out from the atoms, by the electrons which they contain, when an external disturbance displaces the system from its state of stable periodic motion. In such a state the radiations emitted by the various electrons on account of the acceleration which keeps them in their intermolecular orbits compensate one another almost completely from the point of view of energy radiated; so that there is in general no decay of the periodic intermolecular motion.

This conception, this electronic theory of matter in which matter becomes, at least partially, synonymous with electricity in motion, appears to account for an enormous number of facts, which increase constantly under the efforts of physicists impatient to contemplate in a less primitive form the synthesis which it promises to bring forward.

(30) *Stability of the Electron.* The fundamental conception, that of the electron, does not go without raising difficulties still further, besides the impossibility already pointed out of representing to ourselves by material images its displacement with respect to the ether. It seems necessary to admit something else in its structure than its electric charge, an action which maintains the unity of the electron and prevents its charge from being dissipated by the mutual repulsions of the elements which constitute it. The form of the electron is determined by some relation which insures its stability, the condition of incompressibility of the medium being insufficient, since the spherical form corresponds only to unstable equilibrium for an electrified body of given volume in which no force opposes the deformation.

This condition, which belongs to some fundamental property of the medium, determining the charge carried by the electrons, all identical from this point of view, is perhaps closely connected with the third mode of activity of the ether, a third form of energy, the gravitational form, of which our principle of stationary energy ought to take account by the addition of terms to those expressing the electrostatic energy, but of infinitely smaller magnitude.

(31) *Gravitation.* Gravitation remains obstinately outside of our electromagnetic synthesis; the Newtonian forces not only do not appear to be propagated with the velocity of light, but also it seems difficult to found them on electromagnetism without modifying profoundly our fundamental ideas in regard to field and quantity of electricity and the possibility of an attraction of one aggregation of neutral electrons for another aggregation of the same nature.

It appears probable that gravitation results from a mode of activity of the ether and a property of electrons entirely different from the electromagnetic mode, and we must admit besides electric and magnetic energies, a third distinct form, that of gravitation.

It remains to understand how it is possible, and what is the significance of the equivalence, the passage of this third form into one of the first two. Also we are no more capable of understanding, outside of the formal equations which express it, the connection between the electric and magnetic energies themselves and their transformations, the one into the other, by means of the electrons.

(32) *An Experiment Necessary.* It does not seem impossible to connect the forces of cohesion with electromagnetism, especially

from the point of view of the mutual attractions which orientation causes in the constitution of crystalline media, on account of the complex electric and magnetic fields which surround a system of electrons in its immediate vicinity.

Gravitational forces alone remain distinct, superimposed on the electromagnetic forces, and no difficulty comes from this on account of the negative results of the experiments undertaken to show the absolute motion of the earth.

The negative results can be explained, as we shall see, if all the internal forces of matter are of electromagnetic origin; but gravitational force, alone different, can be superimposed on them without introducing an appreciable modification of this result, for its intensity is extraordinarily small compared to electromagnetic actions, even if there is no mutual compensation between them, and in all the experiments in question, interference of light or equilibrium of an elastic system, the gravitational forces play no appreciable rôle.

It would be, indeed, important to obtain a condition in a case of equilibrium where the forces of gravity would play an important part, and if the equilibrium remains independent of the total motion to nearly the second order, if we could only observe the mutual motion to this order of precision, it would be necessary to conclude that the forces of gravitation also are modified by motion of translation in the same manner as the electromagnetic forces, since the equilibrium between the two kinds of forces is not disturbed, and this would be an important indication of the necessity of an electromagnetic representation of gravitation. We would be able, for example, if the sensibility allowed it, to perform the experiment of Trouton and Noble by suspending the condenser with a bifilar to the pan of a balance instead of by an elastic fibre.

Since this test has not been made, since experiments designed to show the absolute motion have not involved weight, it would be more reasonable to consider gravitation as a force distinct from electromagnetic action, which acts at the interior of the electrons in order to insure their stability, without its being possible actually to imagine in what manner we can seek a more profound knowledge of the ether and of the electrons which it incloses.

It does not seem, in any manner and for many reasons, that this can be of the nature of a material and mechanical representation of the ether.

VI. *Cathode Rays*

(33) *The Ratio e/m.* Before examining the consequences involved in the electronic conception of matter, I should like to examine a few points relative to the electrons of two kinds. Those which we know the better, the more intimately, are the negative electrons, which

are always identical with one another in all their properties, whatever may be the matter which has furnished them. We have already seen how the direct measurement of the charge leads always to the same result, The mass, both the longitudinal and transverse mass, having the same value for small velocities, can be determined by the measurement of the ratio of the charge to the mass.

The results obtained for this ratio in the case of cathode rays show some quite marked divergences when different methods of measurement are employed. The first values were given by J. J. Thomson by combining the magnetic deviation of the rays with a measurement of the energy which they possess by means of the heat produced in a thermoelectric couple which receives them, or by combining this magnetic deviation with the deviation in an electrostatic field. The ratio $\frac{e}{m}$ furnished by this second method, the more accurate of the two, is approximately 10^7 electromagnetic units C.G.S.

Another method first pointed out by Schuster was used successively by Kaufmann and Simon. It consists in combining the magnetic deviation with the measurement of the difference of potential under which the rays are produced, considering that this difference of potential is that which exists between the cathode and anode. This hypothesis admitted, the method is capable of great accuracy, and the results which it gives appear to agree with the limiting values, for small velocities of the ratio $\frac{e}{m}$ for the β rays, although the method employed by Kaufmann in this last measurement is different from that of Schuster. The number obtained by Simon is 1.865×10^7, nearly double that of J. J. Thomson. The explanation proposed by the latter for this disagreement, according to which the cathode rays are not produced by the total difference of potential between the cathode and the anode, but originate in a region situated in front of the cathode, does not, however, appear satisfactory, since it does not account for the constancy of the results of Kaufmann and Simon when the conditions of the experiment, the difference of potential in particular, were varied between large limits.

A means of deciding the question would consist in performing a type of experiment already used by Lenard, by subjecting the cathode rays, after their production, to a supplementary and known fall of potential, and determining by the modification which would result in their magnetic deviation the initial fall of potential under which they had been produced.

(34) *The Cathode Corpuscle.* However it may be, we can, owing to the results of Kaufmann, affirm the identity of the cathode rays already found independent of the gas and the electrode contained in the Crookes tube, with the β rays of radium. The measurements

by J. J. Thomson and Lenard of the negative charges emitted by a negatively charged metallic surface under the action of light and of those spontaneously emitted by incandescent bodies also show an identity with the cathode rays. Wehnelt has recently shown that the oxides of the alkaline earths possess in an extraordinary degree this property of spontaneously emitting cathode rays at high temperatures, and furnishes a means of performing, on this particular kind of rays, simple and exact measurements.

Finally, we know that the magnitude of the Zeeman effect, in the case where the spectrum lines considered present the appearance of a normal triplet, leads to the conclusion that the light corresponding to these lines is emitted by negatively electrified centres, present in matter and having the same ratio $\frac{e}{m}$ as the cathode rays.

Moreover, the magnitude of this ratio, one thousand to two thousand times greater than for the hydrogen atom in electrolysis, leads us, as a consequence of the identity of charges established by Townsend, to consider the mass of the cathode corpuscle as one thousand times smaller at least than an atom of hydrogen; a result in perfect agreement with the conception which makes material atoms an agglomeration of electrons of two kinds. On the hypothesis that the mass is entirely of electromagnetic origin, the knowledge of the ratio $\frac{e}{m}$ gives for the electron a sufficiently small radius (10^{-13} centimeters about) in order to be, conformably to our conception also, negligible in comparison with atomic dimensions.

(35) *Flames.* The small mass of the cathode corpuscle, and the possibility of separating from matter electrified centres a thousand times smaller than the smallest atom, is confirmed by the mobility of the negative ions in flames. We obtain enormous mobility compared to that observed in gases at ordinary temperatures, and the methods of the kinetic theory of gases permits us to calculate, by means of this experimental mobility, that the movable negative centres in flames have a mass about a thousand times smaller than the hydrogen atom, and should consequently be identical with the cathode corpuscles. At ordinary temperatures the negative ions are less mobile because the cathode corpuscles surround themselves with neutral molecules by simple electrostatic attraction, and form an agglomeration which the feeble agitation allows to remain stable.

VII. *Positive Electrons — a Rays*

(36) *Goldstein Rays. a Rays.* Our knowledge of the structure of positive charges is much less advanced than for the negative. Two important cases show us the existence of positively charged particles, besides the positive ions in conducting gases, which at ordinary temperatures consist of an agglomeration of neutral molecules around

a charged centre: these are the Kanalstrahlen of Goldstein, an efflux of positive charges toward the cathode, the electric and magnetic deviations of which lead to values for the ratio of $\frac{e}{m}$ varying between wide limits, but always several thousand times smaller than for the cathode rays. The mass of these positive centres is of the order of that of the atoms. The a rays of radioactive bodies, easily absorbed, and particularly easy to observe in the case of polonium and the active bismuth of Marckwald, appear to be, in fact, Kanalstrahlen. The mass of the positively charged particles which constitute these rays is of the same order as that of the hydrogen atom, and their velocity does not exceed 20,000 to 25,000 kilometers per second, so that it is impossible to verify whether their mass is entirely electromagnetic or not. Can we consider them as electrons as simple as the negative corpuscle itself, or are they of much more complex structure; are they, for example, atoms or molecules which have lost a cathode corpuscle?

(37) *Electrons or Atoms.* On the first hypothesis, the great mass of the positive centres would lead us to assign them dimensions much smaller than the cathode corpuscles themselves, the electromagnetic mass of an electrified sphere being inversely proportional to its radius. One is thus led to the result that an electron possesses inertia, I will not say weight, inversely proportional to its radius. H. A. Wilson thinks to find an argument in favor of this conception of a very small and consequently very inert positive electron in the observation that the a rays are much less easily absorbed than the β rays of the same velocity.

Many other reasons lead us to adopt the contrary hypothesis that an a particle is very complex and little different from an atom. Rutherford has given serious reasons for identifying the a particle with the helium atom deprived of a cathode corpuscle; also Stark gives experimental reasons referring to the emission spectra of positive centres in vacuum tubes, which imply a complex structure. Finally the theory of the disruptive discharge attributes the production of cathode rays in part at least to the impact against the cathode of particles which constitute the Goldstein rays; an electron smaller than the cathode particle itself seems scarcely able to produce a surface disturbance sufficiently intense, while on the other hand, an atom, unable to penetrate another atomic structure, and projected with a high velocity, would produce by its impact a considerable local disturbance.

(38) *The Positive charge of the a Rays.* It is perhaps by this considerable disturbance produced by the a or canal rays in matter which they meet that one can explain the interesting fact that the positive charge of the a rays has not been directly shown so far by the negative charge which a polonium salt should spontaneously

acquire if it emits only a rays. However high may be the vacuum around a piece of radioactive bismuth, or polonium, it does not acquire any charge, and loses rapidly, on the contrary, its positive or negative charge. Possibly one might explain this discharge by the ionizing action of the a rays on the gas, however rare. The passage of a particles, projectiles of large dimensions, through the surface of radioactive bodies from which they come, can play the same part as the impact of Kanalstrahlen on the surface of the cathode, and cause the emission of cathode rays of very little penetrating power, whose presence would suffice, added to that of the a rays, to prevent any permanent charge of the radioactive body, whatever may be its sign.

(39) *The Positive Electrons.* If the positive centres, as we know, ought not to be represented as free electrons, it seems, however, necessary to admit the presence of probable electrons which cause the neutralization of the negative charges in the atomic structure, but which for some reason come out of this structure with extreme difficulty, contrary to what is the case for the negative centres. Moreover, it would appear necessary in order that the theory of metals, which ascribes their conductivity to the presence of free electrified centres moving under the action of a field can take account of all the facts, the Hall effect in particular, of variable sign in different metals, that the centres of two kinds coexist in the metal, free to move about in all directions. These positive centres do not appear to be the metallic atoms themselves, necessarily immovable in order to maintain the solid framework of the metal. It is possible that the positive electron, which no known action in a gas can maintain separate from the atomic material, may be free in large numbers in the entirely different medium which constitutes the metal. Many problems present themselves here on the subject of the nature of the positive charges.

VIII. *Theory of Matter. Radioactivity*

(40) *Atomic Instability.* Let us examine now a little more closely the consequences to which we are led by the conception of matter as made up of electrons of two signs, of atoms formed of electrified bodies in motion under their mutual actions. From the first, — outside of gravitation, whose intensity is infinitely small compared to the electromagnetic forces in the interior of atoms which determine all the physical and chemical changes of state, — the elementary laws of action reduce to the forces of Lorentz, which allow us, as we have seen, to calculate the acceleration to which an electron is subjected as function of the electric and magnetic fields produced by the other electrons at the point where the first electron is situated. In the case

where the acceleration is sufficient for it to radiate an appreciable energy to a distance by means of the acceleration wave, it is probably necessary to bring in, by other terms in the equation of motion of the electron, some forces by which it can receive again the energy which it radiates, and which disappear in the case of quasi-stationary motion. It does not seem, however, in any experimental case that these corrective terms can become appreciable.

From the same point of view, the electrons in periodic motion in the material atom are necessarily subject throughout their closed orbits to accelerations which are accompanied by a radiation of energy borrowed from the internal electric and magnetic energy of the atom. This radiation must be extremely small, as in the simple case of several cathode corpuscles circulating at equal distances in the same orbit, and can be compensated for by energy obtained from external radiation. We can suppose that this continual radiation, much more important naturally when the atom, as the result of external shock, is displaced from its most stable equilibrium, is a cause of decay to the atomic structure and which at the end of a certain length of time ought necessarily to give the structure a fundamental rearrangement, as a top falls when its rotation has sufficiently diminished in velocity. A condition of instability is thus reached, the consecutive rearrangement being accompanied by a violent projection of certain electrified centres from the atom. This conception furnishes at least an image of radioactive phenomena, and the successive transformations in the life of an atom, an hypothesis of which has been advanced by Rutherford. It seems, however, that it is not necessary to admit a probable decay of atomic structures, sensible only for radioactive substances. The fact that the dispersion takes place as a function of the time according to a rigorous exponential law, the quantity which is destroyed in a given time being exactly proportional to the quantity present, seems to indicate that the substance not destroyed remains identical with itself. Perhaps the reorganization of the atomic structure might result from its accidental passage through a particularly unstable configuration, the probability that a like configuration should be reproduced being independent, in the mean, of the previous history of the atom, and the mean life of the latter would be short in proportion as this probability is great.

(41) *Internal Energy and Heat set Free.* A very simple calculation shows also that the stock of energy represented by the electric and magnetic fields surrounding the electrons contained in an atom is sufficiently great to supply for ten million years the evolution of heat discovered by Curie in the radium salts. As it appears now well established that the mean life of a radium atom is of the order of a thousand years, it results that the ten-thousandth part only of this reserve of energy is utilized during this especially active period in

the life of the atom. There is then no difficulty in conceiving how the enormous evolution of heat by radium can be ascribed to its internal energy.

No atom being free from this loss of energy due to the radiation of the electrons, one ought to expect on this hypothesis of decay a universality of radioactive phenomena, the atoms which we consider as actually stable suffering only an extraordinarily slow waste.

IX. *Electric Properties*

(42) *Polarization.* It remains now to show in a few words how the preceding conceptions lend themselves easily to a representation of the principal electric and magnetic properties of matter and make possible for the first time a theory of the disruptive discharge and of metallic conduction.

A common property of all forms of matter is electrostatic polarization arising from the variation of the specific inductive power with the nature of the substance.

This polarization results in a manner quite natural by the modification which an external electric field produces in the motions of the electron which constitute the atom. This modification is caused in the mean by an excess of positive centres on the side where the field tends to displace them and by an excess of negative centres on the opposite side. The system takes then on the average an electrostatic polarization.

(43) *Corpuscular Dissociations.* If the electric field becomes sufficiently intense, as, for example, during the passage of one of those brief pulsations which constitute the Roentgen rays, or during the passage through the atomic structure of an α or β particle of very great velocity, the modification produced may be very great, a cathode corpuscle may be separated from the structure which remains positively charged; there is produced thus a corpuscular dissociation which explains the conductivity acquired by insulating mediums under the action of Roentgen or Becquerel rays, and which manifests itself especially in gases, where the electrified centres thus freed can move more easily, although by electrostatic attraction on the neutral molecules, electrically polarizable, they surround themselves with a group of molecules which accompany them during their motion.

It seems well established that the negative ions in particular, also produced in a gas, have a cathode corpuscle for centre, since the penetration of cathode rays into a gas produces in it negative ions identical with those of Roentgen rays, at least from the point of view of their mobility or of their power of condensing supersaturated water vapor. It seems, nevertheless, important to make sure, by measuring the mobility of ions produced by different causes in the interior of gases, whether the differences which appear to exist are real and are caused by the difference in the molecules which adhere to them, or are due to the electrified centres which serve as the nuclei for them.

(44) *Mobility and Recombination.* It is equally important to be able, by measurement of mobility, to follow the modification which a change of temperature produces in the size of the agglomeration and to connect the ions observed at ordinary temperatures with the incomparably more mobile ions which we observe in flames, and which appear to be made up of single electrical centres, cathode corpuscles and perhaps a particles.

The rate of recombination of ions is as yet not well known in respect to the variations with pressure and temperature, although it certainly plays an essential part in the phenomena of disruptive discharge through gases at low pressures; it would be desirable if this point were better fixed.

(45) *Ionization by Impact.* Every actual theory of the disruptive discharge rests on the conception that the impact of an electrified particle in sufficiently rapid motion against a molecule can cause corpuscular dissociation.

This idea was a natural consequence of the known fact that cathode and Becquerel rays, made up of similar particles, make a gas through which they pass a conductor. If the corpuscular dissociation produces in the gas, separated from the molecule, a cathode corpuscle and a positive residue, these fragments can, if a sufficiently intense electric field exists in the gas, acquire a velocity great enough to act as β or a rays and cause from point to point a rapid increase in conductivity.

Townsend has shown how this consequence is capable of exact experimental verification, and he has found that between certain limits of velocity, each impact between the cathode corpuscle and a molecule results in a corpuscular dissociation of the same kind. The velocity acquired ought not, however, to exceed a certain limit beyond which the negative corpuscle or β particle passes through the atomic edifice without producing a sensible disturbance in it.

In order that a disruptive discharge may exist without an external cause to maintain the production of the first electrified centres, it is necessary that the positive centres should be able, like the negative, although with more difficulty, to produce corpuscular dissociation at the moment of their impact with the molecules, as this latter causes the conductivity produced in gases by the a rays.

Townsend has been able, in support of this hypothesis, to determine the exact moment when the disruptive phenomenon is produced, and to analyze the mechanism of it.

In addition to this fundamental conception of ionization by impact, the theory of the disruptive discharge has yet much progress to make.

The extremely varied aspects which this discharge takes, the production of striations, an explanation of which was first given by J. J. Thomson, the influence of a magnetic field on the conditions of the discharge, the phenomena that are produced when the electrodes are only of the order of a micron apart, where the molecules do not appear to take part in the production of the spark, are many of the essential points which to-day attract attention.

(46) *The Electric Arc.* By the side of the ordinary disruptive discharge, by brush or spark, the electric arc, with an entirely different aspect, brings in the new phenomenon of the emission of cathode corpuscles by the surface of incandescent bodies. This incandescence of the electrode, of the cathode especially, is, in fact, characteristic of the arc discharge; the cathode is raised to a sufficiently high temperature by the impact of the positive ions which flow toward it, so that the corpuscles present in the electrode, and which give it its conductivity, experience a true evaporation and carry the greater part of the current. In fact, a filament of incandescent carbon is able to emit, at a much lower temperature than that of the voltaic arc, cathode corpuscles representing a current density of two amperes per square centimeter.

(47) *Evaporation of the Cathode.* This phenomenon, known under the name of the Edison effect, is very general and has been connected in a quantitative manner by Richardson on the fundamental hypothesis of the kinetic theory with the presence of freely moving cathode particles in the interior of conductors.

At ordinary temperatures this emission of corpuscles is diminished to such an extent that electrostatics is possible and a metal can keep a permanent charge. Every corpuscle present in the metal is immersed in a medium of high specific inductive capacity, and a finite amount of work is necessary to make them pass from this medium to a region where the specific inductive capacity is equal to unity. Only the corpuscles having a sufficient velocity would be able to supply this work on leaving the conductor, and their number, absolutely negligible at ordinary temperatures, increases with extreme rapidity with the rise in temperature. Richardson has shown that the variation obtained by experiment agrees very well with that predicted by theory.

(48) *Metals.* The spontaneous dissociation of atoms which the kinetic theory implies, the separation of electrified centres free to move in the interior of the metal, is a consequence of the high specific inductive capacity of the medium, of the ease of electrostatic polarization of metals, owing to the ease with which the metallic atoms lose corpuscles in order to remain positively charged. The potential energy of an electrified particle in such a medium is much smaller than anywhere else, and conformably with the laws of the distribution of

energy given by the kinetic theory, the free particles ought to be more numerous in it.

(49) *Chemical Phenomena.* It is by an action of the same kind that water, of great specific inductive capacity (smaller, however, than that of metals) causes the electrolytic dissociation of salts that are dissolved in it; it would be of great interest to determine the relation between this electrolytic dissociation, especially of liquid conductors, and the corpuscular dissociation common probably to gases and metals.

In electrolytic dissociation, the cathode corpuscles lost by the metallic atoms, instead of remaining free as in corpuscular dissociation, remain united to an atom or to a radical to form the negative ion in electrolytes. This question touches the relations between our actual ideas and chemistry, relations still very obscure, and which it would be very important to clear up. The electric dissociation produced in gases by Roentgen rays does not appear connected with any chemical modification; however, in air all intense ionization is accompanied by the formation of ozone. Here is a domain almost entirely unexplored.

X. *Magnetic Properties*

(50) *Ampère and Weber.* However, the complex phenomena of magnetism and diamagnetism have seemed so far to lead us to expect more difficulties, although the electrons gravitating in the atom in closed orbits furnish at first sight a simple representation of the molecular currents of Ampère, capable of turning under the action of an external magnetic field in order to give birth to induced magnetism, or of reacting by induction, according to the idea of Weber, against the external field so as to make the substance diamagnetic.

Those who have tried to follow out this idea have found it so far sterile; independently, different physicists have come to the conclusion that the hypothesis of electrons in undiminished motion cannot furnish a representation of the permanent phenomena of magnetism or diamagnetism.

I am enough of a parvenu to attempt to show, contrary to the preceding opinion, that it is possible to give, by means of the electrons, an exact signification to the ideas of Ampère and Weber, to find for para- and diamagnetism completely distinct interpretations, conforming to the laws experimentally established by Curie: weak magnetism, an attenuated form of ferromagnetism, varies inversely as the absolute temperature; on the other hand diamagnetism is shown to be, in all observed cases with the exception of bismuth, rigorously independent of the temperature. The theory which I propose takes entire account of these facts and clears up at the same time the complex question of magnetic energy.

I shall give here only the principal results of this work which will, be published in full elsewhere.

(51) *Molecular Currents.* An electrified particle of charge e moving with a velocity v is equivalent to a current of moment ev. One easily deduces from this that a molecular current made up of an electron which describes in the periodic time t an orbit inclosed by the surface S is equivalent from the point of view of the magnetic field produced to a magnet of magnetic moment $M=\frac{eS}{t}$ normal to the plane of the orbit.

There would be a corresponding current for each of the electrons present in a molecule, and the magnetic moment resulting from these would be zero or different from zero, according to the degree of symmetry of the molecular structure.

(52) *Diamagnetism.* If on a group of such molecules we superimpose an external magnetic field, all the molecular currents experience a modification independent of the manner in which the superposition is obtained, whether by the establishment of the field or by motion of the molecule in a preëxisting field. The direction of this modification, due to the induction experienced by the molecular currents, corresponds always to diamagnetism, the increase of the magnetic moment being $\Delta M = -\frac{He^2}{4\pi m}S$ in the case of a circular orbit. H is the component of the magnetic field normal to the plane of the orbit and m the mass of the electron which describes the orbit.

(53) *The Magnetic Energy.* When the molecule is supposed immovable, the work necessary for the modification of the molecular currents is furnished by the electric field produced, according to the equations of Hertz, during the establishment of the magnetic field.

In the opposite case, where the modification is due to the motion of the molecules, the work is furnished to the molecular currents by the kinetic energy of the molecule or by the action of neighboring molecules. The diamagnetic modification produced at the moment of the establishment of the field continues in spite of the molecular agitation.

This modification is manifested in three distinct ways:

1. If the resulting motion of the molecules is zero, the substance is diamagnetic in the ordinary sense of the word, and the order of magnitude of the experimental diamagnetic constants is in good agreement with the hypothesis of molecular currents circulating in intra-molecular paths.

This conception leads to the law of independence established by Curie between the diamagnetic constants and the temperature or the physical state.

2. If the resulting motion of the molecules is not zero, the initial diamagnetic modification is followed by an orientation of the molecules under the action of the external field, which cause a paramagnetism to appear that masks the underlying diamagnetism, the new phenomenon being considerable compared to the first, when the symmetry permits it to appear.

In slightly paramagnetic bodies, such as gases, the heat agitation is opposed to the complete orientation of the molecular magnets, to saturation, and one finds, in seeking what permanent condition is established, the law of Curie, that the variation of paramagnetic constants is in inverse ratio to the absolute temperature.

3. Finally, the change of period of revolution in consequence of the diamagnetic modification corresponds to the Zeeman effect, as general as diamagnetism itself; iron, certain rays of which show the Zeeman effect, is diamagnetic before the orientation of the molecular magnets under the action of the external field makes it appear paramagnetic.

The orbits considered, which represent the molecular currents of Ampère, are also the circuits of zero resistance of the diamagnetism of Weber, with this remarkable peculiarity that the flux which passes through them is not constant, as Weber supposed, if the inertia of the electrons is entirely of electromagnetic origin.

I have shown, on the other hand, that the orbits of the electrons supposed circular, and described under the action of central forces, experience no deformation during the diamagnetic modification, this latter consisting only in a change of velocity of the electrons in their orbits. We can thus form an exact and simple conception of the facts of magnetism and diamagnetism by considering the molecular currents as non-deformable but movable currents, of zero resistance and of enormous self-induction, to which all the ordinary laws of induction are applicable.

XI. *Conclusion*

The rapid perspective which I have just sketched is full of promises, and I believe that rarely in the history of physics has one had the opportunity of looking either so far into the past or so far into the future. The relative importance of parts of this immense and scarcely explored domain appears different to-day from what it did in the preceding century: from the new point of view the various plans arrange themselves in a new order. The electrical idea, the last discovered, appears to-day to dominate the whole, as the place of choice where the explorer feels that he can found a city before advancing into new territories.

The mechanical facts, the most evident of all those of which matter is possessed, from the first attracted the attention of our ancestors, and led them to conceive of the notions of mass and force which appeared a long while the most fundamental, those from which all the others ought to raminate. As the means of investigation have increased, as the more hidden facts have been discovered, we have thought for a long while to be able to reduce them to the old laws, to be able in fact to find an explanation of mechanical origin.

The actual tendency, of making the electromagnetic ideas to occupy the preponderating place, is justified, as I have sought to show, by the solidity of the double base on which rests the idea of the electron; on the one hand by the exact knowledge of the electromagnetic ether which we owe to Faraday, Maxwell, and Hertz, and on the other hand by the experimental evidence brought forward by the recent investigations into the granular structure of electricity. Moreover, this assurance which we express when considering the past is increased, if it is possible, when we consider the future.

Already all views, not only of the ether, but of matter, source and receiver of luminous waves, obtain an immediate interpretation which mechanics is powerless to give, and this mechanics itself appears to-day as a first approximation, largely sufficing in all cases of motion of matter taken in mass, but for which a more complete expression must be sought in the dynamics of the electron.

Although still very recent, the conceptions of which I have sought to give a collected idea are about to penetrate to the very heart of the entire physics, and to act as a fertile germ in order to crystallize around it, in a new order, facts very far removed from one another.

Falling in ground well prepared to receive it, in the ether of Faraday, Maxwell, and Hertz, the idea of the electron, an electrified movable centre which experiment to-day allows us to lay hold of individually, constitutes the tie between the ether and matter formed of a group of electrons.

This idea has taken an immense development in the last few years, which causes it to break the framework of the old physics to pieces, and to overturn the established order of ideas and laws in order to branch out again in an organization which one foresees to be simple, harmonious, and fruitful.

PRESENT PROBLEMS OF RADIOACTIVITY

BY ERNEST RUTHERFORD

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I

Since the initial discovery by Becquerel of the spontaneous emission of new types of radiation from uranium, our knowledge of the phenomena exhibited by uranium and the other radioactive bodies has grown with great and ever increasing rapidity, and a very large mass of experimental facts has now been accumulated. It would be impossible within the limits of this article even to review briefly the more important experimental facts connected with the subject, and, in addition, such a review is rendered unnecessary by the recent publication of several treatises[1] in which the main facts of radioactivity have been dealt with in a fairly complete manner.

In the present article, an attempt will be made to discuss the more important problems that have arisen during the development of the subject and to indicate what, in the opinion of the writer, are the subjects which will call for further investigation in the immediate future.

II. *Nature of the radiations*

The characteristic radiations from the radioactive bodies are very complex, and a large amount of investigation has been necessary to isolate the different kinds of rays and to determine their specific character. The rays from the three most studied radio-elements, uranium, thorium, and radium, can be separated into three distinct types, known as the α, β, and γ rays.

The nature of the α and β rays has been deduced from observations of the deflection of the path of the rays by a magnetic and electric field. According to the electromagnetic theory, a radiation which is deflectable by a magnetic or electric field must consist of a flight of charged particles. If the amount of deflection of the rays from their path is measured when both a magnetic and an electric field of known

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[1] Mme. Curie, *Thèses présentées à la Faculté des Sciences.* Paris, 1903.
H. Becquerel, *Recherches sur une propriété nouvelle de la Matière.* Typographie de Firmin, Didot et Cie. Paris, 1903.
E. Rutherford, *Radioactivity.* Cambridge, University Press, 1904.
F. Soddy, *Radioactivity.* Electrician Co., London, 1904.

strength is applied, the value V of the velocity of the particles and the ratio $\frac{e}{m}$ of the charge carried by the particle to its apparent mass m can be determined. From the direction of the deviation, the sign of the electric charge carried by the particle can be deduced.

Examined in this way, the β rays have been shown to consist of negatively charged particles projected with a velocity approaching that of light. The experiments of Becquerel and Kaufmann have shown that the β rays are identical with the cathode rays produced in a vacuum tube. This relationship has been established by showing that the value of $\frac{e}{m}$ is the same for the two kinds of rays. In both cases the value of $\frac{e}{m}$ has been found to be about 10^7 electromagnetic units, while the corresponding value of $\frac{e}{m}$ for hydrogen atoms set free in the electrolysis of water is 10^4. If the charge on the β particles — or electrons as they may be termed — is the same as that carried by the hydrogen atom, this result shows that the apparent mass of the electrons at slow speeds is about $\frac{1}{1000}$ of that of the hydrogen atom. The β particles from the radio-elements are expelled with a much greater speed than the cathode ray particles in a vacuum tube. The velocity of the β particles from radium is not the same for all particles, but varies between about 10^{10} and 3×10^{10} cms. per second. The swifter particles move with a velocity of at least 95 per cent of that of light. The emission by radium of electrons with high but different velocities has been utilized by Kaufmann to determine the variation of $\frac{e}{m}$ with speed. He found that the value of $\frac{e}{m}$ decreased with increase of velocity, showing that the apparent mass increased with the speed. By comparison of the experimental results with the mathematical theory of a moving charge, he deduced that the mass of the electrons was in all probability electromagnetic in origin, *i. e.*, the apparent mass could be explained purely in terms of electricity in motion without the necessity of a material nucleus on which the charge was distributed. J. J. Thomson, Heaviside, and others, have shown that a moving charged sphere increases in apparent mass with the speed, and that, for speeds small compared with the velocity of light, the increase of mass $m=\frac{2}{3}\frac{e^2}{a}$ where e is the charge carried by the body and a the radius of the conducting sphere over which the electricity is distributed. Kaufmann deduced that the value of $\frac{e}{m}=1.86\times10^7$ for electrons of slow velocity. If the mass of the electrons is electrical in origin, it is seen that $a=10^{-13}$ cms., since the value of $e=3.4\times10^{-10}$ electrostatic units. The results of various methods of determination agree in fixing the diameter of an atom as about 10^{-8} cms. The apparent diameter of an electron is thus minute compared with that of the atom itself.

The highest velocity of the radium electrons measured by Kaufmann was 95 per cent of the velocity of light. The power of electrons of penetrating solid matter increases rapidly with the velocity, and some of those expelled from radium are able to penetrate through more than 3 mms. of lead. It is probable that a few of the electrons from radium move with a velocity still greater than the highest value observed by Kaufmann, and it is important to determine the value of $\frac{e}{m}$ and the velocity of such electrons. According to the mathematical theory, the mass of the electron increases rapidly as the speed of light is approached, and should be infinitely great when the velocity of light is reached. This leads to the conclusion that no charged body can be made to move with a velocity greater than that of light. This result is of great importance, and requires further experimental verification. A close study of the high speed electrons from radium may throw further light on this question.

Only a brief and imperfect statement of our knowledge of electrons has been given in this paper. A more complete and detailed account of both the theory and experiment will be given by my colleague, Dr. Langevin.

III. *The α rays*

The β rays are readily deflected by a magnetic field, but a very intense magnetic field is required to deflect appreciably the α rays. The writer showed by the electric method that the α rays of radium were deflected both by a magnetic and electric field, and deduced the velocity of projection of the particles and the ratio $\frac{e}{m}$ of the charge to the mass. The direction of deflection of the α rays is opposite in sense to the β rays. Since the β rays carry a negative charge, the α particles thus behave as if they carried a positive charge. The magnetic deflection of these rays was confirmed by Becquerel and Des Coudres, using the photographic method, while the latter, in addition, showed their deflection in an electric field and deduced the value of the velocity and $\frac{e}{m}$. The values obtained by Rutherford and Des Coudres were in very good agreement, considering the difficulty of obtaining a measurable deviation.

Observer	*Value of Velocity*	*Value of* $\frac{e}{m}$
Rutherford	2.5×10^9 cms. per sec.	6×10^3 electromagnetic units
Des Coudres	1.6×10^9 cms. per sec.	6×10^3 electromagnetic units

Since the value of $\frac{e}{m}$ for the hydrogen atom is 10^4, on the assumption that the α particle carries the same charge as the hydrogen atom, this result shows that the apparent mass of the α particle is about twice that of the hydrogen atom. If the α particle consists of any known kind of matter, this result indicates that it is either the atom of hydrogen or of helium. The α particles thus consist of heavy bodies projected with great velocity, whose mass is of the same order of magnitude as the helium atom and at least 2000 times as great as the apparent mass of the β particle.

If the α particles carry a positive charge, it is to be expected that the particles, falling on a body of sufficient thickness to absorb them, should under suitable conditions give it a positive charge, while the substance from which they are projected should acquire a negative charge. The corresponding effect has been observed for the β rays. The β particles from radium communicate a negative charge to the body on which they fall, while the radium from which they are emitted acquires a positive charge. This effect has been very strikingly shown by a simple experiment of Strutt. The radium compound, sealed in a small glass tube, the outer surface of which is made conducting, is insulated by a quartz rod. A simple gold-leaf electroscope is attached to the bottom of the glass tube, in order to indicate the presence of a charge. The whole apparatus is inclosed in a glass vessel, which is exhausted to a high vacuum, in order to reduce the loss of charge in consequence of the ionization of the gas by the rays. Using a few milligrams of radium bromide, the gold leaf diverges to its full extent in a few minutes and shows a positive charge. The explanation is simple. A large proportion of the negatively charged particles are projected through the glass tube containing the radium, and a positive charge is left behind. By allowing the gold leaf, when extended, to touch a conductor connected to earth, the gradual divergence of the leaves and their collapse becomes automatic, and will continue, if not indefinitely, at any rate for as long a time as the radium lasts.

When the radium is exposed under similar conditions, but unscreened in order to allow the α particles to escape, no such charging action is observed. This is not due to the equality between the number of positively and negatively charged particles expelled from the radium, for no effect is observed when the radium is temporarily freed from its power of emitting β rays by driving off the emanation by heat. The writer recently attempted to detect the charge carried by the α rays from radium by allowing them to fall on an insulated plate in a vacuum, but no appreciable charging was observed. The β rays were temporarily got rid of by heating the radium in order to drive off its emanation. There was found to be a strong surface ionization set up at the surface from which the rays emerged and the surface on which they impinged. The presence of this ionization causes the upper plate to lose rapidly a charge communicated to it. Although this action would mask to some extent the effect to be looked for, a measurable effect should have been obtained under the experimental conditions, if the α rays were expelled with a positive charge; but not the slightest evidence of a charge was observed. I understand that similar negative results have been obtained by other observers.

This apparent absence of charge carried by the a rays is very remarkable and difficult to account for. There is no doubt that the a particles *behave* as if they carried a positive charge, for several observers have shown that the a rays are deflected by a magnetic field. It is interesting, in this connection, that Wien was unable to detect that the "canal rays" carried a charge. These rays, discovered by Goldstein, are analogous in many respects to the a rays. They are slightly deflected by a magnetic and electric field, and behave like positively charged bodies atomic in size. The value of $\frac{e}{m}$ is not a constant, but depends upon the nature of the gas in the tube through which the discharge is passed. The apparent absence of charge on the a particles may possibly be explained on the supposition that a negatively charged particle (an electron) is always projected at the same time as the positively charged particle. Such electrons if they are present should be readily bent back to the surface from which they came by the action of a strong magnetic field. It will be of interest to examine whether the charge carried by the a rays can be detected under such conditions. Another hypothesis, which has some points in its favor, is that the a particles are uncharged at the moment of their expulsion, but, in consequence of their collision with the molecules of matter, lose a negative electron, and consequently acquire a positive charge. This point is at present under examination. The question is in a very unsatisfactory state, and requires further investigation.

It is remarkable that positive electricity is always associated with matter atomic in size, for no evidence has been obtained of the existence of a positive electron corresponding to the negative electron. This difference between positive and negative electricity is apparently fundamental, and no explanation of it has, as yet, been forthcoming.

The evidence that the a particles are atomic in size mainly rests on the deflection of the path of the rays in a strong magnetic and electric field. It has, however, been suggested by H. A. Wilson that the a particle may in reality be a "positive" electron, whose magnitude is minute compared with that of the negative. The electric mass of an electron for slow speeds is equal to $\frac{2}{3}\frac{e^2}{a}$. Since there is every reason to believe that the charge carried by the a particle and the electron is the same, in order that the mass of the positive electron should be about 2000 times that of the negative, it would be necessary to suppose that the radius of the sphere over which the charge is distributed is only $\frac{1}{2000}$ of that of the electron, *i. e.*, about 10^{-16} cms. The magnetic and electric deflection would be equally well explained on this view. This hypothesis, while interesting, is too far-reaching in its consequences to accept before some definite experimental evidence is forthcoming to support it. The evidence at present obtained strongly supports the view that the α particles are in reality projected matter, atomic in size. The probability that the α particle is an atom of helium is discussed later, in section VIII.

Becquerel showed that the α rays of polonium were deflected by a magnetic field to about the same extent as the α rays of radium. On account of the feeble activity of thorium and uranium, compared with radium and polonium, it has not been found possible to examine whether the α rays emitted by them are deflectable. There is little doubt, however, that the α particles of all the radio-elements are projected matter of the same kind (probably helium atoms). The α rays from the different radioactive products differ in their power of penetration of matter in the proportion of about three to one, being greatest for the α rays from the imparted or "induced" activity of radium and thorium, and least for uranium. This difference is probably mainly due to a variation of the velocity of projection of the α particles in the various cases. The interpretation of results is rendered difficult by our ignorance of the mechanism of absorption of the α rays by matter. Further experiment on this point is very much required.

It is of importance to settle whether the α particles of radium and polonium have the same ratio of $\frac{e}{m}$. Becquerel states that the amount of curvature of the α rays from polonium in a field of constant strength was the same as for the α rays from radium. This would show that the product of the mass and velocity is the same for the α particles from the two substances. The α rays of polonium, however, certainly have less penetrating power than those of radium, and presumably a smaller velocity of projection. This result would indicate that $\frac{e}{m}$ is different for the α particles of polonium and radium. It is of importance to determine accurately the ratio of $\frac{e}{m}$ and the velocity for the rays from these two substances in order to settle this important point.

IV. *The γ Rays*

In addition to the α and β rays, uranium, thorium, and radium all emit very penetrating rays known as γ rays. These rays are about 100 times as penetrating as the β rays, and their presence can be detected after passing through several centimeters of lead. Villard, who originally discovered these rays in radium, stated that they were not deflected in a magnetic field, and this result has been confirmed by other observers. Quite recently, Paschen has described some experiments which led him to believe that the γ rays are corpuscular in character, consisting of negatively charged particles (electrons) projected with a velocity very nearly equal to that of light. This conclusion is based on the following evidence. Some pure radium bromide was completely inclosed in a lead envelope 1 cm. thick, — a thickness sufficient to absorb completely the ordinary β rays emitted by radium, but which allows about half of the γ rays to escape. The lead envelope was insulated in an exhausted vessel, and was found to gain a positive charge. In another experiment, the rays escaping from the lead envelope fell on an insulated metal ring, surrounding the lead envelope. When the air was exhausted, this outer ring was found to gain a negative charge. These experiments, at first sight, indicate that the γ rays carry with them a negative charge like the β rays. In order to account for the absence of deflection of the path of the γ rays in very strong magnetic or electric fields, it is necessary to suppose that the particles have a very large apparent mass. Paschen supposes that the γ particles negative are electrons like the β particles, but are projected with a velocity so nearly equal to that of light that their apparent mass is very great.

Some experiments recently made by Mr. Eve, of McGill University, are of great interest in this connection. He found by the electric method that the γ rays set up secondary rays, in all directions, at the surface of which they emerge and also on the surface of which they impinge. These rays are of much less penetrating power than the primary rays, and are readily deflected by a magnetic field. The direction of deflection indicated that these secondary rays consisted, for the most part, of negatively charged particles (electrons) projected with sufficient velocity to penetrate through about 1 mm. of lead. In the light of these results, the experiments of Paschen receive a simple explanation without the necessity of assuming that the γ rays of radium themselves carry a negative charge. The lead envelope in his experiment acquired a positive charge in consequence of the emission of a secondary radiation consisting of negatively charged particles, projected with great velocity from the surface of the lead. The electric charge acquired by the metal ring was due to the absorption of these secondary rays by it, and the diminution of this charge in a magnetic field was due to the ease with which these secondary rays are deflected. It is thus to be expected that the envelope surrounding the radium, whether made of lead or other metal, would always acquire a positive charge, provided the metal is not of sufficient thickness to absorb all the γ rays in their passage through it.

No conclusive evidence has yet been brought forward to show that the γ rays can be deflected either in a magnetic or electric field. In this, as in other respects, the rays are very analogous to the Roentgen X rays.

According to the theory of Stokes, J. J. Thomson, and Weichert, of rays are transverse pulses set up in the ether by the sudden arrest X the motion of the cathode particles on striking an obstacle. The more sudden the stoppage, the shorter is the pulse, and the rays, in consequence, have greater power of penetrating matter. In some recent experiments Barkla found that the secondary rays set up by the X rays, on striking an obstacle, vary in intensity with the orientation of the X-ray tube, showing that the X rays exhibit the property of one-sidedness or polarization. This is the only evidence so far obtained in direct support of the wave-nature of the X rays.

If X rays are not set up when the cathode particles are stopped, conversely, it is to be expected that X rays should be set up when they are suddenly set in motion. Now this effect is not observable in an X-ray tube, since the cathode particles acquire most of their velocity, not at the cathode itself, but in passing through the electric field between the cathode and anti-cathode. It is, however, to be expected theoretically that a type of X rays should be set up at the sudden expulsion of the β particles from the radio-atoms. The rays, too, should be of a very penetrating kind, since not only is the charged particle projected with a speed approaching that of light, but the change of motion must occur in a distance comparable with the diameter of an atom.

On this view, the γ rays are a very penetrating type of X rays, having their origin at the moment of the expulsion of the β particle from the atom. If the β particle is the parent of the γ rays, the intensity of the β and γ rays should, under all conditions, be proportional to one another. I have found this to be the case, for the γ rays always accompany the β rays and, in whatever way the β-ray activity varies, the activity measured by the γ rays always varies in the same proportion. Active matter which does not emit β rays does not give rise to γ rays. For example, the radio-tellurium of Marckwald, which does not emit β rays, does not give off γ rays.

Certain differences are observed, however, in the ionizing action of γ and X rays. For example, gases and vapors like chlorine, sulphuretted hydrogen, methyl-iodine, and chloroform, when exposed to ordinary X rays, show a much greater ionization, compared with air, than is to be expected, according to the density law. On the other hand, the relative ionization of these substances by γ rays follows the density law very closely. It seemed likely that this apparent difference was due mainly to the greater penetrating power of the γ rays. This was confirmed by some recent experiments of Eve, who found that the relative conductivity of gases exposed to very penetrating X rays from a hard tube approximated in most cases closely to that observed for the γ rays. The vapor of methyl-iodine was an exception, but the difference in this case would probably disappear if

X rays could be generated of the same penetrating power as that of the γ rays.

The results so far obtained thus generally support the view that the γ rays are a type of penetrating X rays. This view is in agreement, too, with theory, for it is to be expected that very penetrating β rays should always appear with the β rays.

No evidence of the emission of a type of X rays is observed from active bodies which emit only α rays. If the α particles are initially projected with a positive charge, such rays are to be expected. Their absence supplies another piece of evidence in support of the view that the α particle is projected without a charge, but acquires a positive charge in its passage through matter.

V. *Emission of Energy by the Radioactive Bodies*

It was early recognized that a very active substance like radium emitted energy at a rapid rate, but the amount of this energy was very strikingly shown by the direct measurements of its heating effect made by Curie and Laborde. They found that one gram of radium in radioactive equilibrium emitted about 100 gram calories of heat per hour. A gram of radium would thus emit 896,000 gram calories per year, or over 200 times as much heat as is liberated by the explosion of hydrogen and oxygen to form one gram of water. They showed that the rate of heat emission was the same in solution as in the solid state, and remained constant when once the radium had reached a stage of radioactive equilibrium. Curie and Dewar showed that the rate of evolution of heat from radium was unaltered by plunging the radium into liquid air, or liquid hydrogen.

It seemed probable that the evolution of heat by radium was directly connected with its radioactivity, and the experiments of Rutherford and Barnes proved this to be the case. The heating effect of a quantity of radium bromide was first determined. The emanation was then completely driven off by heating the radium, and condensed in a small glass tube by means of liquid air. After removal of the emanation, the heat evolution of the radium in the course of about three hours fell to a minimum corresponding to one quarter of its original value, and then slowly increased again, reaching its original value after an interval of about one month. The heat emission from the emanation tube at first increased with the time, rising to a maximum value about three hours after its introduction. It then slowly decreased according to an exponential law with the time, falling to half value in about four days. If Q_{max} is the maximum heating effect of the emanation tube, the heat emission Q at any time t, after the maximum is reached, is given by

$$Q = Q_{max} e^{-\lambda t}$$

where λ is the radioactive constant of the emanation.

The curve expressing the recovery with time of the heating effect of radium from its minimum is complementary to the curve expressing the diminution of the heating effect of the emanation tube with time. The curves of decay and recovery agree within the limit of experimental error with the corresponding curves of decay and recovery of the activity of radium when measured by the α rays. Since the minimum, or non-separable activity of radium, measured by the α rays, after the emanation has been removed, is only one quarter of the maximum activity, these results indicate that the heating effect of radium is proportional to its activity measured by the α rays. It is not proportional to the activity measured by the β or γ rays, since the β or γ ray activity of radium almost completely disappears some hours after removal of the emanation.

These results have been confirmed by further observations of the distribution of the heat emission between the emanation and the successive products which arise from it. If the emanation is left for several hours in a closed tube, its activity measured by the electric method increases to about twice its initial value. This is due to the "excited activity," or in other words to the radiations from the active matter deposited on the walls of the tube by the emanation. The activity of this deposit has been very carefully analyzed, and the results show that the matter deposited by the emanation breaks up in three successive and well-marked stages. For convenience, these successive products of the emanation will be termed radium A, radium B, and radium C. The time T taken for each of these products to be half transformed, and the radiations from each product, are shown in the following table:

Product	T	*Radiations*
Radium		α rays
↓		
Emanation	4 days	α rays
↓		
Radium A	3 mins.	α rays
↓		
Radium B	21 mins.	no rays
↓		
Radium C	28 mins.	α, β, and γ rays

When the emanation has been left in a closed vessel for several hours, the emanation and its successive products reach a stage of approximate radioactive equilibrium, and the heating effect is then a maximum. If the emanation is suddenly removed from the tube by a current of air, the heating effect is then due to radium A, B, and C together. On account, however, of the rapidity of the change of radium A (half value in three minutes), it is experimentally very difficult to distinguish between the heating effect of the emanation and that of radium *A*. The curve of variation with time of the heating effect of the emanation tube after removal of the emanation is very nearly the same as the corresponding curve for the activity measured by the a rays. These results show that each of the products of radium supplies an amount of heat roughly proportional to its activity measured by the a rays. Each product loses its heating effect at the same rate as it loses its activity, showing that the heating effect is directly connected with the radioactive changes. The results indicated that the product, radium *B*, which does not emit rays does not supply an amount of heat comparable with the other products. This point is important, and requires more direct verification.

Since the heat emission is in all cases nearly proportional to the number of a particles expelled, the question arises whether the bombardment of these particles is sufficient to account for the heating effects observed. The kinetic energy of the a particle $\frac{1}{2}mv^2$ can be at once determined since $\frac{e}{m}$ and V are known. The following table shows the kinetic energy of the a particle deduced from the measurements of Rutherford and Des Coudres. The third column shows the number of a particles expelled from 1 gram of radium per second on the assumption that the heating effect of radium (100 gram-calories per gram per hour) is entirely due to the energy given out by the expelled a particles.

Observer	Kinetic energy	Number of a particles expelled per second from 1 gram of radium.
Rutherford	5.9×10^{-6} ergs.	2×10^{-11}
Des Coudres	2.5×10^{-6} ergs.	5×10^{-11}

This hypothesis that the heating effect of radium is due to bombardment of the a particle can be indirectly put to the test in the following way. It seems probable that each atom of radium in breaking up emits one a particle. On the disintegration theory, the residue of the atom, after the a particle is expelled, is the atom of the emanation, so that each atom of radium gives rise to one atom of the emanation. Let q be the number of atoms in each gram of radium breaking up per second. When a state of radioactive equilibrium is reached, the number N of emanation particles present is given by $N=\frac{q}{\lambda}$, where λ is the constant of change of the emanation. Now Ramsay and Soddy deduced from experiment that the volume of the emanation released from 1 gram of radium was about one cubic millimeter at atmospheric pressure and temperature. It has been experimentally deduced that there are 3.6×10^{19} molecules in one cubic centimeter of gas at ordinary pressure and temperature. The emanation obeys Boyle's law and behaves, in all respects, like a heavy gas, and we may in consequence deduce that $N = 3.6 \times 10^{16}$. Now $\lambda = 2.0 \times 10^{-6}$. Thus $q = 7.2 \times 10^{10}$. Now the particles expelled from radium in a state of radioactive equilibrium are about equally divided between four substances, viz., the radium itself, the emanation, radium *A* and *C*. We may thus conclude that the number of α particles expelled per second from 1 gram of radium in radioactive equilibrium is 2.9×10^{11}. The value deduced by this method is intermediate between the values previously obtained (see previous table) on the assumption that the heating effect is entirely due to the α particles.

I think we may conclude from the agreement of these two methods of calculation that the greater portion of the heating effect of radium is a direct result of the bombardment of the expelled α particles, and that, in all probability, about 5×10^{10} atoms of radium break up per second.

The energy carried off in the form of β and γ rays is small compared with that emitted in the form of α rays. By calculation it can be shown that the average kinetic energy of the β particle is small in comparison with that of the α particle. This result is confirmed by comparative measurements of the total ionization produced by the α and β rays, when the energy of the rays is all used up in ionizing the gas, for the total ionization produced by the β rays is small compared with that due to the α rays. The total ionization produced by the γ rays is about the same as that produced by the β rays, showing that, in all probability, the energy emitted in the form of these two types of radiation is about the same. From the point of view of the energy radiated, and of the changes which occur in the radioactive bodies, the α rays thus play a far more important rôle in radioactivity than the β or γ rays. Most of the products which arise from radium and thorium emit only α rays, while the β and γ rays appear only in the last of the series of rapid changes which take place in these bodies.

Since most of the heating effect of radium is due to the α rays, it is to be expected that all radioactive substances, which emit α rays, should also emit heat at a rate proportional to their α ray activity. On this view, both uranium and thorium should emit heat at about one millionth the rate of radium. It is of importance to determine directly the heating effect for these substances, and also for actinium radio-tellurium.

According to the disintegration theory, the α particle is expelled as a result of the disintegration of the atom of radioactive matter. While it is to be expected that a greater portion of the energy emitted should be carried off in the form of kinetic energy by the expelled particles, it is also to be expected that some energy would be radiated in consequence of the rearrangement of the components of the system after the violent ejection of one of its parts. No direct measurements have yet been made of the heating effect of the α particles, independently of the substance in which they are produced. Experiments of this character would be difficult, but would throw light on the important question of the division of the energy radiated between the expelled *a* ray particle and the system from which it arises.

The enormous evolution of energy by the radioactive substances is very well illustrated by the case of the radium emanation. The emanation released from 1 gram of radium in radioactive equilibrium emits during its changes an amount of energy corresponding to about 10,000 gram-calories. Now Ramsay and Soddy have shown that the volume of this emanation is about 1 cubic millimeter at standard pressure and temperature. One cubic millimeter of the emanation and its product thus emits about 10^7 gram-calories. Since 1 centimeter of hydrogen, in uniting with the proportion of oxygen required to form water, emits 3.1 gram-calories, it is seen that the emanation emits about 3 million times as much energy as an equal volume of hydrogen.

It can readily be calculated, on the assumption that the atom of the emanation has a mass 100 times that of hydrogen, that 1 pound of the emanation some time after removal could emit energy at the rate of about 8000 horse-power. This would fall off in a geometrical progression with the time, but, on an average, the amount of energy emitted during its life corresponds to 50,000 horse-power days. Since the radium is being continuously transformed into emanation, and three quarters of the total heat emission is due to the emanation and its products, a simple calculation shows that 1 gram of radium must emit during its life about 10^9 gram-calories. As we have seen, the heat emission of radium is about equally divided between the radium itself and the three other *a* ray products which come from it.

The heat emitted from each of the other radioactive substances while their activity lasts, should be of the same order of magnitude, but in the case of uranium and thorium the present rate of heat emission would probably continue, on an average, for a period of about 1000 million years.

VI. *Source of the Energy emitted by the Radioactive Bodies*

There has been considerable difference of opinion in regard to the fundamental question of the origin of the energy spontaneously emitted from the radioactive bodies. Some have considered that the atoms of the radio-elements act as transformers of borrowed energy. The atoms are supposed to be able, in some way, to abstract energy from the surrounding medium and to emit it again in the form of the characteristic radiations observed. Another theory, which has found favor with a number of physicists, supposes that the energy is derived from the radio-atoms themselves and is released in consequence of their disintegration. The latter theory involves the conception that the atoms of the radio-elements contain a great store of latent energy, which only manifests itself when the atom breaks up. There is no direct evidence in support of the view that the energy of the radio-elements is derived from external sources, while there is much indirect evidence against it. Some of this evidence will now be considered. There is now no doubt that the α and β rays consist of particles projected with great speed. In order for the α particle to acquire the velocity with which it is expelled, it can be calculated that it would be necessary for it to move freely between two points differing in potential by about five million volts. It is very difficult to imagine any mechanism which could suddenly impress such an enormous velocity on one of the parts of an atom. It seems much more reasonable to suppose that the α and β particles were originally in rapid motion in the atom, and, for some reason, escaped from the atomic system with the velocity they possessed at the instant of their release. There is now undeniable evidence that radioactivity is always accompanied by the production of new kinds of active matter. Some sort of chemical theory is thus required to explain the facts, whether the view is taken that the energy is derived from the atom itself or from external sources. The "external" theory of the origin of the energy was initially advanced to explain only the heat emission of radium. We have seen that this is undoubtedly connected with the expulsion of α particles from the different disintegration products of radium, and that the radium itself only supplies one quarter of the total heat emission, the rest being derived from the emanation and its further products. On such a theory it is necessary to suppose that in radium there are a number of different active substances, whose power of absorbing external energy dies away with the time, at different but definite rates. This still leaves the fundamental difficulty of the origin of these radioactive products unexplained. Unless there is some unknown source of energy in the medium which the radioactive bodies are capable of absorbing, it is difficult to imagine whence the energy demanded by the external theory can be derived. It certainly cannot be from the air itself, for radium gives out heat inside an ice calometer. It cannot be any type of rays such as the radioactive bodies emit, for the radioactivity of radium, and consequently its heating effect, are unaltered by hermetically sealing it in a vessel of lead several inches thick. The evidence, as a whole, is strongly against the theory that the energy is borrowed from external sources, and, unless a number of improbable assumptions are made, such a theory is quite inadequate to explain the experimental facts. On the other hand, the disintegration theory, advanced by Rutherford and Soddy, not only offers a satisfactory explanation of the origin of the energy emitted by the radio-elements, but also accounts for the succession of radioactive bodies. On this theory, a definite, small proportion of the atoms of radioactive matter every second becomes unstable and breaks up with explosive violence. In most cases, the explosion is accompanied by the expulsion of an α particle, in a few cases, by only a β particle, and in others by α and β particles together. On this view, there is at any time present in a radioactive body a proportion of the original matter which is unchanged and the products of the part which has undergone change. In the case of a slowly changing substance like radium, this point of view is in agreement with the observed fact that the spectrum of radium remains unchanged with its age.

The expulsion of an α or β particle or both from the atom leaves behind an atom which is lighter than before and which has different chemical and physical properties. This atom in turn becomes unstable and breaks up, and the process, once started, proceeds from stage to stage with a definite and measurable velocity in each case.

The energy radiated is, on this view, obtained at the expense of the internal energy of the radio-atoms themselves. It does not contradict the principle of the conservation of energy, for the internal energy of the products of the changes, when the process has come to an end, is supposed to be diminished by the amount of energy emitted during the changes. This theory supposes that there is a great store of internal energy in the radio-atoms themselves. This is not in disagreement with the modern views of the electronic constitution of matter, which have been so ably developed by J. J. Thomson, Larmor, and Lorentz. A simple calculation shows that the mere concentration of the electric charges, which on the electronic theory are supposed to be contained in an atom, implies a store of energy in the atom so enormous that, in comparison, the large evolution of energy from the radio-elements is quite insignificant.

Since the energy emitted from the radio-elements is for the most part kinetic in form, it is necessary to suppose that the α and β particles were originally in rapid motion in the atoms from which they are projected. The disintegration theory supposes that it is the atoms and not the molecules which break up. Such a view is necessary to explain the independence of the rate of disintegration of radioactive matter, of wide variations of temperature, and of the action of chemical and physical agents at our command. This must be conceded if the term atom is used in the ordinary chemical sense. It is, however, probable that the atoms of the radio-elements are in reality complex aggregates of known or unknown kinds of matter, which break up spontaneously. This aggregate behaves like an atom and cannot be resolved into simpler forms by external chemical or physical agencies. It breaks up, however, spontaneously with an evolution of energy enormous compared with that released in ordinary chemical changes. This question is further considered in section VIII of this paper.

The disintegration theory assumes that a small fraction of the atoms break up in unit time, but no definite explanation is, as yet, forthcoming of the causes which lead to this explosive disruption of the atom. The experimental results are equally in agreement with the view that each atom contains within itself the potentiality of its final disruption, or with the view that the disintegration is precipitated by the action of some external cause that may lead to the disintegration of the atom in the same way that a detonator is necessary to start certain explosions. The energy set free is, however, not derived from the detonator, but from the substance on which it acts. There is another general view which may possibly lead to an explanation of atomic disruption. If the atom is supposed to consist of electrons or charged bodies in rapid motion, it tends to radiate energy in the form of electromagnetic waves. If an atom is to be permanently stable, the parts of the atom must be so arranged that there is no loss of energy by electromagnetic radiation. J. J. Thomson has investigated certain possible arrangements of electrons in an atom which radiate energy extremely slowly, but which ultimately must break up in consequence of the loss of internal energy. According to present views, it is not such a matter of surprise that atoms do break up as that atoms are so stable as they appear to be. This question of the causes of disintegration is fundamental, and no adequate explanation has yet been put forward.

VII. *Radioactive Products*

Rutherford and Soddy showed that the radioactivity was always accompanied by the appearance of new types of active matter which possessed physical and chemical properties distinct from the parent radio-element. The radioactivity of these products is not permanent, but decays according to an exponential law with the time. The activity I_t and at any time t is given by $I_t = I_o e^{-\lambda t}$ where I_o is the initial activity and λ a constant. Each radioactive product has a definite change-constant which distinguishes it from all other products. These products do not arise simultaneously, but in consequence of a succession of changes in the radio-elements; for example, thorium in breaking up gives rise to *Thorium X*, which behaves as a solid substance soluble in ammonia. This in turn breaks up and gives rise to a gaseous product, the thorium emanation. The emanation is again unstable and gives rise to another type of matter which behaves as a solid and is deposited on the surface of the vessel containing the emanation. It was found that the results would be quantitatively explained on the assumption that the activity of any product at any time is the measure of the rate of production of the next product. This is to be expected, since the activity of any substance is proportional to the number of atoms which break up per second; and since each atom in breaking up gives rise to one atom of the next product together with α or β particles or both, the activity of the parent is a measure of the rate of production of the succeeding product.

Of these radioactive products, the radium emanation has been very closely studied on account of its existence in the gaseous state. It has been shown to be produced by radium at a constant rate. The amount of emanation stored up in a given mass of radium reaches a maximum value when the rate of supply of fresh emanation balances the rate of change of the emanation present.

If q be the number of atoms of emanation produced per second by the radium and N the maximum number present when radioactive equilibrium is reached, then $N = \frac{q}{\lambda}$, where λ is the constant of change of the emanation. This relation has been verified experimentally. The emanation is found to diffuse through air like a gas of heavy molecular weight. It is unattacked by chemical reagents, and in that respect resembles the inert gases of the argon family. It condenses at a definite temperature −150°C. Its constant of change is unaffected between the limits of temperature of 450°C and −180°C. Since the emanation changes into a non-volatile type of matter which is deposited on the surface of vessels, it was to be expected that the volume of the emanation should decrease according to the same law, as it lost its activity. These deductions, based on the theory, have been confirmed in a striking manner by the experiments of Ramsay and Soddy. The radium emanation was chemically isolated and found to be a gas which obeyed Boyle's law. The volume of the emanation observed was of the same order as had been predicted before its separation. The volume was found to decrease with the time according to the same law as the emanation lost its activity. Ramsay and Collie found that the emanation had a new and definite spectrum similar in some respects to that of the argon group of gases.

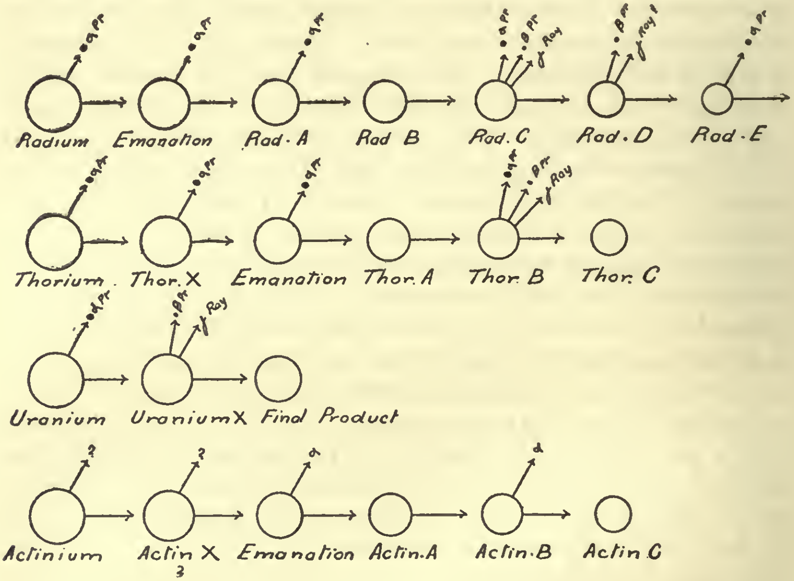
There can thus be no doubt that the emanation is a transition substance with remarkable properties. Chemically it behaves like an inert gas, and has a definite spectrum, and is condensed by cold. But, on the other hand, the gas is not permanent, but disappears, and is changed into other types of matter. It emits during its changes about one million times as much energy as is emitted during any known chemical change.

From the similarity of the behavior of the emanation of thorium and actinium to that of radium, we may safely conclude that these also are new gases which have only a limited life and change into other substances.

The non-volatile products of the radioactive bodies can be dissolved in strong acids and show definite chemical behavior in solution.

They can be partially separated by electrolysis and by suitable chemical methods. They can be volatilized by the action of high temperature, and their differences in this respect can be utilized to effect in many cases a partial separation of successive products. There can be little doubt that each of these radioactive products is a transition substance, possessing, while it lasts, some definite chemical and physical properties which serve to distinguish it from other products and from the parent element.

The radioactive products derived from each radio-element, together with the type of radiation emitted during their disintegration, are shown graphically in Fig. 1.



The radiations from actinium have not so far been examined sufficiently closely to determine the character of the radiation emitted by each product. There is some evidence that a product, actinium X, exists in actinium corresponding to Th X in thorium. It has not, however, been very closely examined.

The question of nomenclature for the successive products is important. The names Ur X, Th X have been retained, and also the term emanation. The emanation from the three radio-elements in each case gives rise to a non-volatile type of matter which is deposited on the surface of the bodies. The matter initially deposited from the radium emanation is called radium A, radium A changes into B, and B into C, and so on. A similar nomenclature is applied to the further products of the emanation of thorium and actinium. This notation is simple and elastic, and is very useful in mathematical discussion of the theory of successive changes. In the following table a list of the products is given, together with the nature of the radiation and the most marked chemical and physical properties of each product. The time T for each of the products to be half transformed is also added.

Radioactive products.	T	*Rays.*	*Some chemical and physical properties.*
Uranium	2.5×10^8 years.	α	Soluble in excess of ammonium carbonate.
↓			
Uranium X	22 days.	β, γ	Insoluble in excess of ammonium carbonate.
↓			
Final product.			
Thorium	10^9 years.	α	Insoluble in ammonia.
↓			
Thorium X	4 days.	α	Soluble in ammonia.
↓			
Emanation	1 min.	α	Inert gas condenses about −120°C.
↓			
Thorium A	11 hours.	no rays.	Attaches itself to negative electrode, soluble in strong acids.
↓			
Thorium B	55 mins.	α, β, γ	Separable from A by electrolysis.
↓			
Final product.			
Actinium			
↓			
Actinium X ?			
↓			
Emanation	3.9 secs.	α	Gaseous product.
↓			
Actinium A	41 mins.	no rays.	Attaches itself to negative electrode, soluble in strong acids.
↓			
Actinium B	1.5 mins.	α	Separable from A by electrolysis.
↓			
Final product.			
Radium	1000 years.	α	
↓			
Emanation	4 days.	α	Inert gas, condenses −150° C.
↓			
Radium A	3 mins.	α	Attaches itself to negative electrode soluble in strong acids.
↓			
Radium B	21 mins.	no rays.	Volatile at 500°C.
↓			
Radium C	28 mins.	α, β, γ	Volatile about 1100°C.
↓			
Radium D	about 40 years.	β, γ	Soluble in sulphuric acid.
↓			
Radium E	about 1 year.	α	Attaches itself to bismuth plate in solution, volatilizes at 1000°C.
↓			

The changes which occur in the active deposits from the emanation of radium, thorium, and actinium have been difficult to determine on account of their complexity. For example, in the case of radium, the active deposit, obtained as a result of a long exposure to the emanation, contains quantities of radium A, B, and C. The changes occurring in the active deposit of radium have been determined by P. Curie, Danne, and the writer. The value of T for the three successive changes is 3, 21, and 28 minutes respectively. Radium *A* gives only α rays, *B* gives out no rays at all, while *C* gives out α, β, and γ rays. These results have been deduced by the comparison of the change of activity with time, with the mathematical theory of successive changes. The variation of the activity with time depends upon whether the activity is measured by the α, β, or γ rays. The complicated curves are very completely explained on the hypothesis of three successive changes of the character already mentioned.

The activity of a vessel in which the radium emanation has been stored for some time rapidly falls to a very small fraction after the emanation is withdrawn. There, however, always remains a slight residual activity. The writer has recently examined the activity in detail. The residual activity at first mainly consists of β rays, and the activity measured by them does not change appreciably during the period of one year. The α ray activity is at first small, but increases uniformly with the time for the first few months that the activity has been examined. These results receive an explanation on the hypothesis that radium *C* changes into a product *D* which emits only β rays. *D* changes into a product *E*, which emits only α rays. This view has been confirmed by separating the α ray product by dipping a bismuth plate into the solution containing radium *D* and *E*. The probable period of these changes can be deduced from observations of the magnitude of the α and β ray activity at any time. It has been deduced that radium *D* is probably half transformed in forty years, and radium *E* is half transformed in about one year. The evidence at present obtained points to the conclusion that radium *E* is the active constituent present in Marckwald's radio-tellurium, and probably also in the polonium of Mme. Curie.

The changes in the active deposit of thorium have been analyzed by the writer, and the corresponding changes in actinium by Miss Brooks.

The occurrence of a "rayless change" in the active deposits from the emanation of radium, thorium, and actinium is of great interest and importance. As these products do not emit either α or β or γ rays, their presence can only be detected by their effect on the amount of the succeeding products. The action of the rayless change is most clearly brought out in the examination of the variation of activity with time of a body exposed for a very short interval in the presence of the emanations of thorium and actinium. Let us consider, for simplicity, the variation of activity with time for thorium. The activity (measured by the α rays) observed at first is very small, but gradually increases with the time, passes through a maximum, and finally decays according to an exponential law with the time falling to half value in 11 hours. The shape of this curve can be completely explained on the assumption of the two successive changes, the second of which alone gives out rays. The matter deposited on the body during the short exposure consists almost entirely of thorium *A*. Thorium *A* changes into *B* and the breaking up of *B* gives rise to the activity measured.

Let n_o = number of particles of thorium *A* deposited on the body during the time of exposure to the emanation.

Let *P* and *Q* be the number of particles of thorium *A* and *B* respectively at any time after removal.

Let λ_1, λ_2 be the constants of the two changes.

The number of particles of *P* existing at any time *t* is given by $P = n_o e^{-\lambda_1 t}$. If each atom of *A* in breaking up gives rise to one atom of *B*, the increase *dQ* in the number of *Q* in the time *dt* is given by the difference between the number of atoms of *B* supplied by the change in *A* and the number of *B* which break up.

Thus, $$\frac{dQ}{dt} = \lambda_1 P - \lambda_2 Q = \lambda_1 n_0 e^{-\lambda_1 t} - \lambda_2 Q.$$

The solution of this equation is of the form $Q = ae^{-\lambda_1 t} + be^{-\lambda_2 t}$. Since for a very short exposure $Q = 0$

$$a = -b = \frac{\lambda_1}{\lambda_1 - \lambda_2}$$

and $$Q = \frac{n_0}{\lambda_1 - \lambda_2}(c^{-\lambda_2 t} - e^{-\lambda_1 t}).$$

If thorium *A* does not give out rays, the activity of the body at any time after removal is proportional to *Q*. Thus the activity at any time *t* is proportional to $e^{-\lambda_2 t} - e^{-\lambda_1 t}$. Now the experimental curve of variation of activity is found to be accurately expressed by an equation of this form. A very interesting point arises in settling the values of λ_1 and λ_2 corresponding to the two changes. It is seen that the equation is symmetrical in λ_1 and λ_2 and in consequence is unaltered if the values of λ_1 and λ_2 are interchanged. Now the constant of the change is determined by the observation that the activity finally decays to half value in 11 hours. The theoretical and experimental curves are found to coincide if one of the two products is half transformed in 11 hours and the other in 55 minutes. The comparison of the theoretical and experimental curves does not, however, allow us to settle whether the period of change of thorium *A* is 55 minutes or 11 hours. In order to settle the point, it is necessary to find some means of separating the products thorium *A* and *B* from each other. In the case of thorium, this is done by electrolysing a solution of thorium. Pegram obtained an active product which decayed according to an exponential law with the time falling to half value in a little less than 1 hour. This result shows that the radiating product thorium *B* has the shorter period. In a similar way, by recourse to electrolysis, it has been found that the change of actinium *B* has a period of 1.5 minutes.

In the case of radium, P. Curie and Danne utilized the difference in volatility of radium *B* and *C* in order to fix the period of the changes.

It is very remarkable that the third successive product of radium, thorium, and actinium should not give out rays. It seems probable that these rayless changes are not of so violent a character as the other changes, and consist either of a rearrangement of the components of the atom or of an expulsion of an α or β particle with so slow a velocity that it fails to ionize the gas. The appearance of such changes in radioactive matter suggests the possibility that ordinary matter may also be undergoing slow "rayless changes," for such changes could not have been detected in the radio-elements, unless its succeeding products emitted rays.

It is seen that the changes occurring in radium, thorium, and actinium are of a very analogous character and indicate that each of these bodies has a very similar atomic constitution.

While there can be no doubt that numerous kinds of radioactive matter with distinct chemical and physical properties are produced in the radio-elements, it is very difficult to obtain direct evidence in some cases that the products are successive and not simultaneous. This is the case for products which have either a very slow or very rapid rate of change compared with the other product. For example, it is difficult to show directly that radium *B* is the product of radium *A* and not the direct product of the emanation. In the same way, there is no direct evidence that radium *C* is the parent of radium *D*. At the same time the successive nature of these products is indicated by indirect evidence.

There can be little doubt that each of the radioactive products is a distinct chemical substance and possesses some distinguishing physical or chemical properties. There still remains a large amount of chemical work to be done to compare and arrange the chemical properties of these products and to see if the successive products follow any definite law of variation. The electrolytic method can in many cases be used to find the position of the product in the electrochemical series. The products which change most rapidly are present in the least quantity in radium and pitchblende. Only the slower changing products like the radium emanation and radium *D* and *E* exist in sufficient quantities to be examined by the balance. It is possible that the products radium *A*, *B*, and *C* may be obtained in sufficient quantity to obtain their spectrum.

VIII. *Connection between the a Particles and Helium*

The discovery of Ramsay and Soddy that helium was produced by the radium emanation was one of the greatest interest and importance, and confirmed in a striking manner the disintegration theory of radioactivity, for the possible production of helium from radioactive matter had been predicted on this theory before the experimental evidence was forthcoming. Ramsay and Soddy found that the presence of helium could not be detected in a tube immediately after the introduction of the emanation, but was observed some time afterwards, showing that the helium arose in consequence of a slow change in the emanation itself or in its further products.

The question of the origin of the helium produced by the radium emanation and its connection with the radioactive changes occurring in the emanation is one of the greatest importance. The experimental evidence so far obtained does not suffice to give a definite answer to this question, but suggests the probable explanation. There has been a tendency to assume that the helium is the final disintegration product of the radium emanation, *i. e.*, it is the inactive substance which remains when the succession of radioactive changes in the emanation have come to an end. There is no evidence in support of such a conclusion, while there is much indirect evidence against it. It has been shown that the emanation which breaks up undergoes three fairly rapid transformations; but after these changes have occurred, the residual matter — radium *D* — is still radioactive, and breaks up slowly, being half transformed in probably about forty years. There then occurs a still further change. Taking into account the minute quantity of the radium emanation initially present in the emanation tube, the amount of the final inactive product would be insignificant after the lapse of a few days or even months. It thus does not seem probable that the helium can be the final product of the radioactive changes. In addition, it has been shown that the a particle behaves like a body of about the same mass as the helium atom. The expulsion of a few a particles from each of the heavy atoms of radium would not diminish the atomic weight of the residue very greatly. The atomic weight of the atoms of radium *D* and *E* is in all probability of the order of two hundred, since the evidence supports the conclusion that each atom expels one a particle at each transformation. In order to explain the presence of helium, it is necessary to look to the other inactive products produced during the radioactive changes. The a particles expelled from the radioactive product are themselves non-radioactive. The measurement of the ratio $\frac{e}{m}$ shows that they have an apparent mass intermediate between that of the hydrogen and helium atoms. If the a particles consist of any known kind of matter they must be either atoms of hydrogen or of helium. The actual value of $\frac{e}{m}$ has not yet been determined with an accuracy sufficient to give a definite answer to the question. On account of the very slight curvature of the path of the a particles in a strong magnetic or electric field, an accurate determination of $\frac{e}{m}$ is beset with great difficulties.

The experimental problem is still further complicated by the fact that the α particles escaping from a mass of radium have not all the same velocity, and in consequence it is difficult to draw a definite conclusion from the observed deviation of the complex pencil of rays.

The results so far obtained are not inconsistent with the view that the α particles are helium atoms, and indeed it is difficult to escape from such a conclusion. On such a view, the helium, which is gradually produced in the emanation tube, is due to the collection of α particles expelled during the disintegration of the emanation and its further products. This conclusion is supported by evidence of another character. It is known that thorium minerals like monazite sand contain a large quantity of helium. In this respect, they do not differ from uranium minerals which are rich in radium. The only common product of the different radioactive substances is the α particle, and the occurrence of helium in all radioactive minerals is most simply explained on the supposition that the α particle is a projected helium atom. This conclusion could be indirectly tested by examining whether helium is produced in other substances besides radium, for example, in actinium and polonium.

The experimental determination of the origin of helium is beset with difficulty on all sides. If the α particle is a helium atom, the total volume of helium produced in an emanation tube should be three times the initial volume of the emanation present, since the emanation in its rapid changes gives rise to three products each of which emits α particles. This is based on the assumption, which seems to be borne out by the experiments, that each atom of each product in breaking up expels one α particle. This at first sight offers a simple experimental means of settling the question, but a difficulty arises in accurately determining the volume of helium produced by a known quantity of the radium emanation. It would be expected that, if the emanation were isolated in a tube and left to stand, the volume of gas in the tube should increase with time in consequence of the liberation of helium. In one case, however, Ramsay and Soddy observed an exactly opposite result. The volume diminished with time to a small fraction of its original value. This diminution of volume was due to the decomposition of the emanation into a non-gaseous type of matter deposited on the walls of the tube, and followed the law of decrease to be expected in such a case, namely, the volume decreased according to an exponential law with the time, falling to half value in four days. The helium produced by the emanation must have been absorbed by the walls of the tube. Such a result is to be expected if the particle is a helium atom, for the α particle is projected with a velocity sufficient to bury itself in the glass to a depth of about $\frac{1}{100}$ mm. This buried helium would probably be in part released by the heating of the tube, such as occurs with the strong electric discharge employed in the spectroscopic detection of helium. Ramsay and Soddy have examined the glass tubes in which the emanation had been confined for some time, to see if the buried helium was released by heat. In some cases, traces of helium were observed.

Accurate measurements of the value of $\frac{e}{m}$ for the a particle, and also an accurate determination of the relative volume of the emanation and the helium produced by it, would probably definitely settle this fundamental question.

Certain very important consequences follow on the assumption that the a particle is, in all cases, an atom of helium. It has already been shown that the radio-elements are transformed into a succession of new substances, most of which in breaking up emit an a particle. On such a view, the atom of radium, thorium, uranium, and actinium must be supposed to be built up in part of helium atoms. In radium, at least five products of the change emit a particles, so that the radium atom must contain at least five atoms of helium. In a similar way, the atoms of actinium and thorium (or if thorium itself be not radioactive, the atom of the active substance present in it) must be compounds of helium. These compounds of helium are not stable, but spontaneously break up into a succession of substances, with an evolution of helium, the disintegration taking place at a definite but different rate at each stage. Such compounds are sharply distinguished in their behavior from the molecular compounds known to chemistry. In the first place, the radioactive compounds disintegrate spontaneously and at a rate that is independent of the physical or chemical forces at our control. Changes of temperature, which exert such a marked influence in altering the rate of molecular reactions are here almost entirely without influence. But the most striking feature of the disintegration is the expulsion, in most cases, of a product of the change with very great velocity — a result never observed in ordinary chemical reactions. This entails an enormous liberation of energy during the change, the amount, in most cases, being about one million times as great as that observed in any known chemical reaction. In order to account for the expulsion of an a or β particle with the observed velocities, it is necessary to suppose that their particles exist in a state of rapid motion in the system from which they escape. Variation of temperature, in most cases, does not seem to affect the stability of the system.

It is well established that the property of radioactivity is inherent in the radio-atoms, since the activity of any radioactive compound depends only on the amount of the element present and is not affected by chemical treatment. As far as observation has gone, both uranium and radium behave as elements in the usual accepted chemical sense.

They spontaneously break up, but the rate of their disintegration seems to be, in most cases, quite independent of chemical control. In this respect, the radioactive bodies occupy a unique position. It seems reasonable to suppose that while the radioactive substances behave chemically as elements, they are, in reality, compounds of simpler kinds of matter, held together by much stronger forces than those which exist between the components of ordinary molecular compounds. Apart from the property of radioactivity, the radio-elements do not show any chemical properties to distinguish them from the non-radioactive elements, except their very high atomic weight. The above considerations thus evidently suggest that the heavier inactive elements may also prove to be composite.

IX. *Origin of the Radio-Elements*

We have seen that the radio-elements are continuously breaking up and giving rise to a succession of new substances. In the case of uranium and thorium, the disintegration proceeds at such a slow rate that in all probability a period of about 1000 million years would be required before half the matter present is transformed. In the case of radium, however, where the process of disintegration proceeds at over one million times the rate of uranium and thorium, it is to be expected that a measurable proportion of the radium should be transformed in a single year. A quantity of radium left to itself must gradually disappear as such in consequence of its gradual transformation into other substances. This conclusion necessarily follows from the known experimental facts. The radium is continuously being transformed into the emanation which in turn is changed into other types of matter. Since there is no evidence that the process is reversible, all the radium present must, in the course of time, be transformed into emanation. The rate at which radium is being transformed can be approximately calculated either from the number of a particles expelled per second or from the observed volume of the emanation produced per second. Both methods of calculation agree in fixing that in a gram of radium about one milligram is transformed per year. From analogy with other radioactive changes, it is to be expected that the rate of change of radium would be always proportional to the amount present. The amount of radium would thus decrease exponentially with the time, falling to half value in about 1000 years. On this point of view, radium behaves in a similar way to the other known products, the only difference being that its rate of change is slower. We have already seen that, in all probability, the product radium D is half transformed in about 40 years and radium E in about one year. In regard to their rate of change, the two substances radium D and E, which are half transformed in about 40 years and 1 year respectively, occupy an intermediate position between the rapidly changing substances like radium *A*, *B*, and *C* and the slowly changing parent substance radium.

If the earth were supposed to have been initially composed of pure radium, the activity 20,000 years later would not be greater than the activity observed in pitchblende to-day. Since there is no doubt that the earth is much older than this, in order to account for the existence of radium at all in the earth, it is necessary to suppose that radium is continuously produced from some other substance or substances. On this view, the present supply of radium represents a condition of approximate equilibrium where the rate of production of fresh radium balances the rate of transformation of the radium already present. In looking for a possible source of radium, it is natural to look to the substances which are always found associated with radium in pitchblende. Uranium and thorium both fulfill the conditions necessary to be a source of radium, for both are found associated with radium and both have a rate of change slow compared with radium. At the present time, uranium seems the most probable source of radium. The activity observed in a good specimen of pitchblende is about what is to be expected, if uranium breaks up into radium. If uranium is the parent of radium, it is to be expected that the amount of radium present in different varieties of pitchblende obtained from different sources should always be proportional to the amount of uranium contained in the minerals. The recent experiments of Boltwood, Strutt, and McCoy indicate that this is very approximately the case. It is not to be expected that the relation should, in all cases, be very exact, since it is not improbable, in some cases, that a portion of the active material may be removed from the mineral, by the action of percolating water or other chemical agencies. The results so far obtained strongly support the view that radium is a product of the disintegration of uranium. It should be possible to obtain direct evidence on this question by examining whether radium appears in uranium compounds which have been initially freed from radium. On account of the delicacy of the electric test of radium by means of its emanation, the question can very readily be put to experimental trial. This has been done for uranium by Soddy and for thorium by the writer, but the results, so far obtained, are negative in character, although, if radium were produced at the rate to be expected from theory, it should very readily have been detected. Such experiments, however, taken over a period of a few months, are not decisive, for it is by no means improbable that the parent element may pass through several slow changes, possibly of a "rayless" character, before it is transformed into radium. In such a case, if these intermediate products are removed by the same chemical process from the parent element, there may be a long period of apparent retardation before the radium appears. The considerations advanced to account for radium apply equally well to actinium, which in all probability, when isolated, will prove to be an element of the same order of activity as radium. The most important problem at present in the study of radioactive minerals is not the attempt to discover and isolate new radioactive substances, but to correlate those already discovered. Some progress has already been made in reducing the number of different radioactive substances and in indicating the origin of some of them. For example, there is no doubt that the "emanating substance" of Giesel contains the same radioactive substance as the actinium of Debierne. In a similar way, there is very strong evidence that the active constituent in the polonium of Mme. Curie is identical with that in the radio-tellurium of Marckwald. The writer has recently shown that the active constituent in radio-tellurium or polonium is, in all probability, a disintegration product of radium (radium *E*). The same considerations apply to the radio-lead of Hofmann, which is probably identical with the product radium *D*. It still remains to be shown whether or no there is any direct family connection between the radioactive substances uranium, thorium, radium, and actinium. It seems probable that some at least of these substances will prove to be lineal descendants of a single parent element, in the same way that the radium products are lineal descendants of radium. The subject is capable of direct attack by a combination of physical and chemical methods, and there is every probability that a fairly definite answer will soon be forthcoming.

X. *Radioactivity of the Earth and Atmosphere*

It is now well established, notably by the work of Elster and Geitel, that radioactive matter is widely distributed both in the earth's crust and atmosphere. There is undoubted evidence of the presence of the radium emanation in the atmosphere, in spring water, and in air sucked up through the soil. It still remains to be settled whether the observed radioactivity of the earth's crust is due entirely to slight traces of the known radioactive elements or to new kinds of radioactive matter. It is not improbable that a close examination of the radioactivity of the different soils may lead to the discovery of radioactive substances which are not found in pitchblende or other radioactive minerals. The extraordinary delicacy of the electroscopic test of radioactivity renders it possible not only to detect the presence in inactive matter of extremely minute traces of a radioactive substance, but also in many cases to settle quickly whether the radioactivity is due to one of the known radio-elements.

The observations of Elster and Geitel render it probable that the radioactivity observed in the atmosphere is due to the presence of radioactive emanations or gases, which are carried to the surface by the escape of underground water and by diffusion through the soil. Indeed, it is difficult to avoid such a conclusion, since there is no evidence that any of the known constituents of the atmosphere are radioactive. Concurrently with observations of the radioactivity of the atmosphere, experiments have been made on the amount of ionization in the atmosphere itself. It is important to settle what part of this ionization is due to the presence of radioactive matter in the atmosphere. Comparisons of the relative amount of active matter and of the ionization in the atmosphere over land and sea will probably throw light on this important problem.

The wide distribution of radioactive matter in the soils which have so far been examined has raised the question whether the presence of radium and other radioactive matter in the earth may not, in part at least, be responsible for the internal heat of the earth. It can readily be calculated that the presence of radium (or equivalent amounts of other kinds of radioactive matter) to the extent of about five parts in one hundred million million by mass would supply as much heat to the earth as is lost at present by conduction to its surface. It is certainly significant that, as far as observation has gone, the amount of radioactive matter present in the soil is of this order of magnitude.

The production of helium from radium indirectly suggests a method of calculation of the age of the deposits of radioactive minerals. It seems reasonable to suppose that the helium always found associated with radioactive minerals is a product of the decomposition of the radioactive matter present. About half of the helium is removed by heating the mineral and the other half by solution. It thus does not seem likely that much of the helium found in the mineral escapes from it, so that the amount present represents the quantity produced since its formation. If the rate of the production of helium by radium (or other radioactive substance) is known, the age of the mineral can at once be estimated from the observed volume of helium stored in the mineral and the amount of radium present. All these factors have, however, not yet been determined with sufficient accuracy to make at present more than a rough estimate of the age of any particular mineral. An estimate of the rate of production of helium by radium has been made by Ramsay and Soddy by an indirect method. It can be deduced from their result that 1 gram of radium produces per year a volume of helium of about 25 cubic mms. at standard pressure and temperature. They, however, consider this to be an underestimate. On the other hand, if the a particle is a helium atom, it can readily be calculated that 1 gram of radium produces per year about 200 cubic mms. of helium.

Let us consider for example the mineral fergusonite. Ramsay and

Travers have shown that it yields about 1.8 cc. of helium per gram and contains about 7 per cent of uranium. It can readily be deduced from known data that each gram of the mineral contains about one four-millionth of a gram of radium. Supposing that one gram of radium produces $\frac{1}{5}$ cc. of helium per year, the age of the mineral is readily seen to be about 40 million years. If the above rate of production of helium by radium is an overestimate, the time will be correspondingly longer. I think there is little doubt that when the data required are accurately known this method can be applied, with considerable confidence, to determine the age of the radioactive minerals.

XI. *Radioactivity of Ordinary Matter*

The property of radioactivity is exhibited to the most marked extent by the radioactive substances found in pitchblende, but it is natural to ask the question whether ordinary matter possesses this property to an appreciable degree. The experiments that have so far been made show conclusively that ordinary matter, if it possesses this property at all, does so to a minute extent compared with uranium. It has been found that all the matter that has so far been examined shows undoubted traces of radioactivity, but it is very difficult to show that the radioactivity observed is not due to a minute trace of known radioactive matter. Even with the extraordinarily delicate methods of detection of radioactivity, the effects observed are so minute that a definite settlement of the question is experimentally very difficult. J. J. Thomson has recently given an account at the Meeting of the British Association of the work done on this subject in the Cavendish Laboratory, and has brought forward experimental evidence that strongly supports the view that ordinary matter does show specific radioactivity. Different substances were found to give out radiations that differed in quality as well as in quantity. A promising beginning has already been made, but a great deal of work still remains to be done before such an important conclusion can be considered to be definitely established.

SHORT PAPER

Professor R. A. Millikan, of the University of Chicago, presented a paper to this Section on "The Relation between the Radioactivity and the Uranium Content of Certain Minerals," of which the following is an abstract:

In March, 1904, the author, assisted by Mr. H. A. Nichols, Assistant Curator of Geology at the Field Columbian Museum (Chicago), began an investigation of the relation between the radioactivity and the uranium content of uranium-bearing minerals with a view to ascertaining whether the radioactive substances found in pitchblende are not all decomposition products of uranium. If such be the case the ratio between the uranium content and the radioactivity of uranium ought obviously to be constant, in case the assumption may be made that the active products of the decomposition are not washed out of the mineral by percolating water or other agencies.

Since the beginning of this investigation some preliminary results have been published in *Nature* by Boltwood which indicate a constancy in this ratio in the case of a few American ores which he has examined. McCoy (*cf. Ber. d. Chem. Ges.* 36, 3043) has also found a similar indication of constancy in the case of the six different kinds of uranium minerals which he has studied.

The present investigation is not yet complete, but so far as it has gone it furnishes additional evidence in support of the view that uranium is the parent of radium, for it extends somewhat the number of minerals for which the ratio between the activity and the uranium content is approximately constant. The following table gives the results thus far obtained.

Name of mineral	*Locality*	*Per cent of uranium contained*	*Activity in terms of uranium oxide*	*% uranium divided by activity*	*% of departure from mean*
Pitchblende	Colorado	59.1	3.24	18.2	4.2
Clevite	Norway	69.3	4.03	17.2	9.4
Gummite	North Carolina	55.4	2.56	21.6	13.6
Pitchblende	Cornwall, Eng.	9.23	.55	16.9	11.6
Autunite	Cornwall, Eng.	6.9	.33	20.8	9.5
Autunite	Saxony	4.0	.205	19.5	3.6
			Mean	19.0	

It will be seen that the departures from the mean value of the ratio amount in some cases to as much as 13 %, but this was found to be no more than the differences which might be obtained by "resurfacing" the same specimen of a given substance.

The measurements on activity were all made as follows: three hundred mg. of the very carefully powdered mineral were spread as uniformly as possible over three square inches of a metal sheet. This sheet was then placed upon the lower plate of an air-condenser which was connected with one pair of quadrants of an electrometer, the other pair being earthed. The condenser-plates were ten cm. on a side and 3 cm. apart. A potential of one hundred and thirty volts was applied to the upper condenser-plate, and the rate of charging of the electrometer noted. The potential to which the needle of the electrometer was charged was one hundred and twenty-five volts. The chemical analyses were all made by Mr. Nichols.

BIBLIOGRAPHY: DEPARTMENT OF PHYSICS

(*Prepared for the Department by the courtesy of Professor Henry Crew*)

GENERAL PHYSICS

ARRHENIUS, Lehrbuch der kosmischen Physik.
GUILLAUME and POINCARÉ, Rapports présentés au Congrès International de physique. (Paris, 1900.)
POYNTING and THOMSON, Text-Book of Physics.
WATSON, Text-Book of Physics (Longmans).
WINKELMANN, Handbuch der Physik, 6 vols. 2d ed.
VIOLLE, Cours de Physique.

DYNAMICS

CLIFFORD, Elements of Dynamic.
HERTZ, Die Principien der Mechanik.
LAGRANGE, Mécanique Analytique.
LAMB, Hydrodynamics.
LOVE, Treatise on the Mathematical Theory of Elasticity.
MINCHEN, Treatise on Statics.
NEWTON, Principia.
THOMSON and TAIT, Treatise on Natural Philosophy.
WEBSTER, Dynamics.
WIEN, Lehrbuch der Hydrodynamik.

SOUND

BLASERNA, Theory of Sound.
DONKIN, Acoustics.
HELMHOLTZ, Sensations of Tone. (Trans. by Ellis.)
RAYLEIGH, Theory of Sound.

HEAT

BOLTZMANN, Vorlesungen über Gastheorie.
EWING, Steam Engine and other Heat Engines.
FOURIER, Analytical Theory of Heat. (Trans. by Freeman.)
GUILLAUME, Thermométrie.
JEANS, Dynamical Theory of Gases.
MAXWELL, Theory of Heat.
MEYER, Kinetic Theory of Gases. (Trans. by Baynes.)
PLANCK, Thermodynamics. (Trans. by Ogg.)
PRESTON, Theory of Heat.

LIGHT

CZAPSKI, Theorie der Optischen Instrumente.
DRUDE, Theory of Optics. (Trans. by Mann and Millikan.)
EDSER, Light for Students.
KAYSER, Handbuch der Spectroscopie.
KELVIN, Baltimore Lectures.
LARMOR, Ether and Matter.

Newton, Opticks.
Schuster, Theory of Optics.

ELECTRICITY AND MAGNETISM

Boltzmann, Vorlesungen über Maxwells Theorie der Electricitat und des Lichtes.
Du Bois, Magnetische Kreise.
Ewing, Magnetic Induction in Iron and other Metals.
Faraday, Experimental Researches.
Hertz, Electric Waves. (Trans. by Jones.)
Maxwell, Treatise on Electricity and Magnetism.
Rutherford, Radioactivity.
Stark, Die Electricitat in Gasen.
Thomson, Conduction of Electricity through Gases.
Thomson, J. J., Recent Researches in Electricity and Magnetism.
Webster, Theory of Electricity and Magnetism.

PHYSICAL PAPERS

Scientific Papers of Abbe, Heaviside, Helmholtz, Hertz, Hopkinson, Joule, Kirchhoff, Maxwell, Rankine, Rayleigh, Reynolds, Rowland, Tait.

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DEPARTMENT X — CHEMISTRY

DEPARTMENT X — CHEMISTRY

(*Hall* 5, *September* 20, 4.15 *p. m.*)

CHAIRMAN: PROFESSOR JAMES M. CRAFTS, Massachusetts Institute of Technology.
SPEAKERS: PROFESSOR JOHN U. NEF, University of Chicago.
PROFESSOR FRANK W. CLARKE, Chief Chemist, U. S. Geological Survey.

THE Chairman of the Department of Chemistry was Professor James M. Crafts, of the Massachusetts Institute of Technology, who in opening the work of the Department spoke of the great stimulus which American chemists owed to European laboratories and the lively remembrance of the freedom of these laboratories and priceless instruction given. The application which Americans make of the scientific methods acquired abroad are characteristic of our nationality, but at the same time strongly reminiscent of other sources.

The decade within which this Congress meets has been one of extraordinary interest in the history of chemistry. I say a decade, although perhaps I should say a half-decade, since we are told by the British Premier, addressing the meeting for the advancement of science at Cambridge, that "until five years ago our race has without exception lived and died in a world of illusions." His admirably turned periods appear to signalize our old conceptions of the constitution of matter as the chief among illusions, and he seems to look forward to the immediate replacement of the false doctrine by a more idealistic conception of the universe. The atomic theory is naturally dismissed with censure, and thus we have taken away from us those blocks with which we built so happily our toy houses in the days of our innocent, childish faith. The last Faraday lecturer has been less cruel, for although he has no faith in the indivisibility of atoms, from which we can knock off electrons, nor in the individuality of the elements, his criticism is not merely negative, but, like a truly scientific engineer, he offers us a new model for our constructions. Professor Ostwald invites us to enter a beautiful stalactite cavern, groping, indeed, in some obscurity, but with the vision of a brighter light beyond.

The observations of the Röntgen and Becquerel rays have led in Germany, France, England, and Canada to a study of emanations, which has been distinguished by extreme skill in the invention of new methods and by the minute study of phenomena, which seemed even a year ago beyond the reach of human ingenuity.

The simplest statement of facts is sufficiently wonderful and mysterious. Although not more than two or three grams of radium have been gathered from the earth's crust, its natural history is already well developed, and at latest news we are told that one gram of radium bromide will evolve 0.0022 milligrams of helium in one year; that the life of a radium atom is 1050 years, or, in another experiment, 1250 years.

It may be said that within this decade the knowledge of the structure of carbon compounds has become so complete that the way to the production of the most useful bodies has become evident in theory, and I need not remind you of the consequent achievements by that happy combination of pure and industrial science in Germany.

Also within this decade, the somewhat neglected study of mineral chemistry has acquired unexpected interest by the discovery in France of metallic carbides and nitrides, formed at temperatures comparable with those of the sun, and these discoveries, besides giving rise to most unexpected industrial applications, show entirely new possibilities for the geology of the primitive rocks.

The active pursuit of physical chemistry has extended over some thirty years. Great dates are the publication, just two decades ago, of van 't Hoff's *Etudes de dynamique chimique*, and one year afterwards of Ostwald's *Allgemeine Chemie;* and, again, ten years ago *Dix Années d'une Théorie.*

Suffice it to say that the title, General Chemistry, has been amply justified. The attractive presentation of bold theories, their rapid confirmation by experiment, and the completeness of treatment by the founders of the new science have led to the immediate acceptance of their views, until the mathematical analysis of chemical phenomena has become the dominating feature of our science, and has transformed our methods of thought, as Kepler and Newton's theories transformed the study of astronomy.

ON THE FUNDAMENTAL CONCEPTIONS UNDERLYING THE CHEMISTRY OF THE ELEMENT CARBON

BY JOHN ULRIC NEF

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Two fundamental conceptions underlie our present system of carbon chemistry. First, the idea of the constant quadrivalence of carbon, which explains most adequately the existence of the vast array of carbon compounds. Second, the conception of substitution or metalepsis, which gives us a basis for interpreting many of the reactions shown by these substances.

These ideas are, however, in the light of investigations of the past twenty years, inadequate; they must be replaced by the conception of a variable valence of carbon and by the conception of dissociation in its broadest sense. A rigid application of the latter conception gives a far simpler basis for interpreting all the reactions of carbon chemistry; they are naturally also applicable to the chemistry of all the other elements.

I. *On the Valence of the Carbon Atom*

The progress of organic chemistry since 1858 is due chiefly to the development of a few very simple ideas concerning the valence of the elements, ideas which were first clearly and fully presented at that time by Kekulé.

Hydrogen, oxygen, and nitrogen are the elements which most frequently combine with carbon to form the so-called organic compounds. Since the compounds of one atom of oxygen, nitrogen, or carbon with hydrogen possess the empyrical formulæ, $O=H_2$, $N\equiv H_3$, $C\equiv H_4$, the conception naturally presents itself that the capacity of the various elements for holding hydrogen atoms varies. Oxygen is capable of holding two such atoms, nitrogen holds three, and carbon four atoms of hydrogen.

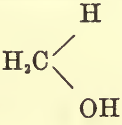
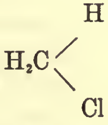
Therefore we assume, taking hydrogen as our unit, that the valence of the element oxygen is two, $-O-$, of nitrogen, three, $-\overset{|}{N}-$, and of carbon, four, $-\underset{|}{\overset{|}{C}}-$.

Without going into much detail concerning the nature of valence, or, what is the same thing, concerning the nature of the forces inherent in our atoms, we assume briefly that every atom of an element possesses one, two, three, four, or more such units of force, and we call the element univalent, bivalent, trivalent, quadrivalent, etc., according to the number of such units it possesses. It is by virtue of the existence of these units of force that the compounds made up of the same or of various elementary atoms exist. We assume that in such a molecular compound the atoms are bound one to another in a definite way by means of their affinity units.

Since the development of these ideas concerning the valence of the elements there has been a great deal of work carried on with the object of determining whether the valence of an element is constant or whether it may vary; the majority of chemists are now convinced that it may vary. The valence of nitrogen may be three or five. The valences of hydrogen, oxygen, and carbon, on the other hand, have, until recently, been assumed always to remain constant, *i. e.*, one, two, and four, respectively.

Since the complexity, the very great variety and number of existing compounds containing carbon are unquestionably to be attributed to the peculiar nature of the forces inherent in the carbon atom, let us consider a little more in detail what hypotheses we make in our present system of carbon chemistry concerning this element. We assume, first, that the valence of the carbon atom is always four; second, that the four valences or affinity units of the carbon atom are equivalent; third, that they are distributed in space in three dimensions and act in tetrahedral directions; fourth, that the carbon atoms can unite with one another by means of one, two, or three affinity units to form what we usually call chains.

These chains may be open, or closed rings or cycles. The number of carbon atoms thus bound to one another may be exceedingly large. The closed chains usually contain three, four, five, six, or seven carbon atoms in the ring. We may have in these chains, whether open or closed, some of the carbon atoms replaced by oxygen, nitrogen, sulphur, or other elements. If now we unite the extra valences of each carbon or other atom — *i. e.*, those affinity units which are not necessary for binding the atoms together in chains — with other atoms or radicals, it is at once evident that we can represent theoretically, by so-called graphical formulæ, molecules of great complexity. It is also at once obvious that with a small number of atoms it must be possible to construct a relatively large number of aggregates which differ from one another simply in the way the atoms are bound together. In 1884, for instance, fifty-five totally different substances of the empyrical-formula $C_9H_{10}O_3$ were actually known. We call them isomers. One of the chief problems of organic chemistry since 1858 has been to determine on the basis of these ideas of valence the "constitution" of the carbon compounds; we determine by methods which are called synthetic, as well as by an exhaustive study of the reactions of a given compound, what may be called the "architecture" of its molecule, *i. e.*, we determine how the various atoms of carbon, nitrogen, oxygen, and hydrogen, etc., of which the substance may be composed are joined together by virtue of their affinity units. How much has been accomplished on the basis of these ideas during the past forty-six years, and how beautifully and simply all the facts known with regard to the almost countless carbon compounds are thus explained, only those can fully appreciate who have a detailed knowledge of the subject. Notwithstanding the large number of workers in the field, it has often required more than a decade of work to determine the molecular architecture of one single carbon compound, and the question at times seriously presents itself whether we must not reach our limitations in this respect. In any case one point is deserving of especial emphasis: this idea of structure which has been applied chiefly to molecules containing the element carbon attributes to them a rigidity which is improbable from a purely dynamic standpoint.

The present system of organic chemistry is thus founded upon the assumption that the valence of all the atoms of carbon, wherever found, remains invariably four. In the earlier part of the last century many attempts were made to isolate the hydrocarbon methylene, $C=H_2$, which must contain bivalent carbon. Dumas and Peligot tried to obtain this substance from methylalcohol,  $H_2C\begin{array}{l}\diagup H\\ \diagdown OH\end{array}$ by loss of water. Perrot tried to isolate it from methylchloride,  $H_2C\begin{array}{l}\diagup H\\ \diagdown Cl\end{array}$ by dissociation into methylene and hydrogen chloride at high temperature. Berthelot, Butlerow, Wurtz, and Kolbe also made many fruitless attempts in this direction. As a final result of these repeated and negative efforts, chemists finally became convinced that compounds containing bivalent carbon could not be isolated, and the conclusion, therefore, that carbon was one of the few elements possessing a constant valence became very general.

There has, however, long existed one very simple compound of carbon which does not adjust itself to this system, — namely, the inactive and poisonous carbon monoxide. If we assume the valence of oxygen as two, then we have here simply a derivative of methylene in which the two hydrogen atoms are substituted by oxygen, $C=O$.

To be sure there were many chemists who preferred to consider the valence of carbon in carbon monoxide as four, thus making the valence of oxygen four, $C \equiv O$; and when we bear in mind that the other members of the oxygen group, sulphur selenium and tellurium, exist as di-, tetra-, and hexavalent atoms, there is some justification for this interpretation. To me personally, however, it seems in the highest degree improbable that two atoms should be thus bound to each other by four affinity units.

About fourteen years ago a series of systematic experiments was undertaken with the object of ascertaining whether carbon can exist in a bivalent condition. The experiments have established this point in a most decisive manner; we have now quite an array of substances which contain bivalent carbon. Furthermore it has been possible to prove, from the experience gained in their study, that methylene chemistry plays an important rôle in many of the simplest reactions of organic chemistry, reactions which have hitherto been explained on the basis of substitution. At the time when these experiments were undertaken there existed besides carbon monoxide several substances which might contain bivalent carbon — namely, prussic acid and its salts the cyanides, $HN=C$ and $MN=C$. Also the so-called carbylamines, $RN=C$, discovered in 1866 by Gautier.

These substances were, therefore, exhaustively studied in order to establish rigidly by experiment whether bivalent carbon was present or absent. The presence of dyad carbon having been established and its properties thus being known, the problem then presenting itself was the isolation of methylene and its homologues.

You are probably all aware that Gay Lussac established in 1815 the existence of a radical, composed of one atom of carbon and one of nitrogen, in prussic acid and the cyanides. This radical, cyanogen, plays in its compounds a rôle similar to that of the elements of the halogen group.

In 1832 Pelouse discovered the alkylcyanides, $R-C\equiv N$, by treating cyanide of potash with alkyliodides or with alkylpotassic sulphates, $KCN + RI$ or $ROSO_2OK \rightarrow R-C\equiv N + KI$ or $KOSO_2OK$, an apparent double decomposition reaction by which we obtain a compound in which the radical $R(=Cn\ H_{2n+1})$ is joined to the cyanogen group by means of carbon. The alkylcyanides thus obtained are neutral, pleasant-smelling, harmless liquids, resembling ether, chloroform, and the alkylhalides, RCl, RBr, and RI.

In 1866 Gautier discovered by treating cyanide of silver with alkyliodides, $RI + AgNC \rightarrow RN=C + AgI$, also an apparent double decomposition reaction, a new class of organic compounds; they are isomeric, not identical, with the alkylcyanides of Pelouse. He called them the carbylamines or isonitriles, and proved that the alkyl group is bound to the cyanogen radical by means of nitrogen $RN=C$ or

$RN ≣ C$. It thus became evident that we must distinguish between two cyanogen radicals, viz., one which in its compounds is bound to alkyl, hydrogen, or metal by means of carbon, $R-C\equiv N$, $H-C\equiv N$, $MC\equiv N$, and another which is joined to these elements or groups by means of nitrogen, $RN=C$, $HN=C$, $MN=C$. We may call the former radical cyanogen, $-C\equiv N$, and the latter isocyanogen,

$$-N=C \text{ or } -N ≣ C;$$

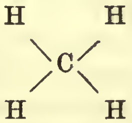
these radicals may obviously combine with each other to form three isomers of the empyrical formula C_2N_2. The substances discovered by Gautier, the alkylisocyanides, $R-N=C$ or $R-N ≣ C$, have properties strikingly different from those of their isomers, the alkylcyanides, $R-C\equiv N$, of Pelouse. They are poisonous, nauseating compounds which affect the throat like prussic acid and color the blood intensely red; they produce violent headaches and vomiting. Their odor is most pronounced and persistent. Hofmann, who, in 1868, discovered another method for making them from primary amines, chloroform, and caustic potash,

$$RNH_2 + 3KOH + CHCl_3 \rightarrow RN=C + 3KCl + 3H_2O,$$

found it impossible to work with them except for very short periods.

An exhaustive study of the reactions of these alkylisocyanides, carried out in 1891–92, led to the definite conclusion that they contain a dyad carbon atom, *i.e.*, they possess the constitution represented by the formula $RN:C$; the other possible formula with quadrivalent carbon and quinquivalent nitrogen, $RN ≣ C$, is excluded by the facts.

The alkylisocyanides belong to the vast category of unsaturated compounds whose chemistry will be briefly discussed from a perfectly general standpoint below; they manifest especially their great chemical activity by absorbing other substances forming new molecules in which the valence of carbon has changed from two to four. Such reactions we call additive. Two molecules simply unite to form one new molecule — the addition product. A molecule containing an unsaturated carbon atom, *i.e.*, one with two of its valences latent or polarized, $RN=C$ or $RN=C]$, cannot *per se* show any chemical activity whatever. This is also true of a system containing a pair of doubly or triply bound carbon atoms, ethylene, $CH_2=CH_2$, and acetylene, $CH\equiv CH$; and finally of a saturated system which we may represent by a paraffine, $C_nH_{2n}+2$, for instance, marsh gas,

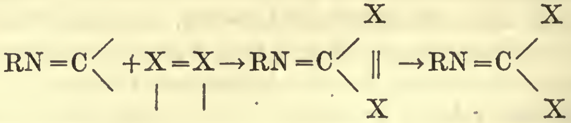


All these substances manifest chemical activity simply because they are to a greater or less degree in a dissociated or what may be called an active condition. A given quantity of alkylisocyanide contains an extremely small per cent of molecules with two free affinity units,

$RN=C\langle$; these are in dynamic equilibrium with the absolutely inert molecules $RN=C$ or better $RN=C]$. That this percentage varies with the nature and mass of R is shown by the fact that various alkylated and arylated isocyanides manifest different degrees of chemical activity. Carbon monoxide possesses relatively a smaller number of such active particles, $O=C\langle$, and consequently is a comparatively inert substance, since the speed of addition reactions shown by unsaturated compounds must naturally be directly in proportion to the per cent of active molecules present. A similar conception obviously explains the relative differences in reactivity shown by the various members of the olefine and acetylene series. Marsh gas, a saturated system, reacts with other substances because it is partially dissociated as follows, $CH_4 \rightleftarrows CH_3- + H-$ and $\rangle CH_2 + 2H-$. From this point of view chemical action depends entirely upon dissociation processes. The reactions often proceed with very great slowness because the percentage of dissociation is extremely low, possibly one tenth to one thousandth of one per cent, or even less.

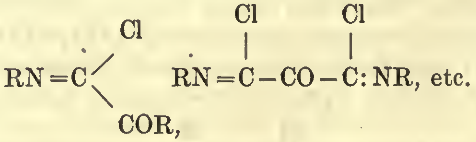
Turning now to a consideration of the reactions of alkylisocyanides; the substances which are absorbed by the unsaturated carbon atom present in the isonitriles are the following.

(1) *Halogens* [(chlorine, bromine, iodine); speed of reaction in the order named].



The reactions, especially those with chlorine and bromine, take place with great evolution of heat at −20°.

(2) *Acidchlorides*, such as $RCO-Cl$, $Cl-OC_2H_5$, $Cl-CO-Cl$, $Cl-CN$, $Cl-COOR$, to form the addition products:

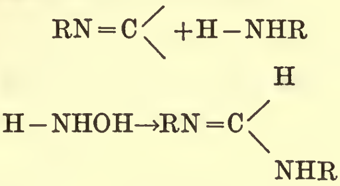


A hyphen denotes the point where the compounds are partially dissociated and consequently absorbed. These reactions, especially those with phosgene and ethylhypochlorite, take place with great violence at −20°.

(3) *Oxygen and sulphur*, to form isocyanates and mustard oils, $RN=C=O$ and $RN=C=S$. Methylisocyanide unites directly at its boiling-point, 58°, with the oxygen of the air. The dry oxides

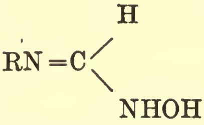
of silver and mercury are reduced to metals with violence at 40°, alkylisocyanates being first formed. This shows the great affinity of bivalent carbon for oxygen.

(4) *Primary amines and hydroxylamine,*



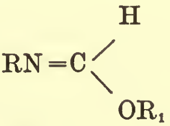
or

or

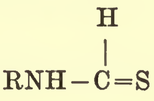


giving amidines or oxyamidines.

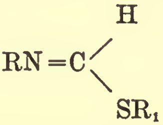
(5) *Alcohols* in the presence of an alkali are absorbed, giving imido ethers,



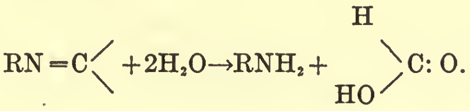
(6) *Hydrogen sulphide and mercaptans* give readily at 100° the addition products



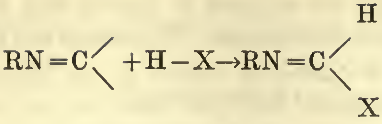
and



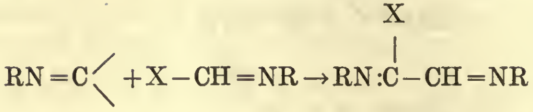
(7) *Acids.* Aqueous mineral acids act with great violence on the isonitriles giving primary amines and formic acid:



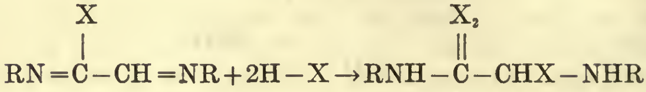
In the absence of water and on diluting the alkylisocyanides with absolute ether, perfectly dry halogen hydride causes the separation of white hygroscopic salt-like substances of the empyrical formula 2RNC, 3HX[X = Cl Br or I]. For this reason Gautier as well as Hofmann supposed the isonitriles to be basic compounds, *i. e.*, substances behaving like ammonia — hence the name carbylamine was given them by Gautier. Further study has shown, however, that this conclusion was erroneous. The isonitriles are entirely devoid of basic properties; the great violence with which they act with halogen hydrides is due to the presence of unsaturated carbon. The reaction probably takes place as follows:



$$RN{=}C\langle + H{-}X \rightarrow RN{=}C\overset{H}{\underset{X}{\langle}} \qquad (1)$$



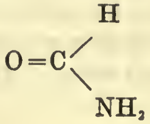
$$RN{=}C\langle + X{-}CH{=}NR \rightarrow RN{:}\overset{X}{\overset{|}{C}}{-}CH{=}NR \qquad (2)$$

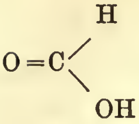


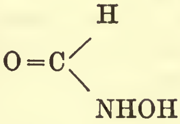
$$RN{=}\overset{X}{\overset{|}{C}}{-}CH{=}NR + 2H{-}X \rightarrow RNH{-}\overset{X_2}{\overset{||}{C}}{-}CHX{-}NHR \qquad (3)$$

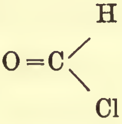
Reversibility of the reactions. The most striking property of the addition products of the isonitriles, $RN{=}C\overset{X}{\underset{Y}{\langle}}$ is their low point of dissociation, *i. e.*, the carbon atom which has absorbed the X – Y, thus becoming quadrivalent, is unable to hold XY above certain temperature limits. There is consequently in every case a temperature, varying with the nature and mass of X and Y as well as with the nature and mass of the groups bound to the other two affinity units of carbon, at which the carbon atom becomes spontaneously dyad and is unable to remain in a quadrivalent condition; it was subsequently possible to prove that this is a perfectly general property of this atom. All the addition products under discussion are partially dissociated, the dissociation $RN{=}C\overset{X}{\underset{Y}{\langle}} \rightleftarrows RN{:}C{<}+XY$, increasing as the temperature is raised, — in other words the valence of carbon at temperatures below the dissociation-point is an equilibrium phenomenon; dynamic equilibrium exists between bivalent and quadrivalent carbon.

The point of complete dissociation of the various addition products of the isonitriles has not been accurately determined in every case. The following data with reference to the dissociation-points of carbon monoxide addition products are of interest and therefore used for illustration in this connection:

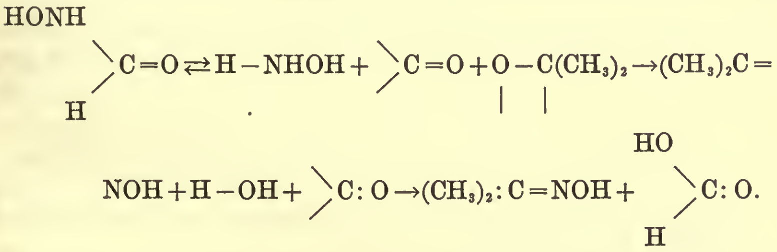
	Dissociation-Point
Formaldehyde, $O{:}C{=}H_2$	600°
Formamide,  $O{=}C\overset{H}{\underset{NH_2}{\langle}}$	about 250°

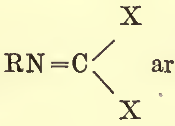
Formic acid,  169°

Formhydroxamic acid,  85°

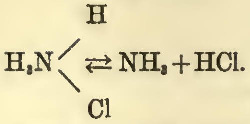
Formylchloride,  below —20°

Since these substances containing quadrivalent carbon decompose spontaneously into carbon monoxide, *i. e.*, cannot exist in the quadrivalent condition at temperatures above those indicated, it is self-evident that at lower temperatures the addition products must be partially dissociated and that in the future we must be able to determine in each case with absolute accuracy the per cent of dissociation at any temperature. A striking experiment with formhydroxamic acid, dissociation-point 85°, proves the correctness of this conclusion; on allowing this crystalline substance to stand at 20° in acetone solution the following reaction takes place quantitatively:



In a similar manner we can prove that the isonitrile addition products, many of which have definite boiling-points and are quite stable, are partially dissociated at ordinary temperatures. Thus the addition products with halogen  are all converted back quantitatively into the alkylisocyanides by treatment with finely divided metals, zinc-dust or sodium, which simply abstract the free halogen.

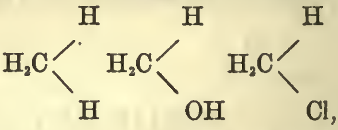
Many of the acylhalide addition products dissociate spontaneously into the components on distillation; these phenomena are perfectly analogous to the dissociation of dry ammonium chloride:



$$H_2N\overset{H}{\underset{Cl}{<}} \rightleftarrows NH_3+HCl.$$

For this reason the majority of the addition products of the isonitriles can be kept only for a short time; this property rendered futile many attempts to isolate definite addition products. The continual dissociation of such products sets free active or dissociated alkylisocyanide particles, and these slowly condense with one another, $xRN=C< \rightarrow (RN=C)x$, giving rise to the so-called alkylisocyanide resins (non-reversible), — products whose molecular weight has not yet been determined and which are perfectly analogous to azulmic or polymerized prussic acid. Consequently in carrying out an addition reaction with an isonitrile, especially if it requires much time or a temperature above 20°, large quantities of these resinous polymers are formed from which it is possible to isolate the addition product only with great difficulty.

Many of the isonitriles themselves even when perfectly pure undergo rapid polymerization to resins so that they can be kept only for a very short time. Phenylisocyanide, $C_6H_5N=C]$, is the most striking instance, as it changes in a few minutes from a colorless to a dark blue liquid, and in a few days condenses to a dark brown resin. Have we not here a possible explanation of the fact that it is impossible to isolate methylene and a large number of its derivatives, although marsh gas, methyl alcohol, and chloride of methyl,



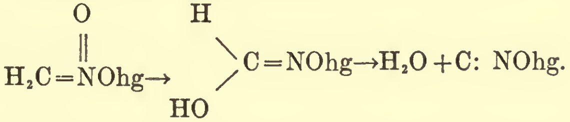
$$H_2C\overset{H}{\underset{H}{<}} \quad H_2C\overset{H}{\underset{OH}{<}} \quad H_2C\overset{H}{\underset{Cl}{<}},$$

all contain a relatively small per cent of active methylene particles at ordinary temperatures?

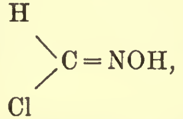
The presence of bivalent carbon in the alkylisocyanides having been established, the next question presenting itself was whether prussic acid and its salts contain the cyanogen or the isocyanogen radical. In the latter case, $H-N=C$, $M-N=C$, these substances must be analogous to Gautier's isonitriles. It had hitherto been considered as established, but without sufficient evidence, that prussic acid and the cyanides were cyanogen compounds analogous to the nitriles of Pelouse.

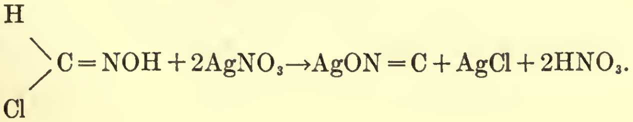
When one considers the physical and physiological properties of prussic acid [boiling-point 25°, specific gravity 0.7, a violent poison] and contrasts these with the corresponding properties of methylcyanide [boiling-point 81°, specific gravity 0.81, sweet-smelling harmless oil] and of methylisocyanide [boiling-point 58°, specific gravity 0.75, a poison], one at once comes to the conclusion that prussic acid as well as its salts must belong to the isocyanogen compounds and consequently must contain bivalent carbon. An exhaustive study of prussic acid and the cyanides establishes this sharply, especially in the case of the salts, from a chemical standpoint. The relation of fulminic acid to prussic acid corroborates the evidence.

You are all familiar with fulminate of mercury — a substance which is made on a commercial scale and used for explosives. It was discovered in 1800 by Howard, and analyzed in 1824 by Liebig in Gay Lussac's laboratory. We obtain it by dissolving mercury in concentrated nitric acid and adding the resulting solution to ordinary alcohol. It has the empyrical formula $HgC_2N_2O_2$, and being obtained from ethylalcohol, CH_3CH_2-OH, fulminic acid was supposed to have two carbon atoms in its molecule, $H_2C_2N_2O_2$. The constitution of this substance was for a long time a great puzzle to chemists. That we have here a substance very closely related to prussic acid was discovered by accident. In working with the mercury salt of isonitromethane it was found that this compound is spontaneously converted at 0° into fulminate of mercury according to the equation,



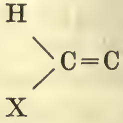
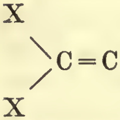
$$H_2C=\overset{\overset{O}{\|}}{N}Ohg \rightarrow \begin{matrix} H \diagdown \\ \\ HO \diagup \end{matrix} C=NOhg \rightarrow H_2O + C\colon NOhg.$$

This synthesis led directly to the conclusion that fulminate of mercury possesses a constitution entirely analogous to cyanide of mercury, $C=Nhg$, *i. e.*, that it contains the isocyanogen radical with bivalent carbon. A further study of the fulminates established this point with precision. Especially striking is the behavior of fulminates towards dilute acids. Liebig and Gay Lussac state in 1824, judging from the odor, that fulminate of silver gives prussic acid with dilute hydrochloric acid. A more careful study of this reaction in 1894 proved that not a trace of prussic acid but a substance formylchloride oxime,  $\begin{matrix} H \diagdown \\ \\ Cl \diagup \end{matrix} C=NOH$, is formed which possesses the following remarkable properties. Long needles, clear as glass, which decompose and explode at 20°; extremely volatile even at 0° and having an odor similar to prussic acid which is obviously due to a partial dissociation into fulminic acid. Aqueous silver nitrate converts it quantitatively into chloride and fulminate of silver,



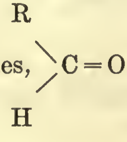
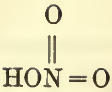
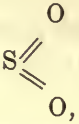
$$\begin{matrix} H \diagdown \\ \\ Cl \diagup \end{matrix} C=NOH + 2AgNO_3 \rightarrow AgON=C + AgCl + 2HNO_3.$$

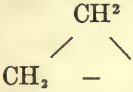
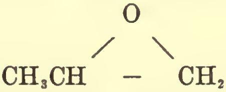
Up to 1897 the presence of bivalent carbon had been established in the following compounds, (1) carbon monoxide, $O=C$; (2) the alkyl and aryl isocyanides, $RN=C$; (3) prussic acid and the cyanides, $HN=C$, $MN=C$; (4) fulminic acid and the fulminates, $HO-N=C$, $MO-N=C$. (2), (3) and (4) are all compounds containing the isocyanogen radical.

In 1897 the presence of bivalent carbon was established in a series of nitrogen free carbon compounds obtained from acetylene. They are the mono-and dihalogen substituted acetylidenes,  $\genfrac{}{}{0pt}{}{H}{X}\!>C=C$ and  $\genfrac{}{}{0pt}{}{X}{X}\!>C=C$ [X = Cl Br or I]. The corresponding members of the acetylene series, $XC\equiv CH$ and $XC\equiv CX$, do not exist, although we have substances like $CH_3C\equiv CI$, $C_6H_5C\equiv C-X$, whose properties are in marked contrast to those of the acetylidene derivatives.

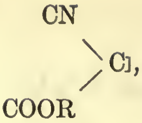
Diiodacetylidene, which possesses an odor deceptively like that of the isonitriles, dissociates at 100° with violence into iodine and diatomic carbon, $I_2=C=C \rightarrow I_2+C=C$; the latter cannot be isolated as such, but polymerizes explosively to graphite and amorphous carbon. The mono- and dihalogen substituted acetylidenes are all poisonous and spontaneously combustible compounds, possessing, therefore, like methylisocyanide a marked affinity for oxygen Up to the present time it has not been possible to isolate compounds containing bivalent carbon other than those mentioned above. We are, however, now in a position to explain clearly why we cannot hope by methods now known to isolate methylene and its homologues as such, although these substances play a great rôle in many of the fundamental reactions of organic chemistry. In order to approach this point more intelligently, let us consider briefly the properties of unsaturated compounds in general, their possibility of existence, etc.

II. *On the Unsaturated Compounds*

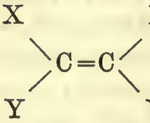
The unsaturated compounds may, first of all, be divided into three categories, namely; (1) those in which two atoms, which may be the same or different, are bound doubly or triply to each other by two or three affinity units, such as olefines, acetylenes, chlorine, $Cl\equiv Cl$, oxygen, $O=O$, aldelhydes,  $\genfrac{}{}{0pt}{}{R}{H}\!>C=O$, alkylcyanides, $RC\equiv N$, nitric acid,  $HO\overset{\overset{\displaystyle O}{\|}}{N}=O$, sulphur trioxide,  etc.; (2), those in which an atom itself is unsaturated, *i. e.*, does not exert its maximum valence capacity, as, for instance, amines, R_3N, thioethers, $R_2=S$], methylene derivatives, etc. We must assume that the remaining affinity units are latent, or, what is far more probable, especially where two or four affinity units are available, that they mutually polarize each other in a manner entirely similar to unsaturated compounds containing doubly or triply linked atoms.

Finally we have a third class of unsaturated compounds, (3) those containing closed atomic chains such as trimethylene,  propyleneoxide,  etc., which show apparently a saturated molecular system like the paraffines, and yet react in a manner perfectly analogous to olefines and methylene derivatives. Fundamentally considered, these three classes of unsaturated compounds manifest their chemical activity in the same way; they absorb a great variety of other molecules and thus form combinations, called addition products. How does this union take place? An unsaturated compound with its affinities polarized represents in reality a saturated system; it cannot *per se* show chemical activity. This is also true of molecular systems in which the atoms are bound to one another by single affinity units. The sole basis for reactivity in either case is the presence of a relatively greater or smaller number of dissociated particles. The reactivity of any unsaturated, as well as of a saturated compound, must in fact be directly proportional to the ratio of such active particles present. If that ratio is very small, the substance may be entirely inert; if it is greater, absorption of reagents proceeds with regularly increasing speed.

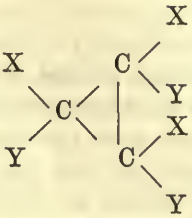
Experience has shown, furthermore, that many unsaturated compounds cannot be isolated, but polymerize spontaneously. It is clear that when the per cent of active particles present in an unsaturated compound becomes relatively great, the possibility of their uniting with each other to form condensed molecules increases — in fact, we may imagine a condition in which the active molecules simply cannot be prevented from combining with each other. This shows us why we cannot isolate and keep substances like formaldehyde, $H_2C=O$, or alkylcyanates, $R-O-C\equiv N$, in the monomolecular form. Similarly in many cases where attempts were made to isolate methylene derivatives like mono- and diphenyl methylene, benzoyl and acetyl methylene, cyanmethylene-carboxylate,



, a spontaneous polymerization to the di- or tri-molecular systems,



or

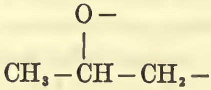


took place.

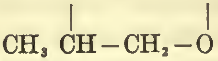
One further point with reference to unsaturated compounds must now be presented.

Intramolecular Rearrangements shown by Unsaturated Systems

From the discussion presented above it is obvious that trimethylene and propyleneoxide, belonging to class 3, must contain a small percentage of active particles; the dissociation of the triatomic ring in the former case can lead to only one form of active molecule, namely, $-CH_2-CH_2-CH_2-$; whereas propyleneoxide may give the following three active molecules:

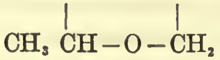


$$CH_3-\overset{\overset{\textstyle O-}{|}}{CH}-CH_2- \qquad (A);$$



$$CH_3\,\overset{|}{C}H-CH_2-\overset{|}{O} \qquad (B);$$

and



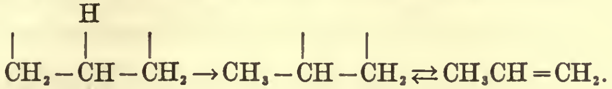
$$CH_3\,\overset{|}{C}H-O-\overset{|}{C}H_2 \qquad (C).$$

Since propyleneoxide absorbs dry ammonia or hydrogen chloride, as was proved by especially careful and exhaustive experiments, giving addition products of the general formula

$$CH_3\,CHOH-CH_2\,X\ [X=Cl \text{ or } NH_2],$$

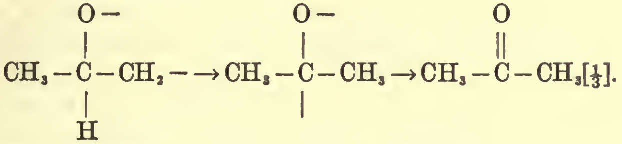
the only possible conclusion that can be reached is that propyleneoxide contains relatively more active *A* than active *B* or *C* molecules; consequently the absorption reactions proceed by preference in *only one* of three theoretically possible directions.

When trimethylene or propyleneoxide is heated or placed in contact with various catalytic agents, the per cent of active particles must naturally increase, and when a definite limit has been reached a spontaneous transformation of trimethylene into propylene and of propyleneoxide into propylaldehyde ($\frac{2}{3}$) and acetone ($\frac{1}{3}$) takes place; both reactions are non-reversible. These results can only be explained in the following manner: aside from the increase in active particles dissociation in other parts of the molecule and especially of hydrogen from carbon must also take place. Consequently the following intramolecular addition reactions finally occur spontaneously:



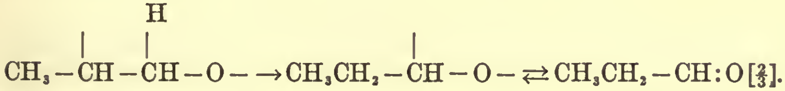
$$\overset{|}{C}H_2-\overset{\overset{H}{|}}{C}H-\overset{|}{C}H_2\rightarrow CH_3-\overset{|}{C}H-\overset{|}{C}H_2\rightleftarrows CH_3CH=CH_2.$$

active trimethylene particles — propylene



$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{O-}{|}}{C}}-CH_2-\rightarrow CH_3-\underset{|}{\overset{\overset{O-}{|}}{C}}-CH_3\rightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_3[\tfrac{1}{3}].$$

active propyleneoxide particles [*A*] — acetone

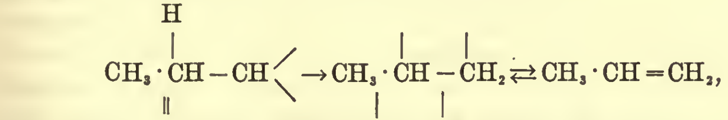


$$CH_3-\overset{|}{C}H-\overset{\overset{H}{|}}{C}H-O-\rightarrow CH_3CH_2-\overset{|}{C}H-O-\rightleftarrows CH_3CH_2-CH:O[\tfrac{2}{3}].$$

active propyleneoxide particles [*B*] — propionaldehyde.

It is interesting to note that the active *B* propyleneoxide molecules which are present in smaller ratio suffer rearrangement more readily than the active *A* molecules. The active *C* molecules, on the other hand, must be present in far smaller amount and certainly no transformation of propyleneoxide to vinylmethyloxide, $CH_2=CH-O-CH_3$, takes place. It is important to realize that propyleneoxide, acetone and propionaldehyde are isomers but do not stand in a tautomeric relation to one another. This is also true of trimethylene and propylene as well as of α and β amylene and isoamylene, etc.

Similarly it can be rigidly shown by experiment that α and β propylidene, $CH_3CH_2-CH=$ and $(CH_3)_2=C\langle$, which are spontaneously combustible substances not capable of isolation as such, transform themselves by intramolecular addition,



$$CH_3\cdot\overset{\overset{H}{|}}{C}H-CH\langle\rightarrow CH_3\cdot\overset{|}{C}H-\overset{|}{C}H_2\rightleftarrows CH_3\cdot CH=CH_2,$$

$$\text{and}\quad CH_3\quad \overset{\|}{C}-CH_2-H\rightarrow CH_3\overset{|}{C}H-\overset{|}{C}H_2\rightleftarrows CH_3\cdot CH=CH_2,$$

into propylene [non-reversible].

There is not the slightest doubt that such intramolecular addition reactions are the basis of the majority of our synthetic methods for making cyclic compounds. The cycloparaffines in Russian petroleum are probably formed from ordinary paraffines by dissociation into hydrogen and methylene derivatives, and the latter then spontaneously transform themselves, by intramolecular addition, into penta- and hexamethylene rings.

On the Reactions of the Paraffines and the Benzene Derivatives

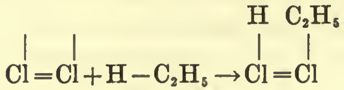
The reactions of the paraffines and the benzene derivatives towards halogens, nitric and sulphuric acids, whereby substitution products are formed, are still interpreted in the text-books from the standpoint of metalepsis or substitution, although a vast amount of evidence has accumulated which makes this axiomatic assumption improbable. The fact that ethane and benzene, for instance, decompose into hydrogen and into ethylene and diphenyl at 800° and 600° respectively proves that an extremely small per cent of these molecules must exist at ordinary temperatures in an active or dissociated condition,

$$CH_3CH_3 \rightleftarrows CH_3CH_2- + H-$$

and $$CH_3CH= + 2H- ;\ \text{or}\ C_6H_6 \rightleftarrows C_6H_5- + H-.$$

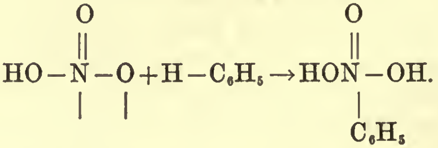
The same is true of ammonia, $H_3N \rightleftarrows H_2N- + H-$ and $HN= + 2H-$ and $N\equiv + 3H$, and of a great variety of other non-ionizable hydrogen compounds.

Consequently when chlorine or nitric acid acts with benzene or ethane to give the monochlor or mononitro substitution products, we have these reagents, in the *active molecular* condition, simply uniting by addition with the dissociated ethane or benzene particles,



$$\overset{|}{Cl}=\overset{|}{Cl} + H-C_2H_5 \rightarrow \overset{\overset{H}{|}}{Cl}=\overset{\overset{C_2H_5}{|}}{Cl}$$

or



$$HO-\underset{|}{\overset{\overset{O}{\|}}{N}}-\underset{|}{O} + H-C_6H_5 \rightarrow HO\underset{\underset{C_6H_5}{|}}{\overset{\overset{O}{\|}}{N}}-OH.$$

The resulting addition products then lose hydrogen chloride and water respectively and thus give the monochlor or nitro substitution product of the mother substance. From this point of view all so-called substitution reactions belong to the category of addition reactions. What is now especially needed in order to place the reactions of organic chemistry on an exact mathematical basis is a precise method of determining the ratio of active particles present at various temperatures in the case of the unsaturated as well as of saturated compounds. As the substances under discussion are almost exclusively non-electrolytes, the sole methods that suggest themselves for this purpose are determinations of the speed of decomposition as well as of addition reactions.

The above discussion makes it evident that all unsaturated compounds belonging to classes 1 and 3 contain a small and relatively varying per cent of active particles with one or more carbon atoms temporarily in an active or *trivalent* condition; the same is true of compounds containing hydrogen bound to carbon-paraffines, $C_nH_{2n+1}-H$, benzene derivatives, etc. The isolation of compounds containing trivalent carbon as such, I believe, however, to be an impossibility. Gomberg's triphenylmethyl, for instance, has recently been proved by him and others to be a bimolecular aggregate $C_{38}H_{30}$, — identical with hexaphenylethane — which, however, like the above-mentioned compounds, contains a very small percentage of active triphenylmethyl, $(C_6H_5)_3\equiv C-$, particles in dynamic equilibrium with the bimolecular aggregate.

We are now in a position to consider the evidence showing that methylene and its homologues play a great rôle in many of the fundamental reactions of organic chemistry which have hitherto been explained on the basis of substitution.

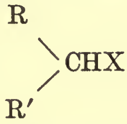
III. *On the Reactions of the Monatomic Alcohols and the Alkylhaloids*

The experiments which first suggest themselves as a means of isolating methylene and its homologues are, (1) dissociation of olefines as ethylene:

$$CH_2=CH_2 \rightleftarrows 2H_2C=,\ \beta \text{ butylene,}$$

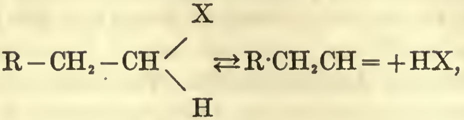
$$CH_3CH\colon CH{\cdot}CH_3 \rightleftarrows 2CH_3CH\langle,\ \text{etc.}$$

Since ethylene gives hydrogen and acetylene by heat and the higher olefines also decompose with evolution of hydrogen, there was little prospect of success by experiments in this direction. (2) Dehydration of the monatomic alcohols, $C_nH_{2n+1}OH$, or removal of halogen hydride from the alkylhalides, $C_nH_{2n+1}X$; naturally only primary and secondary derivatives, RCH_2X and



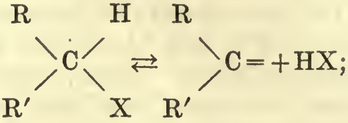
$\begin{matrix}R\\ \\ R'\end{matrix}\!\!>\!CHX$ [X = OH Cl Br or I],

and not tertiary compounds, $R_3\equiv C-X$, can yield methylene and its homologues. Furthermore since many of the alcohols and alkylhalides containing more than one carbon atom in the molecule are known to give olefines by dissociation, dehydration, or treatment with alcoholic potash respectively, the conclusion might naturally at first be drawn that only a direct olefine dissociation existed in these cases. From a purely theoretical standpoint, however, it is clear that a primary or secondary alkylhalide or a corresponding alcohol with more than one carbon atom in the molecule may dissociate with loss of halogen hydride or water in two possible ways: it may undergo (1) methylene dissociation, as



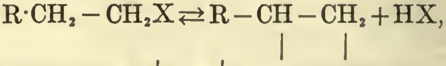
$$R-CH_2-CH\begin{matrix}\diagup X\\ \diagdown H\end{matrix} \rightleftarrows R\cdot CH_2CH= + HX,$$

and



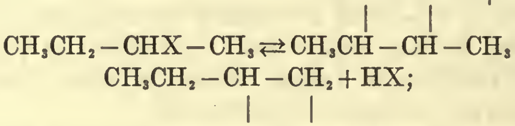
$$\begin{matrix}R\diagdown\\ R'\diagup\end{matrix}C\begin{matrix}\diagup H\\ \diagdown X\end{matrix} \rightleftarrows \begin{matrix}R\diagdown\\ R'\diagup\end{matrix}C= + HX;$$

or (2) olefine dissociation, as



$$R\cdot CH_2-CH_2X \rightleftarrows R-\underset{|}{CH}-\underset{|}{CH_2}+HX,$$

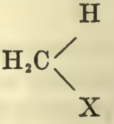
and
and



$$CH_3CH_2-CHX-CH_3 \rightleftarrows CH_3\overset{|}{CH}-\overset{|}{CH}-CH_3$$
$$CH_3CH_2-\underset{|}{CH}-\underset{|}{CH_2}+HX;$$

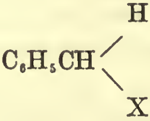
or both kinds of dissociation may take place simultaneously. A third kind of dissociation, where the hydrogen atom does not come from the atom containing the X or from a carbon atom adjacent to it, is also possible, and at times important, but it need not be considered in this connection.

An exhaustive study of the primary and secondary alcohols and alkylhalides covering a period of nine years has proved very conclusively that these substances undergo methylene dissociation only. Preliminary experiments with alcohols and alkylhalides where no olefine dissociation is possible, *i. e.*, in the methane,

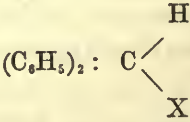


$H_2C\begin{matrix}\diagup H\\ \diagdown X\end{matrix}$

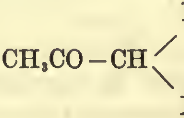
toluene,



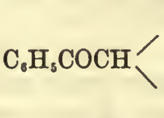
$C_6H_5CH\begin{matrix}\diagup H\\ \diagdown X\end{matrix}$, diphenylmethane



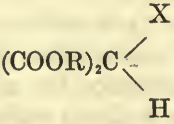
$(C_6H_5)_2:C\begin{matrix}\diagup H\\ \diagdown X\end{matrix}$, acetone and acetophenone,



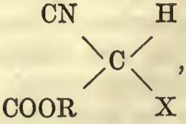
$CH_3CO-CH\begin{matrix}\diagup H\\ \diagdown X\end{matrix}$ and

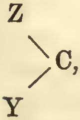
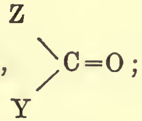


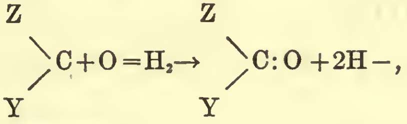
$C_6H_5COCH\begin{matrix}\diagup H\\ \diagdown X\end{matrix}$, malonic and cyanacetic ether series



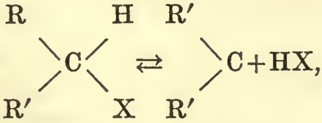
$(COOR)_2C\begin{matrix}\diagup X\\ \diagdown H\end{matrix}$ and

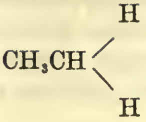
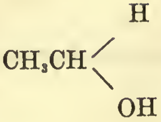
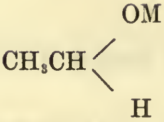
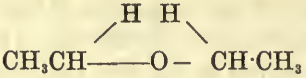
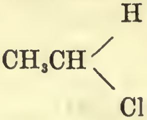
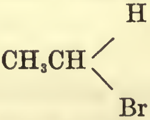
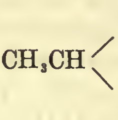
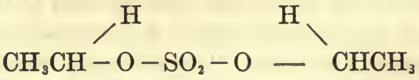
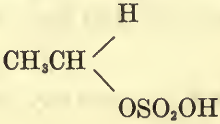
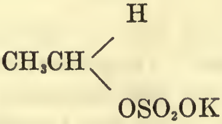
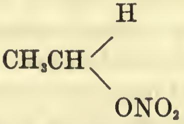


$\begin{matrix}CN\diagdown\\ COOR\diagup\end{matrix}C\begin{matrix}\diagup H\\ \diagdown X\end{matrix}$, have proved that all these compounds have very low dissociation-points — never over 300° in the aromatic nor with few exceptions in the aliphatic series. Nevertheless, it was found impossible to isolate in any case the methylene derivative as such; there was either a spontaneous conversion to a di- or trimolecular polymer, an olefine or a trimethylene derivative, or a conversion to resinous polymers analogous to azulmic acid and the alkylisocyanide resins. Most important was the discovery that these nascent or active methylene residues, , are always spontaneously combustible, burning often with marvelous evolution of heat to the corresponding oxides, ; this was not surprising in view of the properties of the methylene derivatives described above. Furthermore, the affinity of unsaturated carbon for oxygen is strikingly shown by the fact that these residues have the power of decomposing water,

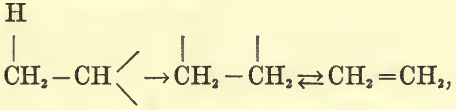


with evolution of hydrogen.

A subsequent investigation of the primary and secondary alcohols and alkylhalides containing more than one carbon atom proved, first of all, that all these substances have comparatively low points of dissociation. In no case was the decomposition-point found to be higher than 700°; it was often as low as 160° to 300°. The products of dissociation are water or halogen hydride and C_nH_{2n} respectively; and the latter, as emphasized above, is invariably methylene or a homologue and never an olefine. This naturally means that all these compounds are partially dissociated in this way at ordinary temperatures, , — relatively more the lower the actual decomposition-point. It is, therefore, possible that in all the interactions of the primary and secondary alkylhalides with other substances, such as salts, ammonia, metals, benzene, etc., they do not act as such, but by virtue of being partially dissociated. An enormous amount of evidence has accumulated in favor of this conclusion. Let us consider chiefly the results obtained in the ethyl series including ethyl alcohol and its derivatives. The dissociation or decomposition-point of the following compounds containing ethyl has been determined with a fair degree of accuracy.

		Decomposition-Point
Ethane,	 $CH_3CH{<}^{H}_{H}$	800°
Ethylalcohol,	 $CH_3CH{<}^{H}_{OH}$	650°
Sodium and potassium ethylate,	 $CH_3CH{<}^{OM}_{H}$	250°
Ethylether,	 $CH_3\overset{H}{C}H-O-\overset{H}{C}H\cdot CH_3$	550°
Ethylchloride,	 $CH_3CH{<}^{H}_{Cl}$	600°
Ethylbromide,	 $CH_3CH{<}^{H}_{Br}$	500°
Ethyliodide,	 $CH_3CH{<}^{H}_{I}$	400°(?)
Diethylsulphate,	 $CH_3\overset{H}{C}H-O-SO_2-O-\overset{H}{C}HCH_3$	200°
Monoethylsulphate,	 $CH_3CH{<}^{H}_{OSO_2OH}$	160°
Ethylpotassium sulphate,	 $CH_3CH{<}^{H}_{OSO_2OK}$	250°
Ethylnitrate,	 $CH_3CH{<}^{H}_{ONO_2}$	200°(?)

Ethane, ethylchloride and bromide, when heated to the temperatures named, give ethylene and hydrogen or halogen hydride respectively, and on cooling these products do not again recombine. We can therefore obtain ethylene quantitatively from chloride or bromide of ethyl by simply passing their vapors through tubes heated to the decomposition-point. Nevertheless, it is impossible to obtain more than very small amounts of ethylene from the ethylhalides by means of alcoholic potash, caustic potash, or quicklime; in these cases ethylether or ethylalcohol is the chief product even when the ethylhalide is passed over quicklime in tubes heated from 300° to 500°. Furthermore, the per cent of ethylene obtained varies remarkably with the temperature, the concentration, and with the nature of the halogen in the alkylhalide used. The conclusions finally reached from these data and also from an exhaustive study of the behavior of the various alkylhalides, nitrates, sulphates, alkylpotassium-sulphates towards heat, sodium ethylate, caustic potash, quicklime, and other salts, are that ethylene cannot possibly be a primary product of dissociation of the ethylhalides, sulphates and nitrates and of free ethylalcohol. The ethylene, when obtained, is formed from ethylidene by an intramolecular addition reaction,

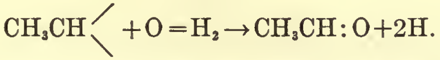


$$\overset{\overset{\textstyle H}{|}}{CH_2}-CH\langle \rightarrow \overset{|}{CH_2}-\overset{|}{CH_2} \rightleftarrows CH_2=CH_2,$$

which is not reversible.

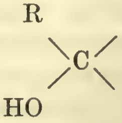
A similar intramolecular change always, in fact, takes place whenever an olefine is formed, whether from a primary or secondary alcohol or from a corresponding alkylhalide sulphate or nitrate. This transformation is perfectly analogous to the conversion, discussed above, of trimethylene and of propylene oxide into propylene, propionaldehyde and acetone.

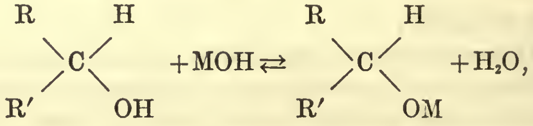
When ethylalcohol or ethylether is heated to its dissociation-point the ethylidene interacts at once in great part with the other dissociation-product, water, to give hydrogen and acetaldehyde,



$$CH_3CH\langle + O=H_2 \rightarrow CH_3CH:O+2H.$$

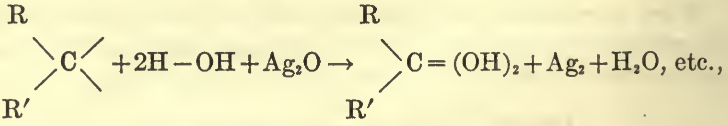
In the case of ether, since there are two ethylidene molecules to one of water, the atomic hydrogen is in part absorbed by ethylidene to give ethane. Finally, a portion of the ethylidene, 20 and 37 per cent respectively, is transformed, by intramolecular addition, into ethylene. The most striking proof that ether is dissociated into water and two C_2H_4 particles is the following: on passing ether vapor over phosphorous pentoxide at temperatures varying from 200° to 400° ethylene is formed quantitatively.

The primary and secondary alcohols and their corresponding ethers being in a state of very slight dissociation at ordinary temperatures, we are able to understand perfectly their behavior towards oxidizing agents. The alkylidenes are all spontaneously combustible substances possessing a great affinity for oxygen. Absolutely pure, dry ethylether, dissociation-point 550°, contains a sufficient per cent of ethylidene particles at ordinary temperatures to burn very slowly in dry oxygen; sodium ethylate, dissociation-point 250°, on the other hand, being dissociated to a far greater extent, burns with great violence in dry air. Ethylalcohol, dissociation-point 650°, is not capable of burning in the air; if, however, we increase the per cent of ethylidene particles by means of catalytic agents, enzymes, platinum sponge, etc., it, too, oxidizes readily, with incandescence with platinum sponge, giving acetic acid. The aldehydes, $RCH=O$, as has long been known, reduce Fehling's solution and silver solutions with great ease. This is due to the presence of oxyalkylidene particles,  $\overset{R}{\underset{HO}{>}}C<$ which burn at the expense of the oxygen of the water. The discovery that all primary and secondary alcohols reduce silver oxide to metallic silver in aqueous solution in the presence of caustic alkalies has only very recently been made. The function of the alkali is obviously to form first the metallic alcoholate,



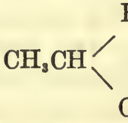
$$\overset{R}{\underset{R'}{>}}C\overset{H}{\underset{OH}{<}} + MOH \rightleftarrows \overset{R}{\underset{R'}{>}}C\overset{H}{\underset{OM}{<}} + H_2O,$$

which, having a far lower dissociation-point than the free alcohol, causes a great increase in the per cent of alkylidene particles present; consequently the following reaction takes place,



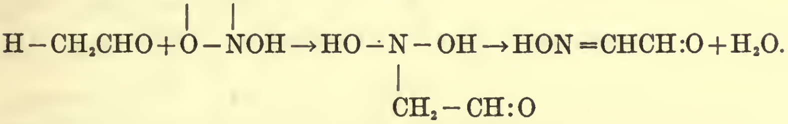
$$\overset{R}{\underset{R'}{>}}C< + 2H-OH + Ag_2O \rightarrow \overset{R}{\underset{R'}{>}}C=(OH)_2 + Ag_2 + H_2O, \text{ etc.},$$

giving as the end result a fatty acid in the case of primary alcohols.

The most striking proof that ethylalcohol is dissociated only into ethylidene and water,  $CH_3CH\overset{H}{\underset{OH}{<}} \rightleftarrows CH_3CH= + H_2O$, *i. e.*, contains no ethylene particles, is the following. Ethylalcohol, containing one molecule of aqueous sodic hydrate, gives in the cold with potassium permanganate solution practically acetic acid only. If any active ethylene particles were present, $CH_3CH_2OH \rightleftarrows \overset{|}{C}H_2 - \overset{|}{C}H_2 + H_2O$, these must necessarily, in view of the work of Wagner with olefines and permanganate, be first converted by oxidation to ethyleneglycol,

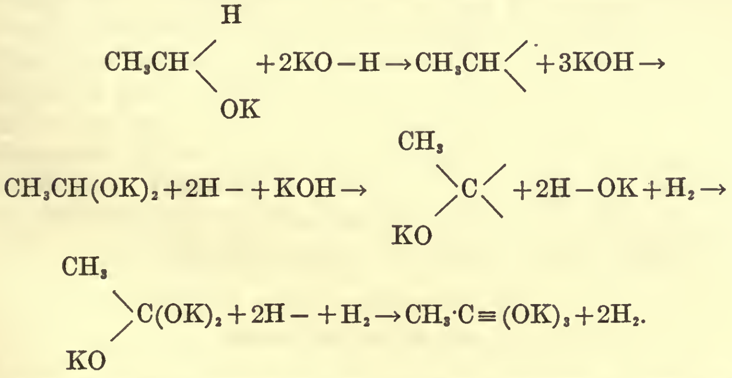
$$3\overset{|}{C}H_2-\overset{|}{C}H_2+6H-OH+2KMnO4\rightarrow OHOH$$
$$3CH_2-CH_2+2MnO_2+2KOH+2H_2O.$$

Analogous results would naturally be expected in the case of all the homologous primary and secondary alcohols. Now a primary alcohol invariably first gives by oxidation with potassium permanganate or other oxidizing agents the corresponding fatty acid; glycols or their oxidation products have never been observed in such cases. The fact that ethylalcohol gives glyoxal, glyoxylic and oxalic acids with nitric acid, is no exception to this rule because these substances result from the hydrolysis and oxidation of isonitrosoacetaldehyde which is formed by the action of nitrous acid on acetaldehyde as follows:



$$H-CH_2CHO+\overset{|}{O}-\overset{|}{N}OH\rightarrow HO-\underset{\substack{|\\ CH_2-CH:O}}{N}-OH\rightarrow HON=CHCH:O+H_2O.$$

The behavior of aldehydes and of primary alcohols towards aqueous or solid caustic potash also leads to the conclusion that only alkylidene dissociation occurs. Ethylalcohol gives at 250°, with an excess of caustic potash, hydrogen and potassium acetate quantitatively,



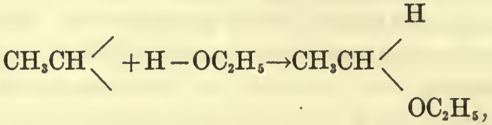
$$CH_3CH{<}^{H}_{OK}\quad+2KO-H\rightarrow CH_3CH{<}\quad+3KOH\rightarrow$$
$$CH_3CH(OK)_2+2H-+KOH\rightarrow {}^{CH_3}_{KO}{>}C{<}\quad+2H-OK+H_2\rightarrow$$
$${}^{CH_3}_{KO}{>}C(OK)_2+2H-\ +H_2\rightarrow CH_3\cdot C\equiv(OK)_3+2H_2.$$

If any of the potassium ethylate, which is first formed, were dissociated into ethylene and caustic potash,

$$CH_3.CH_2OK\rightleftarrows\overset{|}{C}H_2-\overset{|}{C}H_2+HOK,$$

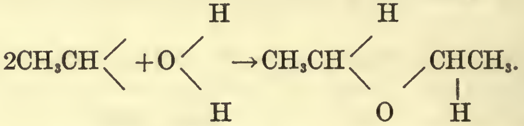
the olefine must naturally give, besides hydrogen, ethylene glycol, $\overset{|}{C}H_2.\overset{|}{C}H_2+2HOK\rightarrow KOCH_2-CH_2OK+H_2$, or its decomposition products; these are, however, not formed. The reaction with potash lime and primary alcohols is so delicate and accurate that it has been suggested by Hell as a means of determining the molecular weight of an unknown primary alcohol.

As mentioned above, ethylether is the chief product when ethylhalides are treated with alcoholic potash or with dry sodium ethylate; this is also true when dry silver oxide and ethylhalides are used. These reactions, which have been interpreted by Williamson and others on the basis of double decomposition or of minute ionization, must obviously be attributed to the absorption by the ethylidene of alcohol or of water which is set free by the action of the halogen hydride particles on the sodium ethylate or silver oxide respectively,



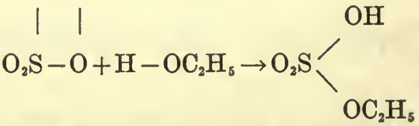
$$CH_3CH\Big\langle + H-OC_2H_5 \rightarrow CH_3CH\Big\langle\begin{matrix}H\\ \\ OC_2H_5\end{matrix},$$

or



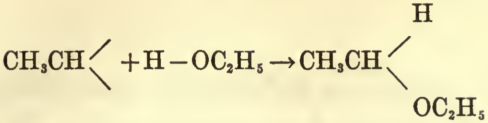
$$2CH_3CH\Big\langle + O\Big\langle\begin{matrix}H\\ \\ H\end{matrix} \rightarrow CH_3CH\Big\langle\begin{matrix}H\\ \\ O\end{matrix}\Big\rangle\begin{matrix}CHCH_3.\\ |\\ H\end{matrix}$$

We are now able to consider an entirely new explanation of the function of sulphuric acid, or of phenylsulphonic acid, in converting ethylalcohol into ether. Sulphuric acid acts first of all with alcohol at ordinary temperatures to give both mono- and diethylsulphate; the first stage in the reaction cannot be ascribed to the union of ethylidene, formed by dissociation of alcohol, with free sulphuric acid, since ethylether, which is relatively more dissociated than alcohol, acts *only very* slowly with concentrated sulphuric acid at ordinary temperatures to give primary ethylsulphate. Furthermore since sulphuric acid itself is completely dissociated into its components, sulphurtrioxide and water, at 400° it is extremely probable that monoethylsulphate is formed by the union of sulphurtrioxide, present by dissociation, $H_2SO_4 \rightleftarrows SO_3 + H_2O$, with alcohol,



$$\overset{|}{O_2S}-\overset{|}{O}+H-OC_2H_5 \rightarrow O_2S\Big\langle\begin{matrix}OH\\ \\ OC_2H_5\end{matrix}$$

Now it is well known that ether formation in a mixture of sulphuric acid and alcohol begins perceptibly only at 95° and proceeds *very* slowly at that temperature. The favorable temperature for ether manufacture is 140°. This is self-evident in view of the following considerations. Primary and secondary ethylsulphate possess the dissociation-points 160° and 200°, respectively; consequently these substances must be dissociated at 140° to a very great extent into sulphuric acid and one or two molecules of ethylidene respectively. Addition of alcohol at 140°, therefore, simply necessitates a combination with the ethylidene particles,



$$CH_3CH\Big\langle + H-OC_2H_5 \rightarrow CH_3CH\Big\langle\begin{array}{l} H \\ OC_2H_5 \end{array}$$

to give ether, and this process can naturally go on indefinitely.

When ethyl alcohol is mixed with an excess of concentrated sulphuric acid and heated to 160° no ether but some ethylene is formed; in fact this method is still suggested and used as the best means of preparing ethylene. The yield of olefine, however, can never be raised above 20 per cent of the theory, and the operation is extremely tedious because carbonization and formation of sulphurdioxide takes place to a very marked extent. These results are now easily understood. The ethylidene molecules, formed by dissociation of ethylated sulphuric acid, burn chiefly at the expense of the oxygen present in sulphuric acid, $CH_3CH\Big\langle + O=SO_2 \rightarrow CH_3CH:O + SO_2$ and the resulting acetaldehyde is then at once charred by the vitriol present. Only twenty per cent at the utmost of the ethylidene particles escape this oxidation by intramolecular conversion to ethylene.

Finally we may summarize the conclusions reached in the above discussion as follows. The valence of carbon is not a constant. At definite temperatures, which vary remarkably with the nature of the groups bound to it, a carbon atom becomes spontaneously dyad. Below these limits there is dynamic equilibrium between bivalent and quadrivalent carbon. The existence of carbon compounds containing bivalent carbon has been definitely established; methylene chemistry plays a great rôle in many of the fundamental reactions of organic chemistry. The conception of substitution or metalepsis, which has been our guide in interpreting the reactions of carbon chemistry since 1833 is no longer tenable. It must be replaced by the conception of dissociation in its broadest sense. Fundamentally speaking, there are but two classes of carbon compounds, — the saturated and the unsaturated compounds. Excluding reactions called ionic, a chemical reaction between two substances always first takes place by their union to form an addition product. The one molecule being unsaturated and partially in an active molecular condition absorbs the second molecule because it is partially split or dissociated into two active portions. The resulting addition product then often dissociates spontaneously, giving two new molecules.

The similarity of such reactions to those called ionic is at once apparent, but their relationship cannot in the present state of our knowledge be clearly understood.

SPECIAL WORKS OF REFERENCE

Liebig, Annalen der Chemie, 1892–1904.
Vol. 270, pp. 267–335; Vol. 280, pp. 263–342;
Vol. 287, pp. 265–359; Vol. 298, pp. 202–374;
Vol. 308, pp. 264–333; Vol. 309, pp. 126–189;
Vol. 310, pp. 316–335; Vol. 318, pp. 1–57 and 137–230;
Vol. 335, pp. 191–333.

THE PROGRESS AND DEVELOPMENT OF CHEMISTRY DURING THE NINETEENTH CENTURY

BY FRANK WIGGLESWORTH CLARKE

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THE history of any science is a record of progress from empiricism to philosophy; from isolated details to systematic knowledge. At the outset, certain facts impress themselves upon the minds of men, either because the observed phenomena are beneficial, or for the opposite reason. Between the facts, the simpler and more obvious relations of cause and effect are first noted, but only in the most superficial way and without deliberate intention. By degrees, after many wanderings along paths that lead nowhere, and in spite of countless misinterpretations, mankind slowly accumulates a mass of data in which something like unity begins to appear, and through which it is seen that the universe is not a creature of caprice, but an existence organized and orderly. This conception lies at the foundation of all science; it is the one article of faith which the student dares not doubt; for rational investigation would be impossible without it. The belief in order, and the hope that we may discover its laws, inspire all scientific researches.

Speaking broadly, the development of science takes place in three stages, which merge one into another and often overlap. First, there is the collection of data; classification follows; and attempts at interpretation come last of all. This is the logical course, which, however, is not always followed. Premature speculations, efforts to determine what the universe should be, are not unknown in the history of human thought, nor have they been altogether futile. Hypotheses, framed in advance of positive knowledge, help to stimulate investigation, and so, despite their errors, lead us ultimately to the truth. In reality, the three stages of growth coexist; experiment and speculation go on side by side; and each one reinforces the others.

At the beginning of the nineteenth century, chemistry was in a transitional, I might almost say a formative, period of its existence. It was just emerging from the morasses of a philosophy unchecked by experiment, and from the vagaries of the alchemists, and was assuming something like its present form. A goodly mass of data had been gathered; they were partly classified, and the work of interpretation was successfully begun. The analyses of air and water, the discrimination between elements and compounds, and a recognition of the constancy of mass, had laid the foundations of the new science. This word "new" I use advisedly. In its earlier days chemistry was only an empirical art, in which discoveries were made by chance, and remembered because of their utility. Chemical facts were secrets in the hands of artisans, or held by initiated priesthoods; and when they were recorded at all it was only in the form of useful recipes or as medical prescriptions. As a science, as an organized body of knowledge with a philosophy of its own, chemistry hardly existed before the time of Boyle. Alchemy, groping in the darkness, had made useful discoveries; but their successful correlation was an affair of a much later period. To Lavoisier, more than to any other one man, the transformation of chemistry from an art into a science must be ascribed. There were greater discoverers than Lavoisier, perhaps, but he was the organizing spirit, and his proof that matter was indestructible made quantitative chemistry a possibility. Without such a basis a rational science would be almost inconceivable. It is a necessary complement to the older philosophical maxim that from nothing nothing can be made. Creation and destruction are equally beyond our powers — a truism which the ancients may have apprehended, but which before the time of Lavoisier rested on speculation alone. Indeed, the conception was defective until the middle of the nineteenth century, when the doctrine of the conservation of energy raised it to completion.

Let us now return to the opening of the century and see how matters stood. The simpler gases, acids, and bases, and the commoner metals were known, and many compounds had been more or less completely examined. Richter and Fischer had shown that reactions took place in proportions which exhibited simple relations to one another; the doctrine of phlogiston had ceased to dominate chemical opinion, and the law of definite proportions, despite the opposition of Berthollet, was generally received. That chemical changes should be governed by fixed quantitative laws was a natural condition to expect, but it needed both proof and explanation. So many reasonable theories had already broken down that a healthy skepticism prevailed, and chemists demanded concrete evidence in favor of every proposition that philosophy might offer for their edification. Rubbish had been cleared away, — what structure should rise in its place? An answer to this question was speedily forthcoming.

It was in October, 1803, that John Dalton published the beginning of his famous atomic theory, but it was not until five years later that he gave it completely to the world. Merely as a speculation, the idea of atoms was as old as philosophy; but in its scientific form it was something entirely new. Under it, the law of definite proportions became necessary and significant; the law of multiple proportions, which had been partially anticipated by others, was made complete; and these considerations alone would have justified the provisional acceptance of the doctrine. It unified the known or suspected laws of chemical combination and gave them philosophic validity. It incited chemists to verify the evidence in its favor, and so led to new discoveries; in short, it fulfilled all the conditions of a good scientific theory. Its chief peculiarity, however, its prime difference from all preceding atomism, remains to be stated. Dalton discovered that to every element a single definite number could be assigned, and that these numbers or their multiples governed the formation of all compounds. Oxygen, for instance, unites with other elements in the proportion of eight parts by weight or some multiple thereof; never in other ratios. These combining numbers, under Dalton's theory, became the relative weights of the atoms; and atomism, hitherto a qualitative notion only, received a quantitative expression. With the help of these atomic weights, or combining numbers, as some anti-theorists preferred to call them, the composition of any substance could be represented by a simple formula; and chemical calculations, which had been empirical and arbitrary, became systematic and easy. In short, Dalton had discovered a new class of constants, the fundamental numbers of quantitative chemistry, whose significance has steadily increased and is probably not even yet completely appreciated. To this point I shall recur later.

The decade following Dalton's unique discovery was chiefly characterized by two lines of research, the study of inorganic compounds, and the investigation of their physical relations. Davy, by decomposing the alkalies and earths, gave precision and definiteness to the conception of a chemical element, while Gay Lussac and Avogadro discovered the laws which connected the volume relations of gases with their chemical composition. To Avogadro we owe the discrimination between atoms and molecules — a distinction which physics, unaided by chemical evidence, could probably not have reached, and which even now is often overlooked by physicists. Maxwell, for example, in his article upon atoms in the Encyclopædia Britannica, deals with molecules throughout, and fails to mention Dalton's work at all. To Maxwell the physical arguments were clear, the chemical relations were not adequately appreciated.

In 1819 Dulong and Petit discovered the law connecting the specific heat of a solid element with its atomic weight, but apart from that investigation chemical research became for thirty years largely a matter of detail. Discoveries were many, successful generalizations were few. During this epoch, Wöhler, by his synthesis of urea, broke down the barrier between organic and inorganic compounds; Liebig and others proved that groups of atoms, the so-called compound radicles, could play the part of pseudo-elements; Dumas established the principle of substitution, and Faraday connected the phenomena of electrolysis with the atomic constants. Inorganic chemistry, however, received the lion's share of attention, and the commanding figure of the period was that of Berzelius. To him we owe the development of chemical formulæ and equations, the thorough determination of many atomic weights, the discovery of new elements, and the investigation of innumerable compounds. And yet his gigantic labors were performed in a laboratory which a modern high school would despise, in which the chemist of to-day would be able to accomplish next to nothing. It was, in fact, a kitchen, wherein cookery and research were carried on almost side by side. Had Berzelius possessed our wealth of resources, could he have achieved a greater success? Perhaps not, for we must remember that he had a virgin field to cultivate, and the implements of the pioneer are less elaborate than those which his successors require. A great part of the work done by Berzelius was necessarily crude, and much of it is still awaiting revision, for the man who clears the ground is not the one to give it the highest cultivation. As knowledge grows, the demands for facilities increase, and we could not return to primitive methods even if we wished to do so. Imagine a modern astronomer with Galileo's telescope, and no more mathematics than Kepler could command! Berzelius labored in the days of small things, and being great he overcame the obstacles that confronted him; we to-day are the slaves of a complexity such as the earlier chemists could never have imagined. I refer now to the material side of science; in its theoretical aspects simplicity has been gained and our range of vision has widened correspondingly. We work in clearer air and with much more powerful appliances than the investigators of earlier times, but to say that we do better would be rash indeed. There are giants in all days, and no age has a monopoly of greatness.

During the Berzelian period, as I have said, inorganic chemistry was the main subject of chemical research. But it was not the only theme, for chemical physics also received a good deal of attention, and organic compounds were by no means neglected. Inorganic substances were apparently simple, the organic were complex; and so the former were naturally considered first, the more obvious problems taking precedence over the less evident. By degrees, however, opinion changed, and the great discoveries of Wöhler, of Liebig, and of Dumas, the theoretical discussions of Laurent and Gerhardt, and perhaps also the physical regularities pointed out by Kopp, turned the current of research into a new channel. Substances that could be arranged in series, with progressive differences in composition and properties, were evidently worth examining; a compound radicle was, in its way, as fascinating an object of study as a new element; the possibilities of substitution and the marvelous chemical plasticity of organic matter were noted, and all of these considerations worked together in effecting a transformation of chemical thought. Organic chemistry became the fashion, and for nearly fifty years it was the central subject of research.

Before entering upon this new period, let us go back and examine the conditions under which progress had previously been made. How was the work done, and what impulses urged it forward? What purposes, what demands, what encouragement, led chemists to pursue their labors? At first, chemistry was a branch of the older natural philosophy, and the discovery of natural laws, the reaching after truth for its own sake, was the chief aim of investigators. These, as a rule, were individuals, working independently, each on his own resources, and without thought of practical results. Science and industry were as yet unallied; chemistry had but a small part in schemes of education; institutions for the aid of research were few, and those which did exist were scantily endowed. Davy, to be sure, had the Royal Institution behind him, and in it he discovered Faraday; Berzelius was secretary of the Academy at Stockholm; but these were exceptional cases, and not by any means the rule. Personal initiative and voluntary effort were almost the sole agencies at work. The great discoveries were made by amateurs, by men who among other labors found some leisure in which to study; and only the occasional man like Cavendish, with ample means, could give his whole time to research. Priestley was a clergyman; Scheele an apothecary; Lavoisier a public official, and these are typical examples. The impulse to investigate came from within, uninfluenced by thought of profit or by any manner of external compulsion. An inspiration, not the pressure of a duty, drove our predecessors forward.

By degrees, however, chemistry was found to be useful, and the commercial demand for chemical services began. Manufacturers discovered that processes and products could be improved, and that waste material had value; metallurgy developed along chemical lines, medicine gained new remedies, and agriculture was turned from its traditional empiricism into scientific courses. A new set of impulses was given to chemistry, and many of its practitioners became professional in expectation of material profit and reward. The field of research was widened, and civilization was thereby advanced. Chemistry was not merely a philosophical amusement, but an agent for "the betterment of man's estate;" and so a double motive existed for its further development. This combination of intellectual interest with utility gave the science a higher place in educational affairs; and when Liebig opened the first university laboratory for students at Giessen, a new era for chemistry began. Before that time the chemist was either self-taught or trained in private laboratories; now he could aspire to scholastic honors and assume his proper position as a learned man. As a discoverer, Liebig was great, but his chief services to chemistry were in his educational work and in the application of science to agriculture. To those achievements his wide reputation is mainly due.

For chemistry, then, the second half of the century opened auspiciously. Chemists were needed for technical purposes and as teachers, and resources were placed at their disposal almost without stint. Discovery was stimulated, investigation became more systematic, theory and practice developed side by side. Practical applications followed the most abstract researches; new industries sprang into existence, and in education mere bookishness gave way to experimental methods. A great but silent revolution had taken place, whose magnitude will be better appreciated by posterity than by ourselves. Had science done no more than to replace supposition by experiment, and chance discovery by orderly research, the revolution would still have been one of the greatest in the history of mankind. Chemistry was not the sole agent in effecting the transformation, but it surely played one of the leading parts.

All of the agencies which I have mentioned helped to encourage the study of organic chemistry. It was systematic, and therefore easily taught, and it was full of suggestiveness both for teacher and pupil. Its practical applications were many, and gave the investigator hope of material rewards; the revelations of coal-tar alone were enough to stimulate chemists to the greatest activity. So it happened that inorganic chemistry fell into neglect, and the majority of chemists followed the leaders into the new field. The conceptions of chemical structure, which had been slowly evolving during many years, were given definiteness by the discovery of valence, and of this the benzene theory was perhaps the most brilliant application. Frankland, Williamson, and Perkin in England; Dumas and Wurtz in France, Kekulé and Hofmann in Germany, and the Russian Butlerow, are the conspicuous names connected with the modern movement. Organic chemistry became an imposing structure, and yet it rested upon the foundations which the older chemists had laid. The constitutional formulæ were built upon atomic conceptions, valence itself was a property of the atom, and complete acceptance of the new ideas was impossible until after Cannizzaro had revised the atomic weights and brought them into harmony with Avogadro's law. Up to that point there was a chaos of rival doctrines, afterward order reigned. The full significance of valence could not appear until the old system of chemical equivalents had been set aside.

Naturally, as the mass of chemical data increased, specialism became necessary. No man could expect to know the whole of chemistry; a small part of it was all that any one could handle, and the inevitable results followed. A specialist may be broad, but the direct tendency of specialism is to narrow one's field of view, and to concentrate the attention upon details rather than generalities. The theories which fit immediate conditions then become satisfactory, and the chance that they may be only partial glimpses of greater laws is disregarded. Only the stronger and more philosophical minds can escape these limitations and see things in their larger aspects.

To the organic specialist, at least in most cases, the doctrine of valence was adequate; for it explained the combinations with which he had to deal. Relatively few of the chemical elements were seriously considered by him, and they offered no insuperable difficulties. Carbon was the typical element, the key to all organic matter; its quadrivalency in terms of the hydrogen unit was assured; its ability to unite with itself in chains or rings was established; with these data constitutional formulæ became truly significant, and useful for the correlation of existing knowledge. Even more can be said in their favor, for they had a certain prophetic ability which guided research and foretold discovery. But, after all, carbon was only one among many elements, and nobody was justified in assuming that its modes of combination represented general laws, or that ideas drawn from the study of organic matter alone were applicable elsewhere. The theory of valence must be tested with regard to all the elements before its full validity could be recognized, and that test implied a renewal of interest in inorganic problems. It was necessary to discriminate between special cases and fundamental principles, and so a much larger field than organic chemistry could offer had to be surveyed. Clues had been found in the study of carbon compounds, but where were they to lead?

So far as actual knowledge went, the chemical elements were distinct entities, and speculation as to their nature had been looked upon generally with disfavor. And yet they had points in common which rendered their classification possible, and it was perfectly evident that they could be arranged in a small number of natural groups. Certain elements were obviously types of others; some were isomorphous, as shown by Mitscherlich, and some exhibited serial relations as in Döbereiner's triads; but no one scheme of classification covered the entire ground. Analogies were numerous enough, but their meaning was not clear. A process of evolution was at work, however, and in due time it culminated in Mendelejeff's development of the periodic system. All partial classifications, all the dim foreshadowings of law, now fell into place together, and one simple generalization occupied the field. The atomic weights became more than ever the fundamental constants of chemistry, and all the properties of the elements were seen to be periodic functions of these quantities. In Mendelejeff's table stress was laid upon valence and the form of compounds which each element could yield; in Lothar Meyer's curves the physical relations were emphasized, and so each statement reinforced the other. Newlands, it is true, had partially anticipated Mendelejeff, but his law of octaves fell just short of completeness.

At first, the periodic classification attracted comparatively little attention, and its general acceptance might have been slow had it not been for certain prophecies. In Mendelejeff's table there were many gaps; these were attributed to the existence of elements as yet unknown, and for three of them the author ventured upon predictions. Each element must have a certain atomic weight, a prescribed density and melting-point, and should form compounds of a stated character. In due time the three unknown elements were actually found, and gallium, scandium, and germanium confirmed all of Mendelejeff's anticipations. The importance of the classification was thus established, and the periodic law became one of the foundation stones of modern chemistry. The conception of valence as a property of the atom acquired a broader significance; in cases that had been doubtful its magnitude could be determined, and with its aid the chaos of inorganic chemistry began to exhibit signs of something like order. The deficiencies of the periodic system I need not mention here, for this is no time for details; neither shall I discuss the obvious difficulties which arise when we seek to apply the doctrine of valence to inorganic compounds; only the larger verities concern us now. In the broadest sense the periodic classification is sound; the principle of valence is general, and the obstacles which now appear will doubtless be overcome by future investigation. That the greatest generalization has been reached, we cannot assume; but so far as we have gone we stand on solid ground, and can continue our explorations in safety.

Up to a certain point organic compounds had been successfully interpreted in terms of valence. Isomerism was explained, and the existence of unknown isomers could be predicted; different atoms were assignable to different positions within the molecule, as in the case of the four hydrogen atoms of acetic acid, one fixed and three replaceable; but after all this had been done there were still some difficulties outstanding. Isomers existed whose chemical structure seemed to be the same, and for their interpretation an extension of chemical theory was needed. This want was supplied by van't Hoff and Lebel, who almost simultaneously pointed out the consequences of assigning a tetrahedral form to the atom of carbon. From the properties of such an atom a new class of structural formulæ could be deduced, by means of which the so-called cases of "physical isomerism" were simply interpreted. The molecules of tartaric and racemic acids, for example, resemble each other as an object resembles its reflection in a mirror, the one being a reversal of the other. Our science acquired a new province, that of stereochemistry, which in less than thirty years has grown to impressive dimensions. The theory of van't Hoff and Lebel did more than to interpret the troublesome known phenomena, it encouraged additional research and led to many discoveries. At first, the asymmetric carbon atom alone was considered, but its peculiar properties are now shared by other elements, and physical or stereochemical isomers are found even among inorganic compounds. When one atom is combined with four other atoms or groups of as many different kinds, optical asymmetry appears, and physical isomerism becomes possible.

During the ninth decade of the century the dominating interest in organic chemistry began to wane, for the reason that other subjects were demanding their share of attention. I do not mean by this that the activity of organic chemists diminished, for their output of discovery was never greater than now; but the centre of the stage was slowly being filled by other groups of actors. Inorganic chemistry was reviving from its long neglect, and physical chemistry loomed large upon the horizon. In each of these branches journals were started, and no difficulty was found in filling their pages with the records of successful investigations. In theory, physical chemistry has made the greatest advances, inorganic research has been more a matter of detail. Let us briefly consider the two themes separately.

To the inorganic chemist several duties were apparent. Old work needed revision, the compounds of many elements were almost undescribed, there was a lack of system to remedy, and the theories derived from organic chemistry were to be tested and applied. A very large part of the work was necessarily descriptive, a preparation for the future, but back of it all lay a fundamental question with which all physical science is connected, for the nature of matter itself was to be determined. In its broadest sense this question demands the coöperation of all science and all philosophy, but to inorganic chemistry one phase of it may be assigned. What is the nature of the chemical elements? Are they one or many? And how shall an element be defined? To these questions there is as yet no final answer, but clues to follow are many, and some of them are offered by the periodic law. To remedy its imperfections is an obvious duty for inorganic chemists to perform.

Near the middle of the Mendelejeff table and of the Lothar Meyer curve there is an area which is partly blank and partly filled with the symbols of uncertain elements. That some of them were tri- and others quadrivalent was well established; but their number was undetermined, and the places which they should occupy were even more doubtful. Some of the uncertainties still remain, and some have been cleared away; but the main problem is as yet unanswered, and therefore the metals of the rare earths are still actively studied. Supposedly definite earths have proved to be mixtures; others, like cerium, lanthanum, yttrium, and scandium, seem to be definitely placed; but what shall we say of the rest? Didymium was thought to be a distinct element, and yet it has been split in two; samarium, gadolinium, erbium, and ytterbium are probably definite; but several other metals are claiming recognition; and so, notwithstanding the progress which has been made, a large part of the field is still obscure. Through the study of the rare earths, one side of our problem, the nature of the elements, is open to attack; but only the outworks have been carried so far.

According to modern ideas, the integrity of an element is determined by two conditions; it must have a distinct spectrum and a definite atomic weight. In the study of the rare earths these criteria have been systematically applied, and to great advantage; but what has been done elsewhere? To answer this question we must go back more than forty years in time and make a new beginning.

It was near the middle of the century that August Comte, seeking to find some limits to positive knowledge, argued that it would be impossible for us ever to determine the nature of the heavenly bodies. Are they composed of matter like that which forms the earth, or are they different in kind? — on that theme we might speculate, but we could never know. The prophecy was futile; Kirchhoff and Bunsen, with the spectroscope, swept the limitations away, and all the universe, as far as eye could reach, was found to contain familiar elements, but under conditions not always like our own. Astronomy, physics, and chemistry had gained a new weapon, and discovery followed discovery along widely different lines.

In the chemical laboratories the value of the new instrument was immediately proved. Two metals, caesium and rubidium, were presently discovered by its aid, thallium and indium were found a little later, and their analogies to other elements made them comparatively easy to classify. The periodic system, which was developed later still, gave them their proper positions among the metals, and they in turn made the classification more complete, and therefore easier to establish. In each case the double criterion was applicable, and definite spectrum was connected with definite atomic weight. I speak now of emission spectra; but they are not the only kind. Certain solutions give absorption spectra, and they have been of great assistance in the study of the rare earths. In the identification of the elements, then, the spectroscope has rendered service of inestimable value, and discovery would have been very slow without it. Quite recently, at the very end of the last century and during the few years of the new, relations have appeared between the wave-lengths of the spectral lines and the atomic weights of the elements; but the general expression which shall connect them all is yet to be revealed.

Another discovery in the realm of inorganic chemistry is deserving of mention now on account of its peculiar significance. The atmosphere was thought to be well known, and yet in 1895 a new element, argon, was discovered in it. This find was quickly followed by others of like kind, and now five gases previously unknown have been extracted from the air. Each gas is identifiable by its spectrum and its density, and from the latter datum the atomic weight can be inferred.

Now the interesting fact concerning these atmospheric gases — helium, neon, argon, krypton, and xenon — is that they represent matter of a new kind. So far as evidence goes, they are monatomic, absolutely inert, and incapable of union with other elements. Their valence is zero, and when the periodicity of the elements is represented by a vibratory curve, they occupy the points of rest, — the nodes. They are matter having physical, but no chemical, properties, and therefore they can be investigated only upon the physical side. This conclusion, perhaps, should be stated provisionally, for it may be reversed by future discovery; but of this possibility we have only one suggestion. Helium was first extracted from the mineral uraninite in which it is firmly held, and we cannot say with certainty that it is not chemically combined. Altered or massive uraninite contains little or no helium; the crystallized varieties yield more, and the most brilliant and perfect crystals are the richest of all. The gas may be merely occluded, but the bare chance of combination should not be overlooked. Either supposition is legitimate; but there is still one more possibility, namely, that helium may be generated by the decay of another substance, and not be an original constituent of uraninite at all. Here we touch the mystery of radium — a body which challenges our former conceptions of an element, for seemingly it can be decomposed.

The discovery of radium by Mme. Curie belongs to the nineteenth century, and therefore it falls within the scope of this essay. How it was found, how laboriously the phenomena of radioactivity were observed in order to isolate traces of the new metal, we all know, and the details need no repetition here. At last pure salts of radium were obtained, and the two criteria of spectrum and atomic weight were satisfied. Radium is clearly a metal of the barium group, it fills a definite place in the periodic table, its claims to elementary rank are on a level with those of other elements, and yet it exhibits an apparent instability which is difficult to explain. Radium gives off material emanations that are different from itself; they are gaseous and inert; in them the spectrum of helium has been observed. From one element another seems to be derived, and all our notions of what an element should be are thrown into temporary confusion. I say "temporary," for I believe that order will be restored, and that a deeper insight into the constitution of matter is close at hand.

Pardon me now if I seem to wander from one part of my subject to another. Between the various departments of knowledge there are no sharp boundaries, and the solution of a problem often depends upon the convergence of testimony from many different directions. The nature of the elements is primarily a question for the inorganic chemist; but physics has much to say upon the subject, and even the serial relations of organic compounds offer suggestive analogies which are entitled to some consideration. The periodic system, with its fulfilled prophecies, tells us that the elements are related one to another by some distinct law; the spectroscope gives us evidence of a different order; electrical phenomena have their share in the story, and the modern phenomena of radioactivity offer the latest testimony of all. What conclusions seem to be foreshadowed by the data now in hand?

One of the earliest achievements of the spectroscope was the rehabilitation of the nebular hypothesis. The resolution of some nebulæ into clusters of stars had shaken faith in Laplace's speculation; but when it was proved that others were really clouds of incandescent gas, belief in the hypothesis was restored. One point, however, was of peculiar interest: in the nebulæ only one or two elements, low in the scale of atomic weights, could be seen; in the whiter and hotter stars a few more substances appeared; colored stars were of still greater complexity, and so on progressively from the simplest constitution to the material heterogeneity of our globe. If suns and planets were evolved from nebulæ, it seemed as if the chemical elements had been successively generated at the same time — a supposition which was certainly legitimate, although it was at first denied by some chemists as unworthy to be heard. At all events, here was testimony bearing upon the problem of the elements, although its full significance was not so clear. It could be pigeonholed, but not thrown away.

Recently, and in great part through the researches of J. J. Thomson, evidence has been obtained of the reverse order. On one side an evolution of the elements is apparently indicated; Thomson's experiments suggest a breaking-down. By studying the ionization of gases, phenomena were observed which point to the existence of particles smaller than the Daltonian atoms, and a beginning has been made toward the identification of matter with electricity. The negative particles, corpuscles or electrons, have been split off from ordinary matter, and they are always the same, regardless of the element from which they separate. Even their mass can be estimated, and it appears to be about the thousandth part of that which represents an atom of hydrogen. These conclusions are perhaps not final, but they are emphasized by the results obtained in the study of radioactivity. The investigations of Rutherford and Soddy, of Ramsay, Dewar, and others, all tend in the same direction, and lead to the suspicion that the atoms are complex and subject to decay. The three most radioactive elements are radium, thorium, and uranium, and these have the highest atomic weights of any substances known. If the elements are complex, these are the most so, and therefore presumably the least stable. If we take this testimony in connection with that given by Thomson, the evidence offered by the spectra of the heavenly bodies, and the regularities of the periodic law, we have a strong argument in favor of the supposition that the so-called elements are not the simplest forms of matter, and that they may be ultimately one. The doctrines of unity of matter and the unity of force are thus philosophically allied, and only negative evidence can be adduced to support a belief in the actual diversity of the elements.

Speaking broadly, organic and inorganic chemistry, at least as they are commonly studied, are essentially descriptive in their character, and they deal with statical phenomena. Physical chemistry, on the other hand, is more concerned with dynamics, and seeks to determine the conditions of chemical equilibrium, and the nature of chemical change. What substances are and what substances do are of course only two phases of the same fundamental problem, which are separable ideally, but not otherwise. Descriptive chemistry lays stress upon one side of the science, physical chemistry emphasizes the other; but they blend together by imperceptible degrees, and no clear line of demarcation can be drawn between them.

Every science, when viewed historically, is seen to have a central line of growth, to which its various branches are naturally related. In chemistry this line is marked by physical phenomena, and from their study the greater generalizations have been derived. Avogadro's law, the law of Dulong and Petit, Faraday's theory of electrolysis, and the periodic classification of the elements are good illustrations of this principle. The atomic theory itself, which connects all of the other relations, is fully as much physical as chemical; valence is best explained in electrical terms, and stereochemistry arose from optical and crystallographic considerations. Physical chemistry is the main stem of our science, and statical conditions are merely the results of dynamical equilibrium. The description of a product is incomplete unless we have noted the physical phenomena, the transformations of energy, which took place during its formation, and to studies of this kind the chemists of the future must devote a large part of their time.

During the last twenty years the importance of physical chemistry, or rather the recognition of its importance, has steadily increased, and to-day it seems to dominate the entire field of chemical research. Laboratories are equipped for its purposes alone, journals are devoted to it, and the activity of investigators has become so great that subdivision has already begun, and men are known as thermo-chemists, electro-chemists, and so on. Electro-chemical societies have been formed and are prosperous; specialism is passing into subspecialism; in short, chemistry is swiftly assuming an entirely new form.

In the evolution of any science successes and disappointments are almost equally influential; the former stimulating, the latter tending to arrest research. The fruitful line is followed, and attracts workers; the barren field is deserted or nearly so. Barrenness, however, may be due not to lack of fertility, but to premature effort; and the truth which is beyond our reach to-day may drop into our hands to-morrow. Thermo-chemistry, for example, has so far failed to repay the labor spent upon it, and has fallen into disfavor; but the future may tell a different story. Its importance is obvious, and its general laws cannot elude discovery forever. The thermal changes which accompany all chemical reactions must sometime be interpreted.

On the other hand, success has followed the physical study of solutions, and thereby chemical theory has been enriched. First, it was found that substances in solution exerted pressure — a phenomenon attended by depression of the melting-point and increased temperature for boiling. This pressure resembled that observed in gases, and a relation between the two was apparent. It was van 't Hoff's privilege to trace the connection, and to develop a kinetic theory of solutions. Avogadro's law was completely paralleled, and equal volumes of solutions at equal osmotic pressures were shown to contain equal numbers of molecules. For both laws, the liquid and the gaseous, however, there were certain apparent exceptions, which, for gases, were easily explained as the result of dissociation. Arrhenius applied this explanation to the exceptional solutions, taking into consideration also the ionic conceptions developed in the study of electrolysis, and the abnormalities vanished. A salt in dilute solution is electrically dissociated into its ions, which remain in equilibrium although separate. From these generalizations several important consequences followed. First, it became a simple matter to determine the molecular weights of soluble substances — a class of measurements that had previously been possible for gases alone. Secondly, much light was thrown upon the subject of reactions between dissolved salts, especially such as involve precipitation or double decomposition. In most cases, although not invariably, the phenomena are ionic, and the molecules are first broken down. In the third place, the uniform heat of neutralization between acids and bases was explained by showing that in all cases it represented one and the same change, namely, the union of hydrogen and hydroxyl ions to form water — a conclusion which gave a significant datum to thermo-chemistry. In brief, many distinct lines of physico-chemical research converge in the kinetic theory of solutions — a theory whose development has hardly more than begun. Like most successful theories, its importance may at first be exaggerated; we have not yet the perspective which shall enable us to judge it truly; in all probability, it is but one phase of some larger law; but, notwithstanding all difficulties and all objections, it is a stride forward, and will bring us to new truth.

We now reach a point where it is difficult to disentangle the many threads of investigation, and to determine their relations to one another and to the past. Current work is more or less confusing, for it is too near our eyes, and its ultimate significance is not easily apprehended. The theory of solutions, the law of mass-action enunciated by Guldberg and Waage, and the phase rule of Willard Gibbs interact in so many ways, and are so rapidly developing, that I for one dare not attempt to predict what the outcome shall be. Chemistry is becoming more and more a mathematical science, and so is gaining in precision; but mathematical reasoning leads to correct conclusions only when its premises are secure. The data must be verified and reverified before we can certainly determine their meaning, and in the enthusiasm of new investigation this necessary duty is often deferred. The pioneer leaves much undone behind him, and patient laborers are needed to follow in his lead. The first glimpse of truth is rarely the whole truth, for that is best gained by what we may call the method of successive approximations.

If prophecy is difficult, retrospection is easy; we may therefore retrace our steps and see what road we have followed. Boyle, Priestley, Scheele, and Lavoisier prepared the way for Dalton, and his atomic theory, the first quantitative theory of its kind, has been for a century the key to all chemistry. All of the great advances in our science have hinged directly upon Dalton's conception, and his atomic weights, as developed by Berzelius and Cannizzaro, are now seen to be fundamental constants, with whose aid the physical relations of different substances are easiest interpreted. The periodic law is based upon the atomic weights, valence is an atomic function, in stereochemistry we have a hint of atomic form, isomerism is intelligible only upon the assumption of variable atomic position, and the structure of a molecule depends upon atomic groupings. The ions of physical chemistry and the molecules of thermodynamics are either atoms or groups of atoms; and, in short, whichever way we turn in physical science we find ourselves, consciously or unconsciously, thinking in atomic terms. And yet we are sometimes told that the atomic theory is outworn, and that some other conception should replace it. We may well ask, therefore, whether atomism has any basis in reality. Is it the truth or only an illusion — a concrete fact, or misinterpretation of testimony?

That the atomic theory has rendered great service to chemistry, and that it correlates our positive data, is clear; but after all it is hypothetical, for no atom has been isolated and seen. The molecule and the atom are inferred from the properties of matter in mass; and if we need a theory at all, there is none other at hand. The attempts to evade it are agnostic in character, and are based upon the tacit assumption that it is unscientific to speculate upon ultimate questions, which, in the nature of things, can never be absolutely solved. We can observe and classify relations, but it is useless to ask what they mean. The phase rule has been suggested as a basis for our classification, and under it the different kinds of matter become different phases of something which we may or may not be able to comprehend. Perhaps I misrepresent the position of the anti-atomists; but if so it is because their statements are to my mind far from clear. If we object to the atom, we must object to the ether, for that is equally unknowable; we cannot divorce matter and motion, for they are never observed apart; in short, we must reconstruct all physical science and keep within the limits of things known. But is the agnostic position sound? Is not the imagination as truly an instrument of science as is the reason? May we never look forward and anticipate what is to come, shall we always observe and experiment without the help of ideals? To do so we must assume limitations where no limits can be seen, and the human mind refuses to work in that way. Speculation is the guide of science; an indispensable assistant in our exploration of the unknown; a good servant, but the worst of masters. Scientific methods differ from unscientific methods partly by their use of system, and partly in their employment of disciplined as against unrestrained speculation.

That the atomic theory has been a useful tool no one can deny; but can we, in the light of present knowledge, imagine a universe without it? We see that matter differs in its properties from point to point, and all of our experiments end in records of these differences. But is not difference a proof of discontinuity? How could a plenum vary? Even the ether itself, that mysterious medium which is thought to pervade all space, is now believed to have a granular structure, or, in other words, to be atomic. Several mathematicians have worked upon this phase of the problem with curious results; but their conclusions lie outside of my theme. The chemical atom alone concerns us now, regardless of its ultimate or physical nature, which may be exceedingly complex. The conception is so bound up with all modern chemical ideas that we cannot abandon it if we would, so long as nothing better is offered us in its place.

The chemist, then, may legitimately claim that matter, as we know it, is made up of small, distinct particles, which, so far as they have been chemically defined, are of few kinds. These particles gather into clusters, through some form of attraction whose nature is still unknown, and in which differences of position probably represent differences of chemical structure. Allotropy and isomerism are thus explainable, two phenomena that are perhaps the same, and for which the atomic theory alone has offered any reasonable interpretation. But this is not all. Certain numerical constants, commonly known as the atomic weights, have been discovered, one for each element, which are fundamental for all quantitative chemistry and for an important part of physics. These constants are real; they represent definite, measurable relations; and in one form or another they will remain in use, apart from all changes in theory. Whether they are independent of one another is yet to be determined; there are indications that they may be connected by some mathematical law; and should such an expression, a quantitative periodicity, be discovered, it would go far towards enlightening us as to the real nature of the elements themselves. The exact determination of the atomic weights is therefore a matter of supreme importance and one bearing directly upon the profounder problems of chemistry. If the atoms are separable into electrons, the masses of the latter should bear some relation to the atomic weights and give us clues to their mathematical interpretation. Future investigations along this line are certain to be made, and we may fairly hope that they will prove successful.

The nineteenth century is often called the age of steam, and its latter half the age of electricity. May we not, with equal propriety, name it the age of chemistry? During the passage of its years chemistry has developed from an art into a science, with a clear philosophy of its own, and with useful applications which affect all other sciences and many industries. A great university may now employ twenty chemists as teachers where fifty years ago there was barely work for one. Training in chemical research has become a recognized feature in higher education; the student is taught to think and investigate; the production of new knowledge is seen to be a distinct function of the teacher. Scholarship is now rated according to its fertility; and the man who merely knows, no matter how thoroughly, the work of his forerunners, is given a low rank in the thinking world. In the industries, chemical thought is translated into action, and so becomes doubly creative, yielding at the same time new knowledge and material wealth. Governments maintain public laboratories; it may be in preparation for warfare, for sanitary purposes, as aids in the enforcement of revenue laws, or for their own protection as purchasers of supplies; and so the usefulness of chemistry is felt along innumerable lines. The science advances with ever-increasing rapidity and there are as yet no signs of slackening. What shall the future be? We can distinguish necessities and express our hopes, even if we cannot prophesy. An essay of this kind would have small value if it failed to offer any helpful suggestions for the work that is to be done.

In the realm of descriptive chemistry certain work is obviously needed and is therefore likely to be done. Part of this, and the least attractive part, is revisionary — a verification of the older data with the correction of venerable errors. On the inorganic side we may predict many advances, and some of the possible lines of research we have already considered. In order to complete the periodic table the rare earths must be exhaustively studied, and the irregularities shown by iodine and tellurium, or by potassium and argon, ought to be explained. The problems of chemical structure which are offered by complex bases and acids and by double salts require elucidation, and here physico-chemical methods are likely to be most applicable. The correlation of chemical structure with crystalline form is sure to receive much attention; but what direction researches of this kind may take is not easy to foresee.

For organic chemistry I am hardly qualified to speak, at least not with regard to the more immediate urgencies. It is plain, however, to every one that there are large and important groups of compounds which await constitutional interpretation, the alkaloids and albuminoids being among them. Organo-metallic bodies also deserve a good deal of attention, for in them the two departments of descriptive chemistry meet, and each one, organic or inorganic, can be made to shed light upon the other. Finally, the relations between physical properties and chemical composition are most easily investigated upon the organic side, and here are problems enough to keep men busy for a good part of the present century. All the properties of a substance should be calculable from its composition; but the adequate data and the conclusive theory are far beyond our reach. We have a few beginnings, nothing more.

In physical chemistry, it seems to me, we find the unifying principles which are to bind all the subdivisions of our science into one. Some of the problems mentioned under the heading of descriptive chemistry are almost wholly physical in their nature; only they are statical, and leave dynamics untouched. They deal with equilibria established by transformations of energy — a statement which holds true whether we connect it with the atomic theory or base it upon the phase rule. The laws of chemical equilibrium are fundamental, beyond question; but antecedent to their application there was an interplay of active forces whose statutes are more general still. What is the nature of chemical change, and what laws govern its transformations of energy? These, to my mind, are the most general questions of dynamical chemistry. They are raised by every reaction, and they involve the consideration of all the physical forces. The problems of thermo-chemistry, of electro-chemistry, of optical chemistry, are mere special cases arising under the more universal general laws, and they will cease to exist when the latter have been discovered. So ideal a condition may never be reached, but we can approach it.

How, now let me ask, shall the work of the future be done? Hitherto individual initiative has been the chief agency in effecting progress, and each man has handled his own problems in his own way. By individual geniuses the greatest discoveries are made, but they are tried and tested by the collective intelligence of many laborers, more humble, perhaps, but also more patient and thorough. The genius is fortunate, but science has use for plodders as well, who furnish the commonplace facts that are the raw material from which laws and generalizations are developed. The great thinker needs only opportunity and encouragement; the rank and file of investigators, it seems to me, require something more. We need not fear that personal effort will cease; and still we may fairly ask whether it is sufficient for the tasks which are now waiting to be done.

One result of individualism in scientific research is evident. Our knowledge increases irregularly, unsymmetrically — with one phase over-developed and another neglected. In every group of data there are gaps to be filled, side by side with needless duplications. One man finishes a research only to find himself anticipated by some more fortunate worker, and he feels that his labor has been thrown away. Competition is a good thing, but coöperation is better, for it insures that economy of effort which is as important in intellectual affairs as it is in the factory or in commerce. Can we, without stifling enthusiasm, without harming the individual, encourage the organization of research, and so give to science a swifter growth and a more perfect symmetry? That vague but potent agency, "the spirit of the time," has taken "organization" for one of its watchwords, and we cannot escape from its spell. Collectivism and individualism, however, are not necessarily antagonistic; they are two forces acting side by side, and each helping the other. A man best develops himself when he works in harmony with his fellows.

Chemical societies are an invention of the nineteenth century, and they stand for one step in the right direction. In their meetings, by conference and discussion, and in their publications, by making research effective, they have done much to encourage investigation, and to avert, in some measure, useless duplications of effort. Through committees, they sometimes direct the growth of science, not by the exercise of compulsion, but by classifying work that has been done and showing where work is needed. An extension of this process might easily be devised, in such manner that a definite field of study should be divided among a number of scholars, each doing his own share and earning whatever independent credit he deserved. In astronomy we already have an example to follow, for observatories have divided a part of their work in exactly this manner, each institution mapping a zone of stars assigned to it by mutual agreement. Coöperative research upon a well-considered plan ought to be possible among chemists. Some overlapping, some duplication, cannot be avoided, but the waste can at least be diminished.

There is one other step which needs to be taken, and one which I have repeatedly urged on other occasions. There should be laboratories organized, equipped, and manned for systematic chemical research upon those problems which are too large for individuals to handle. The exhaustive determination of constants, for example, must precede the development of laws, and few chemists laboring singly care to attempt work of so tedious a nature. Each one often feels the need of data which do not exist, wants that he is unable personally to supply, and such a laboratory as I have in mind could render invaluable service. Astronomy has its observatories, biology is provided with experimental stations, physics is represented by institutions like the Reichsanstalt, while chemistry is almost unaided. Chemistry, the creator of wealth, receives few endowments, and those which have fallen to its share have been in aid, not of research, but of teaching. Great things have been and will yet be achieved in the universities, but their laboratories can cover no more than a small portion of the field. A laboratory for research would not compete with them; it would, on the other hand, reinforce their efforts. When, a hundred years hence, the progress and development of chemistry during the twentieth century is summed up, investigations carried on under endowments will fill a conspicuous portion of the stage. I have faith in the future; I believe it will be better than the past; and to my mind the great advances in science which we celebrate are only a beginning.

SECTION A—INORGANIC CHEMISTRY

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(*Hall* 16, *September* 21, 10 *a. m.*)

CHAIRMAN: PROFESSOR JOHN W. MALLET, University of Virginia.
SPEAKERS: PROFESSOR HENRI MOISSAN, The Sorbonne; Member of the Institute of France.
SIR WILLIAM RAMSAY, K.C.B., Royal Institution, London.
SECRETARY: PROFESSOR WILLIAM L. DUDLEY, Vanderbilt University.

INORGANIC CHEMISTRY: ITS RELATIONS WITH THE OTHER SCIENCES

BY HENRI MOISSAN

(*Translated from the French by Professor R. S. Woodworth, Columbia University*)

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CHEMISTRY, though young as a science, traces its first applications back to the very cradle of the human race. As soon as man in his struggle with nature had come into possession of his individuality, his observing intelligence enabled him to take cognizance of some of the phenomena occurring about him, and to engage in the study of them. He saw the importance of fire, and soon recognized that certain metallic substances could take the place of flint in the manufacture of weapons. Thereupon he devoted himself to that primitive metallurgy of copper, of which we still find so many examples, more or less transformed, in the earliest foundations of Babylon; these remain as witnesses, not dumb, though far from explicit, of the most remote of our civilizations.

The importance of metal in the different stages of human development is so well recognized that a single name is used to cover all the centuries that have made use of the same metal.

To the age of copper succeeds the age of bronze. At the same time gold, being found in the native state, becomes known, and is wrought with the hammer. Iron, since its preparation is much more difficult, cannot be utilized till later.

In these distant times, the epoch most fertile in chemical applications was that of the Egyptian civilization. After many industrial experiments, this people succeeded in dyeing fabrics with purple, in working the rare metals, in making enamels by fusion, in producing and fashioning glass, and in preparing fermented liquors.

On the other hand, a little people, whose part in everything was to throw the most brilliant light on it without inventing new applications, sought to explain, philosophically, these transformations of matter. The Greek philosophers discussed this subject at length. Empedocles reduced all the bodies that nature can present to four elements: fire, air, water, and earth. For him, these elements were composed of a multitude of minute particles, indivisible and insecable. Such a theory leads easily to the atoms of Democritus. Whether these elements were considered as symbols or as a veritable classification of matter, the idea of Empedocles, adopted by Aristotle, and taught by all the schools, was destined to maintain for centuries the position of a doctrine that could not be disputed.

Later, Epicurus revives the theory of atoms, and Lucretius, in a poetic divination, can write:

> Principio, quoniam terra corpus, et humor
> Aurarumque leves animae, calidique vapores,
> E quibus haec rerum consistere summa videtur,
> Omnia nativo ac mortali corpore constant,
> Debet eodem omnis mundi natura putari.[1]

The idea of the four elements reappears unchanged among the Arabian chemists, and among the alchemists of the Middle Ages; though it undergoes various transformations at the hands of Paracelsus who recognized five elements: spirit; mercury; phlegm or water; salt, sulphur, or oil; and earth, — and later at the hands of Beecher who admits the existence of three essences in earth, — vitrifiable, inflammable, and mercurial earth.

The theory of four elements reigns without contest up to the moment when Stahl, professor at the University of Halle, develops his important conception of phlogiston. For Beecher, combustible bodies and metals contained his three sorts of earth combined. For Stahl, "inflammable earth" becomes phlogiston. Carbon, by its combustion, gives heat and light; it therefore contains phlogiston. When a calx, that is to say, a metallic oxide, is heated with carbon, it extracts and fixes the phlogiston, and becomes a metal. These were important conceptions, because they made it possible to unite in one body of doctrine the phenomena of oxidation and of reduction.

Such was the state of the science when Lavoisier followed up his memorable experiments by developing the notion of simple substances. This great savant showed that the same body could change its state, and he separated clearly, among the phenomena of chemistry, on the one side the weight of the reacting bodies, and on the other

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[1] "First, since earth, and water, and the light breath of air, and glowing fire — of which our world seems to be composed — all consist of matter that is subject to birth and to death, we must think that the whole universe is made up of this same sort of matter."

side the heat set free. By weighing the simple substances that were combined and also the compound produced, he definitely established the weight equation of the chemical reaction. By measuring with the calorimeter the amounts of heat set free, he separated ponderable matter from the imponderable agents. All these views were, in addition, logically bound up with each other, and it would have been impossible to study properly the phenomena of combustion if he had not been forming an exact idea of the passage of a body from the solid to the liquid and gaseous states.

We need not here recall his memorable experiments on the composition of air and of water, on the increase of the weight of metals during their oxidation, on the phenomena of combustion, respiration, and the production of animal heat, and on fermentation, or finally his creation of the nomenclature. These new ideas overthrew the theory of phlogiston. They brought light into the midst of the laborious researches of the alchemists, they prepared the way for organic and physiological chemistry, they gave rigor and exactitude to chemical reactions. In a word, they established chemistry in the position of a science.

Starting from this epoch, we can divide into three great periods the numerous researches that were pursued in different countries. In the first period, the modern idea of elements takes shape; in the second, the chemical laws are established; and in the third, the atomic weights of the elements are determined.

The first period includes the studies of a great number of investigators, but among them four names emerge above all others, — Scheele, whose chemical genius enriched our science; Priestley, a mind at once original and conservative; Cavendish, whose analyses have never been surpassed; and finally Humphry Davy, who, by the discovery of the metals of the alkalies and alkaline earths, explained the composition of the earths and won definitive acceptance for the conception of elements.

The second period presents to us the legislators of our science. Wenzel, following up the work of Rouelle, gives precision to the knowledge of salts and of double decompositions. Richter publishes the first tables of neutralization for acids and bases. Proust formulates the law of the constancy of proportions (1806); and Dalton, at the same time, gives a complete exposition of the law of multiple proportions, a first sketch of which he had presented, in 1803, to the literary and scientific society of Manchester. As we shall see further on, the importance of Dalton's law was not appreciated at its full value till much later. Finally, in 1808, Gay Lussac indicated the laws, so simple, of the combination of gases. By their promulgation, Gay Lussac gave to the concept of combination a truly mathematical exactitude.

After that, the study of the weight of the different elements which enter into combination could be pursued with success, especially when Mitscherlich's law of isomorphism (1819) and Dulong and Petit's law of specific heat (1819) became known. In this third period, in which experimental precision was carried to its furthest limits, alongside of the researches of Victor Regnault, Faraday, Marignac, and many others, the most important works published on the subject that we are considering are those of Berzelius, Dumas, and Stas.

The magnificent effort of Berzelius provided a study, as complete as possible, of most of our simple substances. This line of experiment was taken up with the greatest care by Dumas, who first determined the composition, by weight, of water and of air; and then by means of simple and elegant experiments gave us a certain number of atomic weights, among them that of carbon, the pivot of all organic chemistry. Stas next took up the study of these questions, and, *à propos* of William Prout's hypothesis of the unity of matter, showed clearly that the atomic weights are not simple multiples of unity. Stas's experiments will remain in our science as models of precision.

During this splendid period, which requires about a century, the theories by which we bind together the innumerable details of our science had time to change more than once.

We have already seen how Lavoisier's ideas replaced the theory of phlogiston. Later, Humphry Davy, after his splendid discoveries, assigned a predominating rôle to electricity and created the electrochemical theory, which was adopted and modified by Berzelius. Then came the investigations of vapor density, and, after prolonged discussions, many chemists abandoned the numbers of Berzelius, and followed the so-called notation of equivalents, proposed by Wollaston and adopted by Gmelin, Liebig, and Dumas. But soon Gerhardt, considering as equivalents the quantities of hydrochloric acid, water, and ammonia, which correspond to equal volumes, proposed a system of atomic weights, which won as adherents: in France, Laurent, Wurtz, Friedel; in England, Williamson, Frankland; in Germany, Hofmann, Kekulé, Baeyer; in Italy, Cannizaro. The hypothesis of Avogadro and Ampère took on new life, and a sharp distinction between atoms and molecules made possible a reconstitution of the atomic theory on the basis of the great law of Dalton.

Considerably before this time chemistry was divided into two great chapters: inorganic and organic.

The study of organic chemistry had begun with the investigations of Lavoisier. During the succeeding century and more, chemists tried first of all to isolate the proximate principles of vegetables and animals. These studies, pursued on all sides with varying success, endowed chemistry with a great number of clearly defined compounds, some of which possessed important therapeutic properties.

The analysis of all these substances was a rather delicate task, and, as is the rule in the sciences, no definitive results could be established until the methods of analysis were carried to a sufficient point of exactness. Only after this preliminary work was it possible to classify these innumerable compounds. Various theories then followed, till at last synthesis came to complete the work that had been begun. We recall the great researches of Berthelot on this subject: synthesis of the proximate principles of the animal fats, of the alcohols, acids, carbides (acetylene in particular), camphor, different essences. The vital force accepted by Berzelius, Liebig, and Gerhardt no longer existed. Though man's power was limited in so many things, he could make by synthesis inert organic matter.

Soon appears Kekulé's schema giving a new orientation to organic chemistry; and the synthesis of the most complicated compounds is successfully attempted. Graebe and Liebermann accomplish the synthesis of alizarin; and later, in a magnificent study of indigo, Baeyer is able to state that the position of every atom in the molecule of this dye has been experimentally determined. From these researches issue the different syntheses of indigo. Finally Emil Fischer achieves the syntheses of the sugars and so opens new horizons to biology.

For fifty years, the chemistry of carbon has formed a separate chapter, and has presented a marvelous spectacle in its development and in its important industrial applications. From the standpoint of research, organic chemistry — the fruitful theories of which have been slowly transformed — no longer finds any difficulty in determining the composition of the innumerable derivatives that it studies. Inorganic chemistry, on the contrary, though it has aroused so many efforts to establish the qualitative and quantitative analysis of its various compounds, is still far from completion. It is still in a stage of evolution, in spite of the recent work of Gooch, Clarke, and so many others. The reason for this is that some of the elements are as yet very incompletely studied. The large number of simple bodies included in inorganic chemistry increases the difficulty.

When a good part of the atomic weights had been established, the amount of effort that had to be devoted to organic chemistry caused the number of researches in inorganic chemistry to decrease. To-day, however, when the main lines of organic chemistry have been traced, and when in place of the virgin forest, as Hofman called it, there appears a complete city, beautifully laid out, the study of inorganic chemistry has come again into honor.

However, inorganic chemistry has been continuing its discoveries in the mean time. A certain number of new, and for the most part rare, elements have been isolated in the last thirty years. Lecoq de Boisbaudran, in 1875, obtained from Asturian blende a new and curious metal melting at 50°, gallium. Winkler, after very delicate analysis, obtained germanium from Freiberg argyrodite. Also, in 1886, the author of this lecture succeeded in isolating fluorin, which, though having a fairly wide distribution in nature, had previously resisted the efforts of Humphry Davy, Louyet, the Knox brothers, Fremy, and Gore.

Within the last few years, another series of discoveries has aroused the keen interest of the scientific world. As the result of delicate experiments for determining the density of nitrogen when prepared by chemical reaction, and when obtained from the air, Lord Rayleigh declared that the difference, which affected only the third decimal of his figures, was to be attributed to the existence of a gaseous element heavier than nitrogen, present in the atmosphere. Following up this physical determination, Lord Rayleigh and Sir William Ramsay isolated argon; and Sir William Ramsay obtained the satellites of argon, such as krypton, xenon, and neon. These studies led him also, turning his attention to the surface of the earth, to observe and study helium, the spectrum of which had been simultaneously discovered in the sun's rays by Sir Norman Lockyer and by Janssen.

These are splendid results, and they are the more curious since they deal with a series of gaseous bodies which, because of their chemical inertness, are a great embarrassment to the scientist and the philosopher.

But there is a group of metals which, in spite of the continued efforts of chemists, has never yet been fully studied. I refer to the rare earths, divided into the two series of cerium and yttrium.

In 1751, Cronstedt discovered cerite in a mine at Bastnaës. In 1794, Gadolin pointed out a rare earth, yttria, in a heavy black mineral which was found abundantly in the neighborhood of Ytterby, and which was afterwards named gadolinite. Cerium was characterized as an element, in 1804, by Berzelius and Hisinger in Sweden, and by Klaproth in Germany.

This first work was followed by numerous rather confused investigations, until Mosander, in 1839 and 1842, separated lanthanum and didymium from the true cerium. The study of cerium and its compounds was completed by the masterly researches of Cleve, and by Marignac, Brauner, Wyrouboff, and Verneuil. Still later, Mosander's didymium was separated by Auer von Welsbach into two elements, praseodymium and neodymium.

Samarium was studied by Cleve, Lecoq de Boisbaudran, Demarçay, Brauner, and Bettendorf. While examining the action of samarium, Demarçay proved the existence of a new element, europium.

Terminating his work on cerium, Mosander at once took up the study of yttria and from it separated erbia and terbia. This study was continued by Cleve, Marignac, Crookes, Delafontaine. In 1879, Cleve made it certain that erbia was a mixture of several earths, and since that epoch, many researches have followed up this subject. Four elements, yttrium, ytterbium, erbium, and Nilson's scandium, seem proved beyond question. The splendid work of Cleve has shown that there are yet other elements belonging to this group, in particular holmium. From the yttria group, too, Marignac has isolated an earth which has been named by Lecoq de Boisbaudran, oxide of gadolinium.

In spite of the continued efforts of the Swedish school, in spite of the researches of so many authorities, Berzelius, Mosander, Cleve, Nilson, Crookes, Marignac, Lecoq de Boisbaudran, Demarçay, Brauner, Wyrouboff, and Verneuil, this great problem of the rare earths is far from being finished. The separation of these different oxides remains one of the most difficult operations of chemistry, and yet when one compares elements so closely akin as these, one feels what interest for science would attach to a complete study of them.

In short, inorganic chemistry has never ceased progressing; and it has taken advantage of all the discoveries achieved in the other sciences.

The most striking example of this is spectral analysis. We may recall that Wollaston had in 1802 indicated the discontinuity of the solar spectrum. Later, in 1815, Frauenhofer studied the darkened rays of the solar radiation, and the luminous rays of certain spectra. Though numerous studies of this subject were made by Brewster, Wheatstone, Alter, Ångström, Masson, and Plücker, it was not till Kirchhoff's great discovery, in 1860, that the perfect correspondence between the luminous rays of different spectra and the black portions of the solar and stellar radiations became known.

Spectral analysis was thereupon inaugurated by Kirchhoff and Bunsen, and its value was immediately demonstrated by their discovery of the new elements, rubidium and cæsium. Inorganic chemistry appropriated the new method. Sir William Crookes indicated the existence of thallium, which was isolated soon after by Lamy. Reich and Richter discovered indium. Next came the discovery of gallium. Finally, in the hands of many authorities, Bunsen, Thalén, Cleve, Nilson, Crookes, Lecoq de Boisbaudran, Demarçay, Becquerel, Benedicks, this method was applied to that difficult problem of the rare earths.

The simple phenomenon of reversed lines was to extend the field of analytical chemistry to the limits of the furthest visible stars. It was destined to demonstrate that the same matter was distributed throughout the whole universe. In fact, Kirchhoff detected in the atmosphere of the sun the presence of sodium, calcium, and barium; of manganese, iron, chromium, copper, and zinc. Subsequently, Ångström and Thalén proved the existence in the sun of hydrogen, magnesium, and aluminium. Sir Norman Lockyer, in his beautiful spectral studies on the analysis of the heavenly bodies, showed that the sun contained also cadmium, strontium, cerium, lead, and potassium. Higgins followed this up by examining the spectra of stars and nebulæ, in which he met with the same elements. Le P. Secchi showed that the spectrum of comets gave the rays of the hydrocarbons.

This whole great question was reviewed and put into shape by use of new methods, by Rowland, professor in the university at Baltimore. He has given us the most important results that we possess on the composition of the sun as determined by the study of its spectrum. He has distinguished 20,000 rays, only a third of which are surely coincident with our terrestrial rays. It is true, however, that among the coincidences occur the most powerful rays of elementary bodies. Rowland concludes from this that if the earth were raised to the temperature of the sun, it would give almost the same spectrum.

Inorganic chemistry has further utilized spectral analysis for the study of band spectra, which serve the chemist as a means of analysis.

Were there any need of another example to show the fusion of inorganic chemistry and physics, we could recall the many applications of electrolysis which are utilized by chemists. Scarcely had Volta published his great discovery of the electric pile when Carlisle and Nicholson put it into use for the decomposition of water, and only a few years afterwards Humphry Davy prepared by this process the metals of the alkalies and alkaline earths. These metals in their turn served for the isolation of boron, silicon, magnesium, and aluminium.

Since that time, not a year passes without calling in electrolysis to enlarge the field of our discoveries. Many metalloids and metals are obtained to-day by this means, and the most active agent in inorganic chemistry, fluorin, could be isolated by no other method. But we ought also to recall that the study of electrochemistry, and the splendid researches of Faraday on electric conductivity, completed and extended as they were by Kohlrausch, have started chemistry in a new direction which has led to most valuable results. So true is this that Lord Rayleigh could say, at the Montreal meeting of the British Association, "It is by the study of electrolysis that we can hope to increase our knowledge of chemical reactions and of the forces that produce them; in my opinion, the next advance of the science will be by that road."

This penetration of physics into chemistry became more complete as the result of the masterly studies of Henri Sainte Claire Deville on dissociation. By systematically examining the incomplete decompositions of a certain number of substances and by showing the close connection between this dissociation and evaporation, Deville broke down the barriers that separated physical and chemical phenomena. He explained many little-understood reactions, and showed how inverse reactions were produced and how the minerals were formed in metallic veins.

Henri Debray soon demonstrated the value of Deville's ideas by his elegant experiments on the decomposition of carbonate of lime and of hydrated salts.

This matter of dissociation had also certain points of contact with the phenomena of equilibrium of which mention was made in the important memoirs of Berthelot and Péan de Saint Gills, on speeds of etherification. But I do not wish to enter upon the history of this question, for my colleague Mr. van't Hoff will speak to you about it at the Congress of Physical Chemistry, much better than I could. I will only say that at all times the two sciences of physics and chemistry have been of mutual aid and support. Victor Regnault began this great movement of physical chemistry, illumined by the brilliant discoveries of Deville, enlarged by the work of Joule, and continued with such success by Gibbs, van der Waals, van 't Hoff, Arrhenius, and Ostwald.

Passing to a different order of ideas, we may recall the splendid work of Pasteur on molecular dyssymmetry, from which started the very original investigations of Le Bel and van't Hoff on the isomerism of substances possessing rotatory power.

At every turn, inorganic chemistry depends on the data of physics. The determination of physical constants is an everyday performance in our laboratories, and often is the only guarantee of the purity of our preparations. In doubtful cases, when it becomes difficult to establish an atomic weight, the law of Dulong and Petit gives us valuable information. The whole of thermo-chemistry, indeed, founded with such success by Berthelot and by Thomson, makes use only of the methods of calorimetry.

There is another branch of physics which is called upon to render service to inorganic chemistry, and which has had a great development in the last few years; I refer to the easy production of high and low temperatures.

Metallurgy and ceramics have for thousands of years made use, industrially, of high temperatures for obtaining metals, glass, and terra-cotta. These high temperatures were secured by the combustion of wood or coal. Later, savants concentrated the solar heat by means of mirrors or burning-glasses for accomplishing some interesting experiments. Two centuries ago, the importance of the action of heat in the different reactions was so well appreciated that it served as the basis for Stahl's theory of phlogiston. And when chemistry established itself as a science, the ideas of Lavoisier on combustion were the starting-point of this profound transformation.

The employment of the oxyhydrogen blowpipe enabled Robert Hare, professor in Philadelphia, to obtain, in 1802, temperatures higher than those of the most powerful industrial furnaces, and to carry out on a small scale several very curious experiments, such as the fusion of platinum and the volatilization of silica. You know how happily Deville and Debray later applied the oxyhydrogen jet for studying the metallurgy of the platinum group. The question of the heating of ordinary furnaces was after long discussion answered both practically and theoretically by the work of Ebelmen and the important researches of Siemens.

Each of these advances was followed by a set of chemical discoveries consisting either in the more profound study of certain reactions or in the appearance of new compounds which enriched first science, and finally industry.

But the oxyhydrogen jet does not permit the attainment of a higher temperature than 1800°. The melting-point of platinum, as determined by M. Violle, is 1775°. It would be useful to study our chemical reactions above that temperature.

When we wished to reproduce the diamond, we soon saw that our study must be extended to include the various forms of carbon. So generalized, the question included the interesting topic of the solubility of carbon in melted metals. Now, as some of the metals had very high melting-points, we tried experiments with the aid of the oxyhydrogen blowpipe. Under these conditions, the fusion of the metal, in presence of an excess of carbon, occurred in an atmosphere rich in watery vapor, and therefore oxidizing. On the other hand, the combustion of the coal, and the vapor of carbon, furnished a reducing medium. The consequence was that unless a constant temperature was maintained, it was impossible to get a definite equilibrium between these opposite reactions. Besides, in these conditions complete reactions could not be obtained, and the results were variable from one experiment to another.

Already different investigators, among both scientific and industrial workers, had tried to utilize the high temperature of the electric arc, discovered a century ago by Humphry Davy. But these attempts could not be successful until the perfection of the dynamo-electric machine. Gramme's discovery and the gradual improvement of the dynamo finally placed in the hands of chemists a powerful source of electric current which was easily transformed into heat.

By a curious coincidence, our science has been able, within a few years, to thrust back the known frontiers of both heat and cold. After the important experiments of M. Cailletet, which served as the starting-point of these new studies, and after the original investigations of Raoul Pictet, Olszewski and Wroblewski, Sir James Dewar was able to obtain liquid hydrogen in the static condition, and by vaporizing this to reach the lowest temperature yet attained, that of the solidification of hydrogen, −252.5°, or 20.5° above absolute zero. Thus the usable scale of temperature has been considerably lengthened.

Less fortunate than Sir James Dewar, we have not succeeded, in a long series of experiments made by use of the electric furnace, in determining exactly the extreme limit of temperature reached. As the outcome of some delicate experiments, M. Violle has assigned as the boiling-point of carbon the temperature of 3500°. But as we shall prove further on, the temperature of the arc increases with the intensity of the current, and the measurement of these high temperatures requires further investigation. In order to fix the conditions of our experiments, we carefully stated the voltage and amperage of the current and the duration of each experiment. The diameter of the electrodes and the capacity of the furnace had been determined beforehand, and remained constant.

At the very start, we found that at the temperature of our electric furnace, the metallic oxides, hitherto regarded as irreducible, were easily decomposed. Also reactions which were only partial at the highest temperatures of ordinary furnaces became total here. A large number of compound substances were dissociated at these high temperatures, and on the other hand, new series of combinations, definite and crystallized, were obtained. We thus prepared unknown compounds of great stability, such as the carbides, borides, and silicides. Most of these new binary compounds can also be partly or wholly broken up by still further increasing the intensity of the current and with it the temperature.

Some of these carbides will furnish us a very definite scale of dissociation. We also meet here, in the neighborhood of 3000°, the same general laws which govern the decomposition of substances by heat at lower temperatures. Moreover, the boiling of a mixture of copper and lead, of tin and lead, or of copper and tin, presents the same peculiarities between 2000° and 3000° as does a mixture of water and ether, of water and alcohol, or of water and formic acid, at much lower temperatures. The laws of the fractional distillation of two liquids apply therefore to the boiling of metals at very high temperatures.

In using our electric furnace, we operate in a reducing atmosphere, and if a strong enough current is employed we get very quickly a constant temperature, which is the boiling-point of quicklime. If, on the contrary, the substance to be studied is put very close to the arc, that is to say, very close to the gaseous conductor composed of carbon vapor which unites the electrodes, the temperature rises with the intensity of the current. A chemical reaction proves this. With a current of 100 amperes and 50 volts, the reduction of titanic acid by the carbon gives an oxide of an indigo blue color. With

500 amperes and 70 volts, a fused mass of yellow nitride is obtained; while the high temperature of an arc of 1200 amperes and 70 volts gives a carbide of titanium free from nitrogen. With so intense a current as this last the nitride of titanium can no longer be formed; its dissociation by heat is complete and only the carbide can remain.

In pursuing this study, we have found still other examples of combination and then decomposition under the action of an electric arc of greater and greater intensity.

Organic chemistry comes into contact with biology; whence its greatness and also its difficulties.

Biological chemistry could not be developed till after a systematic study of the chemistry of carbon had been made. For a century it was thought that physiological chemistry needed in its manifold transformations only the four elements, carbon, hydrogen, nitrogen, and oxygen. But in recent years our ideas on this point have changed considerably. It has long been known that iron was indispensable in both the animal and vegetable kingdoms. Further, Raulin had proved by some curious experiments the important influence of traces of foreign metals on the culture of aspergillus niger. These experiments had been forgotten; they came too early.

But to-day discoveries relating to this point appear in constantly greater numbers. For example, the fine work of Frederick and of Henze has shown that copper is a constituent of hemocyanin in the blood of cuttlefishes and crustacea. We know now that iodin and bromin should be found in the thyroid gland; these elements are seen to be indispensable to the regular course of normal life. The existence of arsenic in animal tissues was a thing unheard of a few years ago. Professor Armand Gautier has now established by very delicate experiments that arsenic is always present in the horny tissues and in the thyroid gland; and M. Gabriel Bertrand has demonstrated the normal existence of arsenic in the living cells of fishes taken from the sea-bottom at a depth of 3000 meters.

In the same way, a trace of another element, such as manganese, may intervene in the form of a soluble ferment, in the oxydases. One understands then the importance of the different elements and sees that sometimes, in traces, they may play a physiological rôle of capital importance. We have long known that sulphur forms part of the proteid molecule, although we are still quite ignorant of the transformations which bring this element into complex compounds.

It is quite evident that on this point great discoveries still await their realization. We are only beginning to-day the study of the different elements in their combinations with carbon, from the physiological point of view; it may be said that the physiology of the cell remains wholly to be made. We are happy to know that a start in this direction is being made by means of microchemical reactions.

Biology therefore unites again inorganic and organic chemistry. The truth is, there is but one chemical science; every separation is artificial. Just as energy is one, chemistry is one. The splendid researches of Curtius on nitrohydric acid, and our own investigations of the metallic carbides and of the hydrides, of the alkalies and alkaline earths, show how the two chemistries constantly interpenetrate, and demonstrate the unity of the science.

It is true, however, that inorganic chemistry has a technique of its own. To make discoveries there, the precision of physics must be applied. A few examples will make my thought clearer.

Lavoisier only overthrew the theory of Stahl as the result of rigorous experiments prepared with the greatest care and exactitude. We may refer in this connection to his experiments on combustion, on respiration, and on fermentation.

Cavendish, when studying the action of the electric spark on a mixture of oxygen and nitrogen, pushed the experiment till there remained but a very small quantity of gas incapable of uniting with oxygen. He mentions its existence. Since his time, over a century ago, in how many universities, lycea, and gymnasia has this experiment of Cavendish been repeated? And yet no one, during the century, completed the experiment. It was always begun, but never finished. Any one who had carried it on patiently till the nitrogen was entirely absorbed would have discovered argon. It was needful that Lord Rayleigh should determine the densities of the gas, vouching for the third decimal place, in order that the discovery should be realized. The method is elegant, but the path of discovery is rather circuitous.

Shall I cite you another example? When Gay Lussac, in 1815, discovered cyanogen, that first example of a compound playing the part of an element, that first radical formed of nitrogen and carbon, he prepared it by moderately heating pure, dry cyanide of mercury. The cyanide in these conditions split into cyanogen gas and mercury. The experiment is of the simplest. Only a few years before, Proust also had heated cyanide of mercury in a retort. He had obtained ammonia, an apparently oily compound, nitrogen, carbon dioxide and monoxide. The reason was that Proust used damp cyanide. This difference in manner of conducting the same experiment between two men of the ability of Gay Lussac and Proust seemed to me very interesting.

To return to Gay Lussac's preparation of cyanogen. He had left in the bottom of his retort a small quantity of a black powder. After establishing the formula of cyanogen, the existence of hydrocyanic acid and of the cyanides and cyanates, he made an analysis of this powder. It had exactly the same composition as cyanogen. Gay Lussac notes this fact, but he takes care not to go farther, and chemistry had to wait till the researches of Troost and Hautefeuille, published in 1873, before knowing the laws of the transformation of cyanogen into its polymere paracyanogen.

I might further cite for you on this point Humphry Davy's method of work; I might recall to your minds the fact that Wöhler was a master of chemical analysis, and outline for you the excellent studies of Berzelius or of Stas. If I have lingered on this topic, it is because I regard it as most important. Many great investigations remain to be made in inorganic chemistry, but to get them done, the methods must be refined and attain great precision. In a word, experimental research in chemistry should have the rigor of physical experiments.

But to return to the relations of chemistry with the other sciences. We have already spoken of physics and biology. I do not wish to enlarge beyond measure on this point. I will remind you that astronomy, thanks to spectrum analysis, the joint product of physics and chemistry, has been able to extend and develop certain of its theories to include the remotest star visible in our horizon. Moreover, the spectroscopic method of Doppler and Fizeau has been of great service in determining the speed of the heavenly bodies. . .

Our chemistry also comes into contact with mathematics at two important points. It comes into contact with statics in stereochemistry and the special grouping of atoms, in questions of symmetry and in combinational analysis which studies the combinations of objects associated in different conditions. It comes into contact with mathematics also on the dynamic side, in that it involves the principles of molecular mechanics in connection with the conservation of energy and the mechanical theory of heat.

Chemical analysis is one of the foundations of mineralogy. It is of the greatest service to geology, which could not do without it. The majority of the sciences have need of its assistance, and even the historian comes to it to inquire the age of the successive foundations of the ruins of Babylon, bringing to it the bronze or copper objects which the latest excavations have put into his hands.

When it comes to industrial applications of the various sciences, very few of them are not in debt to chemistry. The engineer has constant need of it. Studies of the metals and their alloys have given all their efficiency to machines, ships, and firearms. Two chapters, however, in the applications of science will depend absolutely on the progress of chemistry; we refer to the chemical industry and to rural economy, — so important that they change the destinies of nations, mingle the stocks of peoples, and modify the conditions of their existence.

It is not our part to enlarge upon this side of the question; it is enough to have mentioned it, and to recall, in closing, the vast sum of effort which these researches have demanded. In the midst of these incessant transformations, this continued progress, we see that scientific research has never had but one method: experiment. Faraday's dictum is always true: "Chemistry is essentially an experimental science."

THE PRESENT PROBLEMS OF INORGANIC CHEMISTRY

BY SIR WILLIAM RAMSAY

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To discuss the "present problems of inorganic chemistry" is by no means an easy task. The expression might be taken to mean an account of what is being actually done at present by those engaged in inorganic research; or it might be taken to relate to what needs doing — to the direction in which research is required. To summarize what is being done in an intelligible manner in the time at my disposal would be an almost impossible task; hence I will choose the latter interpretation of the title of my address. Now, a considerable experience in attempting to unveil the secrets of nature has convinced me that a deliberate effort to discover some new law or fact seldom succeeds. The investigator generally begins unmethodically, by random and chance experiments; or perhaps he is guided by some indication which has struck his attention during some previous research; and he is often the plaything of circumstances in his choice. Experience leads him to choose problems which most readily admit of solution, or which appear likely to lead to the most interesting results. If I may be excused the egotism of referring to my own work, I may illustrate what I mean by relating the following curious coincidence: After Lord Rayleigh had announced his discovery that "atmospheric nitrogen" was denser than "chemical nitrogen," I referred to Cavendish's celebrated paper on the combination of the nitrogen and the oxygen of the air by means of electric sparks. Fortified by what I read, and by the knowledge gained during the performance of lecture-experiments that red-hot magnesium is a good and fairly rapid absorbent of nitrogen, it was not long before a considerable quantity of nearly pure argon had been separated from atmospheric nitrogen. Now it happens that I possess two copies of Cavendish's works; and some months afterwards I consulted the other copy and found penciled on the margin the words "look into this." I remembered the circumstance which led to the annotation. About ten years before, one of my students had investigated the direct combination of nitrogen and hydrogen, and I had read Cavendish's memoir on that occasion. I mention this fact to show that, for some reason which I forget, a line of work was not followed up, which would have been attended by most interesting results; one does not always follow the clue which yields results of the greatest interest. I regard it therefore as an impossible task to indicate the lines on which research should be carried out. All that I can do is to call attention to certain problems awaiting solution; but their relative importance must necessarily be a matter of personal bias, and others might with perhaps greater right suggest wholly different problems.

The fundamental task of inorganic chemistry is still connected with the classification of elements and compounds. The investigation of the classification of carbon compounds forms the field of organic chemistry; while general or physical chemistry deals with the laws of reaction, and the influence of various forms of energy in furthering or hindering chemical change. And classification centres at present in the periodic arrangement of the elements, according to the order of their atomic weights. Whatever changes in our views may be concealed in the lap of the future, this great generalization, due to Newlands, Lothar Meyer, and Mendeléeff, will always retain a place, perhaps the prominent place, in chemical science.

Now it is certain that no attempt to reduce the irregular regularity of the atomic weights to a mathematical expression has succeeded; and it is, in my opinion, very unlikely that any such expression, of not insuperable complexity, and having a basis of physical meaning, will ever be found. I have already, in an address to the German Association at Cassel, given an outline of the grand problem which awaits solution. It can be shortly stated then: While the factors of kinetic and of gravitational energy, velocity, and momentum, on the one hand, and force and distance, on the other, are simply related to each other, the capacity factors of other forms of energy; — surface, in the case of surface-energy; volume, in the case of volume-energy; entropy for heat; electric capacity when electric charges are being conveyed by means of ions; atomic weight, when chemical energy is being gained or lost; — all these are simply connected with the fundamental chemical capacity, atomic weight, or mass. The periodic arrangement is an attempt to bring the two sets of capacity factors into a simple relation to each other; and while the attempt is in so far a success, inasmuch as it is evident that some law is indicated, the divergences are such as to show that finality has not been attained. The central problem in inorganic chemistry is to answer the question, why this incomplete concordance? Having stated the general question, it may conduce to clearness if some details are given.

(1) The variation of molecular surface-energy with temperature is such that the surface-energy, for equal numbers of molecules distributed over a surface, is equal for equal intervals of temperature below the temperature at which surface-energy is zero — that is, the critical point. This gives a means of determining the molecular weights of liquids, and we assume that the molecular weight of a compound is accurately the sum of the atomic weights of the constituent elements.

(2) The volume-energy of gases is equal at equal temperature from that at which volume-energy is zero — *i. e.*, absolute zero. And it follows that those volumes of gases which possess equal volume-energy contain equal numbers of molecules — again, a close connection with atomic weights.

(3) The specific heats of elements are approximately inversely proportional to their atomic weights; and of compounds to the quotient of their molecular weights divided by the number of atoms in the molecule. Specific heat and entropy are closely related; hence one of the factors of thermal energy is proportional (nearly) to the reciprocal of the atomic weights.

(4) The ion carries in its migration through a solution one or more electrons. Now, the ion is an atom carrying one or more charges — one for each equivalent. Here we have the capacity for electric charge proportional to the equivalent.

(5) The factors of chemical energy are atomic weight and chemical potential; and as the former is identical numerically, or after multiplication by a simple factor with equivalent, electric potential is proportional to chemical potential.

We see, therefore, that surface, volume, thermal, electrical,and, no doubt, other forms of energy have as capacity factors magnitudes, either identical with, or closely related to, units of chemical capacity; while kinetic and linear energy are not so related, except through the periodic arrangement of the elements.

It appears, therefore, to be a fundamental problem for the chemist to ascertain, first, accurate atomic weights, and, second, to investigate some anomalies which still present difficulties. In America, you have excellent workers in the former branch. Mallet, Morley, Richards, and many others have devoted their time and skill to perhaps the best work of this kind which has been done; and F. W. Clarke has collated all results and afforded incalculable help to all who work at or are interested in the subject. Valuable criticisms, too, have been made by Hinrichs; but it must be confessed that in spite of these, which are perhaps the best determinations which have been made, the problem becomes more, and not less, formidable.

There are lines of work, however, which suggest themselves as possibly likely to throw light on the question. First, there is a striking anomaly in the atomic weight of nitrogen, determined by analysis and determined by density. Stas obtained the number 14.04 ($O = 16$), and Richards has recently confirmed his results; while Rayleigh and Leduc consistently obtained densities which, even when corrected so as to equalize the numbers of molecules in equal volumes, give the lower figure 14.002. The difference is 1 in 350; far beyond any possible experimental error. Recently, an attempt to combine the two methods has led to a mean number; but that result can hardly be taken as final. What is the reason of the discrepancy? Its discovery will surely advance knowledge materially. I would suggest the preparation of pure compounds of nitrogen, such as salts of hydrazine, methylanine, etc., and their careful analysis; and also the accurate determination of the density and analysis of such gaseous compounds of nitrogen as nitric oxide and peroxide. I have just heard from my former student, R. W. Gray, that he has recovered Stas's number by combining $2NO$ with O_2; while the density of NO leads to the lower value for the atomic weight of nitrogen.[1]

The question of the atomic weight of tellurium appears to be settled, at least so far as its position with regard to the generally accepted atomic weight of iodin is concerned; recent determinations give the figures 127.5 (Gutbier), 127.6 (Pellini), and 127.9 (Köthner). But is that of iodin as accurately known? It would appear advisable to revise the determination of Stas, preparing the iodin preferably from an organic compound, such as iodoform, which can be produced in a high state of purity. The heteromorphism of selenates and tellurates, too, has recently been demonstrated; and it may be questioned whether these elements should both belong to the same group.

The rare earths still remain a puzzle. Their number is increasing yearly, and their claim to individuality admits of less and less dispute. What is to be done with them? Are they to be grouped by themselves as Brauner and Steele propose? If so, how is their connection with other elements to be explained? Recent experiments in my laboratory have convinced me that in the case of thorium, at least, ordinary tests of purity such as fine crystals, constant subliming point, etc., do not always indicate homogeneity; or else that we are sadly in want of some analytical method of sufficient accuracy. The change of thorium into thorium *X* is perhaps hardly an explanation of the divergences; yet it must be considered; but of this, anon.

To turn next to another problem closely related to the orderly arrangement of the elements, — that of valency, — but little progress can be chronicled. The suggestions which have been made are specu-

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[1] Note added February, 1906: Researches by Gray and by Guye have since shown that Stas's results are in error; and determinations by Richards allow the same conclusion to be drawn. The actual atomic weight cannot differ much from 14.007.

lative, rather than based on experiment. The existence of many peroxidized substances, such as percarbonates, perborates, persulphates, and of crystalline compounds of salts with hydrogen peroxide, makes it difficult to draw any indisputable conclusions as regards valency from a consideration of oxygen compounds. Moissan's brilliant work on fluorides, however, has shown that SF_6 is capable of stable existence, and this forms a strong argument in support of the hexad character of sulphur. The tetravalency of oxygen, under befitting conditions, too, is being acknowledged, and this may be reconciled with the existence of water of crystallization, as well as of the per-salts already mentioned. The adherence of ammonia to many chlorides, nitrates, etc., points to the connecting link being ascribable to the pentavalency of nitrogen; and it might be worth while investigating similar compounds with phosphoretted and arseniuretted hydrogen, especially at low temperatures.

The progress of chemical discovery, indeed, is closely connected with the invention of new methods of research, or the submitting of matter to new conditions. While Moissan led the way by elaborating the electric furnace, and thus obtained a potent agent in temperatures formerly unattainable, Spring has tried the effect of enormous pressure, and has recently found chemical action between cuprous oxide and sulphur at ordinary temperature, provided the pressure be raised to 8000 atmospheres. Increase of pressure appears to lower the temperature of reaction. It has been known for long that explosions will not propagate in rarefied gases, and that they become more violent when the reacting gases are compressed: but we are met with difficulties, such as the non-combination of hydrogen and nitrogen, even at high temperature and great pressure; yet it is possible to measure the electromotive force (0.59 volt) in a couple consisting of gaseous nitrogen and gaseous hydrogen, the electrolyte being a solution of ammonium nitrate saturated with ammonia. Chemical action between dissolved hydrogen and nitrogen undoubtedly occurs; but it is not continuous. Again we may ask, Why? The heat evolution should be great; the gain of entropy should also be high were direct combination to occur. Why does it not occur to any measurable extent? Is it because for the initial stages of any chemical reaction, the reacting molecules must be already dissociated, and those of nitrogen are not? Is that in any way connected with the abnormally low density of gaseous nitrogen? Or is it that, in order that combination shall occur, the atoms must fit each other; and that, in order that nitrogen and hydrogen atoms may fit, they must be greatly distorted? But these are speculative questions, and it is not obvious how experiments can be devised to answer them.

Many compounds are stable at low temperatures which dissociate when temperature is raised. Experiments are being made, now that liquid air is to be purchased or cheaply made, on the combinations of substances which are indifferent to each other at ordinary temperatures. Yet the research must be a restricted one, for most substances are solid at −185°, and refuse to act on each other. It is probable, however, that at low temperatures compounds could be formed in which one of the elements would possess a greater valency than that usually ascribed to it; and also that double compounds of greater complexity would prove stable. Valency, indeed, appears to be in many cases a function of temperature; exothermic compounds, as is well known, are less stable, the higher the temperature. The sudden cooling of compounds produced at a high temperature may possibly result in forms being preserved which are unstable at ordinary temperatures. Experiments have been made in the hope of obtaining compounds of argon and helium by exposing various elements to the influence of sparks from a powerful induction coil, keeping the walls of the containing-vessel at the temperature of liquid air, in the hope that any endothermic compound which might be formed would be rapidly cooled, and would survive the interval of temperature at which decomposition would take place naturally. But these experiments have so far yielded only negative results. There is some indication, however, that such compounds are stable at 1500°. It might be hoped that a study of the behavior of the non-valent elements would have led to some conception of the nature of valency; but so far, no results bearing on the question have transpired. The condition of helium in the minerals from which it is obtainable by heat is not explained; and experiments in this direction have not furnished any positive information. It is always doubtful whether it is advisable to publish the results of negative experiments; for it is always possible that some more skilled or more fortunate investigator may succeed, where one has failed. But it may be chronicled that attempts to cause combination between the inactive gases and lithium, potassium, rubidium, and cæsium have yielded no positive results; nor do they appear to react with fluorin. Yet conditions of experiment play a leading part in causing combination, as has been well shown by Moissan with the hydrides of the alkali-metals, and by Guntz, with those of the metals of the alkaline earths. The proof that sodium hydride possesses the formula NaH, instead of the formerly accepted one, removes one difficulty in the problem of valency; and SrH_2 falls into its natural position among hydrides.

A fertile field of inorganic research lies in the investigation of structure. While the structure of organic compounds has been elucidated almost completely, that of inorganic compounds is practically undeveloped. Yet efforts have been made in this direction which appear to point a way. The nature of the silicates has been the subject of research for many years by F. W. Clarke; and the way has been opened. Much may be done by treating silicates with appropriate solvents, acid or alkaline, which differentiate between uncombined and combined silica, and this in some cases, by replacement of one metal by another, gives a clue to constitution. The complexity of the molecules of inorganic compounds, which are usually solid, forms another bar to investigation. It is clear that sulphuric acid, to choose a common instance, possesses a very complicated molecule; and the fused nitrates of sodium and potassium are not correctly represented by the simple formulæ $NaNO_3$ and KNO_3. Any theory of the structure of their derivatives must take such facts into consideration; but we appear to be getting nearer the elucidation of the molecular weights of solids. Again, the complexity of solutions of the most common salts is maintained by many investigators; for example, a solution of cobalt chloride, while it undoubtedly contains among other constituents simple molecules of $CoCl_2$, also consists of ions of a complex character, such as $(CoCl_4)''$. And what holds for cobalt chloride also undoubtedly holds for many similar compounds.

In determining the constitution of the compounds of carbon, stereochemistry has played a great part. The ordinary structural formulæ are now universally acknowledged to be only pictorial, if, indeed, that word is legitimate; perhaps it would be better to say that they are distorted attempts at pictures, the drawing of which is entirely free from all rules of perspective. But these formulæ may in almost every case be made nearly true pictures of the configuration of the molecules. The benzene formula, to choose an instance which is by no means the simplest, has been shown by Collie to be imitated by a model which represents in an unstrained manner the behavior of that body on treatment with reagents. But in the domain of inorganic chemistry, little progress has been made. Some ingenious ideas of the geologist Sollas on this problem have hardly received the attention which they deserve; perhaps they may have been regarded as too speculative. On the other hand, Le Bel's and Pope's proof of the stereo-isomerism of certain compounds of nitrogen; Pope's demonstration of the tetrahedral structure of the alkyl derivatives of tin; and Smiles's syntheses of stereo-isomeric sulphur compounds give us the hope that further investigation will lead to the classification of many other elements from this point of view. Indeed, the field is almost virgin soil; but it is well worth while cultivating. There is no doubt that the investigation of other organo-metallic compounds will result in the discovery of stereo-isomerides; yet the methods of investigation capable of separating such constituents have in most cases still to be discovered.

The number of chemical isomerides among inorganic compounds is a restricted one. Werner has done much to elucidate this subject in the case of complex ammonia derivatives of metals and their salts;

but there appears to be little doubt that if looked for, the same or similar phenomena would be discoverable in compounds with much simpler formulæ. The two forms of SO_3, sulphuric anhydride, are an instance in point. No doubt formation under different conditions of temperature and pressure might result in the greater stability of some forms which under our ordinary conditions are changeable and unstable. The fact that under higher pressures than are generally at our disposal different forms of ice have been proved to exist, and the application of the phase rule to such cases will greatly enlarge our knowledge of molecular isomerism.

The phenomena of catalysis have been extensively studied of recent years, and have obviously an important bearing on such problems. A catalytic agent is one which accelerates or retards the velocity of reaction. Without inquiring into the mechanism of catalysis, its existence may be made to influence the rate of chemical change, and to render bodies stable which under ordinary conditions are unstable. For if it is possible to accelerate a chemical change in such a way that the usually slow and possibly unrecognizable rate of isomeric change may be made apparent and measurable, a substance the existence of which could not be recognized under ordinary circumstances, owing to its infinitesimal amount, may be induced to exist in weighable quantity, if the velocity of its formation from an isomeride can be greatly accelerated by the presence of an appropriate catalytic agent. I am not aware that attempts have been made in this direction. The discovery of catalytic agents is, as a rule, the result of accident. I do not think that any guide exists which would enable us to predict that any particular substance would cause an acceleration or a retardation of any particular reaction. But catalytic agents are generally those which themselves, by their power of combining with or parting with oxygen, or some other element, cause the transfer of that element to other compounds to take place with increased or diminished velocity. It is possible, therefore, to cause ordinary reactions to take place in presence of a third body, choosing the third body with a view to its catalytic action, and to examine carefully the products of the main reaction as regards their nature and their quantity. Attempts have been made in this direction with marked success; the rate of change of hydrogen dioxide, for example, has been fairly well studied. But what has been done for that compound may be extended indefinitely to others, and doubtless with analogous results. Indications of the existence of as yet undiscovered compounds may be derived from a study of physical, and particularly of electrical, changes. There appears to be sufficient evidence of an oxide of hydrogen containing more oxygen than hydrogen dioxide, from a study of the electromotive force of a cell containing hydrogen dioxide; yet the higher oxide still awaits discovery.

The interpretation of chemical change in the light of the ionic theory may now be taken as an integral part of inorganic chemistry. The ordinary reactions of qualitative and quantitative analysis are now almost universally ascribed to the ions, not to the molecules. And the study of the properties of most ions falls into the province of the inorganic chemist. To take a familiar example: The precipitation of hydroxides by means of ammonia-solution has long led to the hypothesis that the solution contained ammonium hydroxide; and indeed, the teaching of the text-books and the labels on the bottles supported this view. But we know now that a solution of ammonia in water is a complex mixture of liquid ammonia and liquid water; of ammonium hydroxide, NH_4OH; and of ions of ammonium $(NH_4)'$, and hydroxyl $(OH)'$. Its reactions, therefore, are those of such a complex mixture. If brought into contact with a solution of some substance which will withdraw the hydroxyl ions, converting them into water, or into some non-ionized substance, they are replaced at the expense of the molecules of non-ionized ammonium hydroxide; and these, when diminished in amount, draw on the store of molecules of ammonia and water, which combine, so as to maintain equilibrium. Now the investigation of such changes must belong to the domain of inorganic chemistry. It is true that the methods of investigation are borrowed from the physical chemist; but the products lie in the province of the inorganic chemist. Indeed, the different departments of chemistry are so interlaced that it is impossible to pursue investigations in any one branch without borrowing methods from the others; and the inorganic chemist must be familiar with all chemistry, if he is to make notable progress in his own branch of the subject. And if the substances and processes investigated by the inorganic chemist are destined to become commercially important, it is impossible to place the manufacture on a sound commercial basis without ample knowledge of physical methods, and their application to the most economical methods of accelerating certain reactions and retarding others, so as to obtain the largest yield of the required product at the smallest cost of time, labor, and money.

I have endeavored to sketch some of the aspects of inorganic chemistry with a view to suggesting problems for solution, or at least the directions in which such problems are to be sought. But the developments of recent years have been so astonishing and so unexpected, that I should fail in my duty were I not to allude to the phenomena of radioactivity, and their bearing on the subject of my address. It is difficult to gauge the relative importance of investigations in this field; but I may be pardoned if I give a short account of what has already been done, and point out lines of investigation which appear to me likely to yield useful results.

The wonderful discovery of radium by Madame Curie, the preparation of practically pure compounds of it, and the determination of its atomic weight, are familiar to all of you. Her discovery of polonium, and Debierne's of actinium, have also attracted much attention. The recognition of the radioactivity of uranium by Becquerel, which gave the first impulse to these discoveries, and of that of thorium by Schmidt, is also well known.

These substances, however, presented at first more interest for the physicist than the chemist, on account of the extraordinary power which they all possess of emitting "rays." At first, these rays were supposed to constitute ethereal vibrations; but all the phenomena were not explicable on that supposition. Schmidt first, and Rutherford and Soddy later, found that certain so-called "rays" really consist of gases; and that while thorium emits one kind, radium emits another; and no doubt Debierne's actinium emits a third. The name "emanations" was applied by Rutherford to such radioactive bodies; he and Soddy found that those of radium and thorium could be condensed and frozen by exposure to the temperature of liquid air, and that they were not destroyed or altered in any way by treatment with agents which are able to separate all known gases from those of the argon group, namely, red-hot magnesium-lime, and it was later found that sparking with oxygen in presence of caustic potash did not affect the gaseous emanation from radium. The conclusion therefore followed that in all probability these bodies are gases of the argon group, the atomic weight of which, and consequently the density, is very high; indeed, several observers, by means of experiments on the rate of diffusion of the gas from radium, believe it to have a density of approximately 100, referred to the hydrogen standard. This conclusion has been confirmed by the mapping of the spectrum of the radium emanation, which is similar in general character to the spectra of the inactive gases, consisting of a number of well-defined, clearly cut brilliant lines, standing out from a black background. The volume of the gas produced spontaneously from a given weight of radium bromide in a given time has been measured; and it was incidentally shown that this gas obeys Boyle's law of pressures. The amount of gas thus collected and measured, however, was very minute; the total quantity was about the forty-thousandth of a cubic centimeter.

Having noticed that those minerals which consist of compounds of uranium and thorium contain helium, Rutherford and Soddy made the suggestion that it might not be impossible that helium is the product of the spontaneous change of the emanation; and Soddy and I were able to show that this is actually the case. For, first, when a quantity of radium salt which has been prepared for some time is dissolved in water, the occluded helium is expelled, and can be recognized by means of its spectrum; further, the fresh emanation shows no helium spectrum, but after a few days the spectrum of helium begins to appear, proving that a spontaneous change is in progress; and last, as the emanation disappears its volume decreases to zero; and on heating the capillary glass tube which contained it, helium is driven out from the glass walls, into which its molecules had been imbedded in volume equal to three and a half times that of the emanation. The *a* rays, as foreshadowed by Rutherford and Soddy, consist of helium particles.

All these facts substantiate the theory, devised by Rutherford and Soddy, that the radium atom is capable of disintegration, one of the products being a gas, which itself undergoes further disintegration, forming helium as one of its products. Up till now, the sheet-anchor of the chemists has been the atom. But the atom itself appears to be complex, and to be capable of decomposition. It is true that only in the case of a very few elements, and these of high atomic weight, has this been proved. But even radium, the element which has by far the most rapid rate of disintegration, has a comparatively long life; the period of half-change of any given mass of radium is approximately 1100 years. The rate of change of the other elements is incomparably slower. This change, too, at least in the case of radium and its emanation, and presumably also in the case of other elements, is attended with an enormous loss of energy. It is easy to calculate from heat measurements (and independent and concordant measurements have been made) that one pound of emanation is capable of parting with as much energy as several hundred tons of nitroglycerine. The order of the quantity of energy evolved during the disintegration of the atom is as astonishing as the nature of the change. But the nature of the change is parallel to what would take place if an extremely complicated hydrocarbon were to disintegrate; its disruption into simpler paraffins and olefines would also be attended with loss of energy. We may therefore take it, I think, that the disintegration hypothesis of Rutherford and Soddy is the only one which will meet the case.

If radium is continually disappearing, and would totally disappear in a very few thousand years, it follows that it must be reproduced from other substances, at an equal rate. The most evident conjecture, that it is formed from uranium, has not been substantiated. Soddy has shown that salts of uranium, freed from radium, and left for a year, do not contain one ten-thousandth part of the radium that one would expect to be formed in the time. It is evident, therefore, that radium must owe its existence to the presence of some other substances, but what they are is still unascertained.

During the investigation of Rutherford and Soddy of the thorium emanation, a most interesting fact was observed, namely, that precipitation of the thorium as hydroxide by ammonia left unprecipitated a substance, which they termed thorium X, and which was itself highly radioactive. Its radioactive life, however, was a short one; and as it decayed, it was reproduced from its parent thorium at an equal rate. Here is a case analogous to what was sought for with radium and uranium; but evidently uranium is not the only parent of radium; the operation is not one of parthenogenesis. Similar facts have been elicited for uranium by Crookes.

The α rays, caused by the disintegration of radium and of its emanation, are accompanied by rays of quite a different character; these are the β rays, identical with electrons, the mass of which has been measured by J. J. Thomson and others. These particles are projected with enormous velocity, and are capable of penetrating glass and metal screens. The power of penetration appears to be proportional to the amount of matter in the screen, estimated by its density. These electrons are not matter; but, as I shall relate, they are capable of causing profound changes in matter.

For the past year, a solution of radium bromide has been kept in three glass bulbs, each connected to a Topler pump by means of capillary tubing. To insure these bulbs against accident, each was surrounded by a small beaker; it happened that one of these beakers consisted mainly of potash glass; the other two were of soda glass. The potash-glass beaker became brown, while the two soda-glass beakers became purple. I think there is every probability that the colors are due to liberation of the metals potassium and sodium in the glass. They are contained in that very viscous liquid, glass, in the colorless ionic state; but these ions are discharged by the β rays, or negative electrons, and each metal imparts its own peculiar color to the glass, as has been shown by Maxwell Garnett. This phenomenon, however interesting, is not the one to which I desire to draw special attention. It must be remembered that the beakers have been exposed only to β rays; α rays have never been in contact with them; they have never been bombarded by what is usually called matter, except by the molecules of the surrounding air. Now these colored beakers are radioactive, and *the radioactive film dissolves in water*. After careful washing, the glass was no longer radioactive. The solution contains an emanation, for on bubbling air through it, and cooling the issuing air with liquid air, part of the radioactive matter was retained in the cooled tube. This substance can be carried into an electroscope by a current of air, after the liquid air has been withdrawn, and as long as the air-current passes, the electroscope is discharged; the period of decay of this emanation, however, is very rapid, and on ceasing the current of air, the leaves of the electroscope cease to be discharged. In having such a short period of existence, this emanation resembles the one from actinium.

Owing to the recess, only a commencement has been made with the investigation of the residue left on evaporation of the aqueous solution. On evaporation, the residue is strongly active. Some mercurous nitrate was then added to the dissolved residue, and it was treated with hydrochloric acid in excess, to precipitate mercurous chloride. The greater part of the active matter was thrown down with the mercurous chloride, hence it appears to form an insoluble chloride. The mercurous chloride retained its activity unchanged in amount for ten days. The filtrate from the mercurous chloride, on evaporation, turned out to be active; and on precipitating mercuric sulphide in it, the sulphide precipitate was also active; but its activity decayed in one day. The filtrate from the mercuric sulphide gave inactive precipitates with ferric salts and ammonia, with zinc salts and ammonium sulphide, with calcium salts and ammonium carbonate; and on final evaporation, the residue was not radioactive. Hence the active matter forms an insoluble chloride and sulphide. The precipitated mercurous chloride and mercuric sulphide were dissolved in *aqua regia*, and the solution was evaporated. The residue was dissolved in water, and left the dish inactive. But the solution gave an insoluble sulphate, when barium chloride and sulphuric acid were added to it; hence the radioactive element forms an insoluble sulphate, as well as an insoluble chloride and sulphide.

This is a sample of the experiments which have been made. It may be remarked that the above results were obtained from a mixture of the potash and soda glass; somewhat different results were obtained from the potash glass alone. These changes appear to be due to the conversion of one or more of the constituents of the glass into other bodies. Needless to say, neither of the samples of glass contained lead.

I have mentioned these experiments in detail, because I think they suggest wholly new lines of investigation. It would appear that if energy can be poured into a definite chemical matter, such as glass, it undergoes some change, and gives rise to bodies capable of being tested for; I imagine that radioactive forms of matter are produced, either identical with or allied to those at present known. And just as radium and other radioactive elements suffer degradation spontaneously, evolving energy, so I venture to think that if energy be concentrated in the molecules of ordinary forms of matter, a sort of polymerization is the result, and radioactive elements, probably elements with high atomic weight, and themselves unstable, are formed. Of course further research may greatly modify these views; but some guide is necessary, and Mr. Ternent Cook, who has helped me in these experiments, and I, suggest this hypothesis (in the words of Dr. Johnstone Stoney, an hypothesis is "a supposition which we hope may be useful") to serve as a guide for future endeavor.

In the light of such facts, speculation on the periodic arrangement of the elements is surely premature. It is open to any one to make suggestions; they are self-evident. Most of you will agree with the saying, "It is easy to prophesy after the event." I prefer to wait until prophecy becomes easy.

I must ask your indulgence for having merely selected a few out of the many possible views as regards the Problems of Inorganic Chemistry. I can only plead in excuse that my task is not an easy one; and I venture to express the hope that some light has been thrown on the shady paths which penetrate that dark region which we term the future.

SECTION B — ORGANIC CHEMISTRY

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(*Hall* 16, *September* 21, 3 *p. m.*)

CHAIRMAN: PROFESSOR ALBERT B. PRESCOTT, University of Michigan.
SPEAKERS: PROFESSOR JULIUS STIEGLITZ, University of Chicago.
PROFESSOR WILLIAM A. NOYES, National Bureau of Standards.

THE Chairman of the Section of Organic Chemistry was Professor Albert B. Prescott, of the University of Michigan, who opened the proceedings by saying that "we are indebted to every one of the speakers so far heard in the Department of Chemistry for important studies of the element carbon, whether studies of the history, the present problems, or the co-relations of chemical science. We are under special obligations to the departmental address, yesterday, on the 'Fundamental Conceptions of Chemical Change,' by a devotee and a master of the investigation of carbon compounds. We found the keenest interest, this morning, in the utterances of authority and mature judgment upon questions touching the nature and relationship of chemical elements in general, all bearing upon the character of this element, whose unlimited synthetic powers have enlisted so large a share of the labor of the chemical world. It but exemplifies the unity of scientific truth, that all the divisions of chemical science interweave with each other, so that each is strengthened and directed by the growth of all the others. And in the addresses in Sections to-morrow, in Physical Chemistry at ten and in Physiological Chemistry at three, I confidently expect that organic chemists will find no less direct an interest bearing upon their own labors."

THE RELATIONS OF ORGANIC CHEMISTRY TO OTHER SCIENCES

BY JULIUS STIEGLITZ

[**Julius Stieglitz,** Professor of Chemistry, University of Chicago, since 1905. A.M. and Ph.D., University of Berlin, 1889; University Scholar, Clark University, 1890; Chemical Laboratory, Detroit, 1890–92; Docent in Chemistry, University of Chicago, 1892–93; Assistant, *ibid.* 1893–94; Instructor, *ibid.* 1894–97; Assistant Professor, *ibid.* 1897–1902; Associate Professor, *ibid.* 1902–05.]

THE very name of the branch of chemistry on whose relations to other sciences I have the privilege of addressing you to-day tells us with what sciences in particular, other than sister branches of chemistry itself, organic chemistry must stand in closest relationship. Since Wöhler in 1828 by the synthesis of urea showed that there is no fundamental difference between compounds prepared in the laboratory and the same compounds formed in living organisms under the influence of what until then was known as "vital force," organic chemistry has become knitted more and more closely with all branches of the great science of organic life. Its achievements in the past culminated, we may say, in Fischer's synthesis of the important hexoses and his magnificent development, with the aid of van 't Hoff and Le Bel's great theory, of the fact that there is an intimate connection between the stereochemical configurations of organic compounds and their production and assimilation in living organisms. Great as these and similar achievements have been, they can be but an earnest of what must still be done and is being done to have organic chemistry do its full duty in the study of life's development, its maintenance, its decay. The very fact that every stage of life in the animal and the vegetable kingdom, in the lowest and the highest orders, is indissolubly connected with the formation or transformation of very complex organic compounds shows us where the path of the organic chemist must lead to, difficult as the way may be. The plant physiologists, physiological chemists, physiologists, anatomists, bacteriologists have piled up questions for us at a far greater rate than we have been able to answer them.

Before this host of questions there is one to which I wish to call your attention in particular this afternoon in the time at our disposal, and to whose answer I wish to bring a small contribution based on work done with Messrs. Derby, McCrackon, and Schlesinger. The composition, structure, and configuration of the innumerable compounds connected with vital phenomena are problems of the highest importance. But the questions as to *how* and *why* such molecules are formed and transformed seem equally important, for if the transformation ceases, life also ceases, even in the presence of abundance of valuable molecules that build up organisms. Now we are all aware of the fact that there is almost no vital transformation of matter that is not regulated by so-called "catalytic" agents,—enzymes, acids, bases, salts, — in fact, as not long ago was pointed out, an organism seems an almost perfectly regulated machine for the transformation of matter, and the regulators seem to be the catalytic agents! They determine the speed of chemical changes, and, as Euler states, it seems almost certain that without the catalyzer there would be no transformation, no chemical action at all. When, a short time ago, Jacques Loeb startled the world by the artificial fertilization of eggs of sea-urchins and other marine animals by salt solutions of definite composition and concentrations of their ions, he suggested in one of his addresses that the key to his results would most likely be found in the fact that in all eggs there is a tendency to develop, but that if the development were not hastened so as to reach a certain stage within a given time-limit, death would follow without the production of the young animal. But if the development were accelerated sufficiently, a normal development of life would follow. According to Loeb, then, even this fundamental life-fact, the fertilization of eggs, involves probably to a large extent a question of an accelerated reaction, or, as we may say, a "catalytic" problem. In Loeb's experiments and hundreds of others we know what the ultimate results of the catalytic reactions are, but we are just beginning to have any experimental answers to the question why and how catalyzers exert their marvelous accelerating influences. It may be there is no general answer possible to this question which would cover all cases — we can only know after the study of a large number of individual cases. In this semi-darkness we may distinguish for the present two classes of catalytic reactions, first those produced by so-called heterogeneous or physical agents, like platinum black, and secondly those produced by what may be called homogeneous chemical catalyzers such as acids, alkalies, salts. In an endeavor to ascertain in some individual case the exact manner in which a catalytic agent acts, a reaction of the second simpler class was chosen, namely, the thoroughly studied catalysis of an ester like methyl acetate under the influence of acids and water. As we all know, the facts are the following: the saponification of methyl acetate by water according to the equation

$$CH_3CO_2CH_3 + H_2O \rightleftarrows CH_3CO_2H + CH_3OH$$

proceeds exceedingly slowly. Acids greatly accelerate the saponification proportionately to the concentration of the hydrogen ions used. It has been established by Knoblauch and Kistiakonsky that the ultimate condition of equilibrium of the reversible reaction is not sensibly altered by the catalyzer, in other words, that the acid accelerates the reaction velocity in either direction to the same extent. In the third place, the catalytic agent appears to act by its presence simply; it appears, at least, to remain unchanged throughout the course of the reaction. These three properties have been assumed by some to be necessary and typical characteristics of catalytic action. But in this investigation, in order not to overlook possibly the real answer to our problem, the vital fact of acceleration alone was considered as characteristic and it was left to the rigorous application of well-known fundamental laws of chemistry to develop why, incidentally, in this and similar cases the equilibrium is not disturbed sensibly and why the catalyzing acid appears to have no share in the reaction. From this point of view, in endeavoring to imagine just how an acid could affect the speed of the above reaction, the most fundamental fact concerning acids was recalled, the fact that they have the power to form salts with bases and oxides. Here we have the acid and the oxide, and the idea was at once suggested that methyl acetate has basic properties and that salt formation with the acid is the cause of its catalysis. It was clear, however, that the basic functions of a substance like methyl acetate must be far too weak for quantitative measurements of its constants and for a rigorous quantitative test of the idea just developed. Under these circumstances it was thought best to study all these conditions in a class of closely related bodies, the imido-esters, with which quantitative measurements of all important factors could readily be carried out. As the name implies, these are esters in which we have an imide group (: NH), replacing the oxygen atom of the ester, as in imidomethyl acetate, $CH_3C(:NH)OCH_3$. They are markedly basic substances which form well-defined salts. The free bases, for instance benzimido-esters, are very slowly decomposed by water, chiefly according to the reaction

$$C_6H_5C(:NH)OCH_3 + H_2O \rightarrow C_6H_5CONH_2 + CH_3OH \qquad (1)$$

and yet more slowly according to

$$C_6H_5C(:NH)OCH_3 + H_2O \rightarrow C_6H_5CO_2CH_3 + NH_3 \qquad (2)$$

Both reactions are practically non-reversible. The addition of hydrochloric acid enormously increases the velocity of the second reaction, and it becomes almost the exclusive one. Again the question arises, *how* does the acid accelerate the action. Of course the acid forms the hydrochloride, but as imido-esters are weak bases we have in the aqueous solution partial hydrolysis and a condition of equilibrium according to

$$C_6H_5C(NH_2Cl)OCH_3 + H_2O \rightleftarrows C_6H_5C(NH_2OH)OCH_3 + HCl \qquad (3)$$

The reaction presents, therefore, at least three possibilities, — the velocity may be proportionate to the concentration of the salt present at any moment, or to that of the free base, or to either indifferently, to the total substance, as expressed in:

$$\text{(I)} \qquad \frac{dx}{dt} = k_s x \text{ (Salt)}$$

$$\text{(II)} \qquad \frac{dx}{dt} = k_b x \text{ (Base)}$$

$$\text{(III)} \qquad \frac{dx}{dt} = k_{su} x \text{ (Substance)}$$

In order to decide between these three possibilities and thus answer our question, it was necessary to determine two things experimentally, first the actual change, x in time t, and second the proportions of salt, free base, and acid present at any moment t. The latter may be determined on the basis of the well-known equation for the solution of a hydrolyzed salt, namely, according to Arrhenius:

$$\frac{(\text{Positive Ion})}{(\text{Base})\ x\ (\text{H})} = \frac{k_{\text{base}}}{k_{\text{water}}} = k_{\text{hydrolysis}}$$

The constant k was determined experimentally by conductivity measurements, and with its aid the concentrations of salt, base, and acid for the above differential equations calculated. The experimental results show unmistakably that the true course of the reaction is given by equation (I), which alone leads to a true constant.

For instance, we have among our many results for methyl imido benzoate:

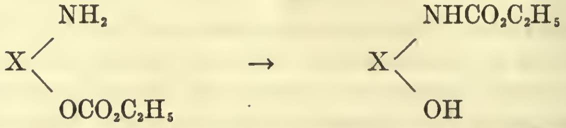
$43430\ k_{\text{salt}} = 246;\ 246;\ 256;\ 238;\ 236;\ 234.$
$257;\ 239;\ 259;\ 249;\ 237;\ 242;\ 252;\ 248.$
$43430\ k_{\text{subst}} = 202;\ 184;\ 183;\ 172.$
$231;\ 201;\ 188;\ 175;\ 168;\ 163;\ 158;\ 138.$
$100\ k_{\text{base}} = 72;\ 67;\ 59;\ 51;\ 46;\ 42.$
$58;\ 49;\ 44;\ 41;\ 35;\ 33.$

For the corresponding nitrobenzoate we have:

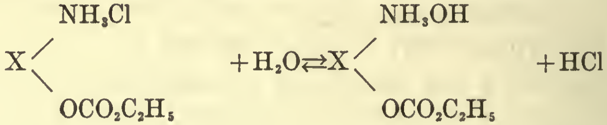
$10{,}000\ k_{\text{salt}} = 256;\ 252;\ 246;\ 255;\ 252;\ 248;\ 263;\ 261;\ 257.$
$4343\ k_{\text{subst}} = 102;\ 98;\ 96;\ 93;\ 90;\ 87;$
$k_{\text{base}} = 1.17;\ 1.23;\ 1.01;\ 0.78;\ 0.69.$

It is therefore certain that hydrochloric acid, which enormously increases the velocity of saponification of the imido-ester according to equation (II), does so simply and quantitatively through salt formation, as was expected. As the experiments were carried out in dilute solutions in which the salts are practically completely ionized, it is obvious that it is the positive ion which is decomposing in the direction given and the acceleration is exclusively due to the formation of more such active or unstable ions.

The accelerating, or let us call it the catalytic, action of the acid is here surely due then to salt or ion formation, or in other words, to the formation of a different, less stable, or more reactive molecule. Now if this is the correct explanation of the catalytic action of acids, it is clear that by this same salt or ion forming power, they should in certain cases *retard* action instead of accelerating it, provided the ion or salt is more stable than the free base. That must be an inevitable consequence of this theory, and we have brought its complete experimental confirmation in work recently published on the molecular rearrangement of certain organic bases according to



by a shifting of a carbethoxy group. The bases are exceedingly weak ones, and their salts, again, are hydrolyzed according to



Hydrochloric acid retards but does not prevent the rearrangement, and it was proved that it retards it quantitatively by salt formation and that the velocity of the rearrangement remains rigorously proportionate to the concentration of the free base present at any moment. For instance the velocity constant was found to be $k_{\text{base}} =$ .0566 at the beginning of the reaction, and .0567 at its end ten hours later.

Now these great changes in speed of reaction are the main characteristics of catalytic action; and we have in these cases a very simple explanation of it. It remained, however, to ascertain whether the two other important characteristics for many catalytic reactions are also in agreement with our conception of salt formation when rigorously applied — first, as explained for the catalysis of methyl acetate, the fact that the catalyzing acid need not *appear* to combine with any of the reacting substances, and second the fact that in a reversible reaction it need not measurably change the final condition of equilibrium. These points were tested by the application of our fundamental conception to the catalysis of methyl acetate. The intimate connection with the work on the imido-ethers is recognized as follows: we found above the velocity of saponification of imido-esters to be

$$\frac{dx}{dt} = \mathrm{k} \times (\mathrm{Salt})$$

But according to Walker and Arrhenius

$$(\mathrm{Salt}) = K \times (\mathrm{Base}) \times (\mathrm{H})$$

and therefore

$$\frac{dx}{dt}=k'\times(\text{Base})\times(\text{H})$$

But this is exactly the velocity equation for the ester catalysis, (Ester) being substituted for (Base):

$$\frac{dx}{dt}=k\times(\text{Ester})\times(\text{H})$$

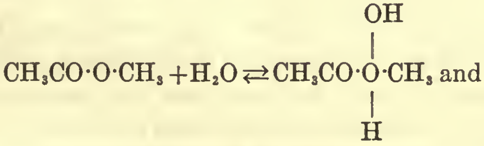
And so if the ester could form salts with acids its saponification could undoubtedly be due to the saponification only of its salt or positive ion. This important link in the chain of argument has been supplied by the discovery of Baeyer and others that the esters do form well-defined salts with acids, very unstable ones, but still salts. They are almost certainly salts of quadrivalent oxygen bases or oxonium salts. Coehn has proved that they are true electrolytes by showing that the positive ion of dimethyl pyronium hydrochloride moves to the negative pole when the solution is electrolyzed.

Now if we start from the idea that it is only the positive ion of methyl acetate which is saponified by water, we can put for the reaction:

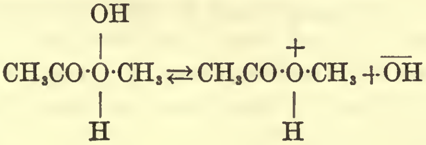
$$CH_3CO_2CH_3+H_2O\rightarrow CH_3CO_2H+CH_3OH$$

$$\frac{dx}{dt}=k_{\text{sap}}\times(\text{Posit. Ester Ion})\times(H_2O)$$

as was proved experimentally for the imido-esters. For the combination of methyl acetate with water to form an oxonium base and for the ionization of this base, we have



$$CH_3CO\cdot O\cdot CH_3+H_2O\rightleftarrows CH_3CO\cdot\underset{\displaystyle H}{\overset{\displaystyle OH}{O}}\cdot CH_3\ \text{and}$$



$$CH_3CO\cdot\underset{\displaystyle H}{\overset{\displaystyle OH}{O}}\cdot CH_3\rightleftarrows CH_3CO\cdot\underset{\displaystyle H}{\overset{+}{O}}\cdot CH_3+\overline{OH}$$

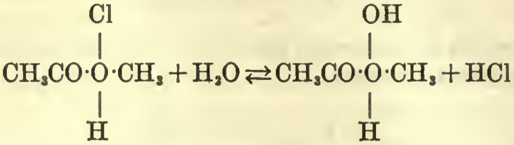
and consequently

$$(\text{Posit. Ester Ion})=\frac{K_{\text{base}}}{K'}\times(\text{Ester})\times(\text{H})$$

By the substitution of this value for the concentration of the positive ester ion in the above equation, we obtain for the velocity of saponification of methyl acetate by water alone

$$V_{\text{sap}}=\text{k}_{\text{sap}}\times\frac{K^{\text{base}}}{K'}\times(\text{Ester})\times(\text{H})\times(H_2O)$$

If we add hydrochloric acid some salt must be formed, which will be almost completely hydrolyzed according to



$$CH_3CO\cdot\overset{Cl}{\underset{H}{O}}\cdot CH_3 + H_2O \rightleftarrows CH_3CO\cdot\overset{OH}{\underset{H}{O}}\cdot CH_3 + HCl$$

Then according to Arrhenius's equation for hydrolyzed solutions of salts of weak bases with strong acids we have

$$(\text{Posit.Ester Ion}) = \frac{K_{\text{base}}}{K'} \times (\text{Ester}-y) \times (\text{H}')$$

For an almost completely hydrolyzed salt the change in the concentration of the ester will not be perceptible, y will be entirely negligible, and we obtain then for the velocity of saponification of methyl acetate in the presence of hydrochloric acid:

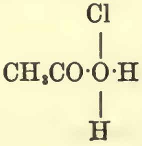
$$V_{\text{sap (HCl)}} = k_{\text{sap}} \times \frac{K_{\text{base}}}{K'} \times (\text{Ester}) \times (\text{H}') \times (H_2O)$$

By a comparison of the two velocity equations, for the reaction in the presence of water alone and in the presence of added acid, we find that the velocity must in fact increase directly proportionate to the concentration of the hydrogen ions, since all other factors remain unchanged. This consequence of our theory is evidently in perfect agreement with the well-known experimental results.

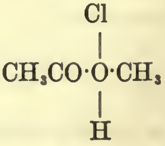
And now we come to the last important fact, namely, that the reaction is a reversible one, viz.:

$$CH_3CO\cdot O\cdot H + CH_3OH \rightarrow CH_3COOCH_3 + H_2O$$

and that the velocity of this reaction is also accelerated by the addition of hydrochloric acid. Following out our idea rigorously, this increased velocity under the influence of an acid must be due to minimal basic properties of acetic acid or methyl alcohol. It could easily be shown, if time permitted, that it is to the basic properties of acetic acid that we must look in this instance. This conclusion is not so surprising as it may appear at first glance, we have so many substances that are both basic and acid, and

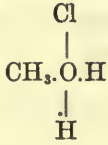


$CH_3CO\cdot\overset{Cl}{\underset{H}{O}}\cdot H$ is not more different from

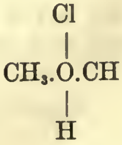


$CH_3CO\cdot\overset{Cl}{\underset{H}{O}}\cdot CH_3$

than



$CH_3.\overset{Cl}{\underset{H}{O}}.H$ is from



$CH_3.\overset{Cl}{\underset{H}{O}}.CH$

It may be added that Rosenheim from a comparison of compounds of acetic acid and its esters with metal chlorides arrived by a different way at the conclusion that acetic acid must form oxonium salts. Euler has also decided that acetic acid must have some basic functions. Applying again this conception and the laws of equilibrium to the study of the velocity of esterification, we find the velocity, in the absence of any acid, in the same way as was used above,

$$V_{\text{est}} = k_{\text{est}} \times (\text{Posit. Acetate Ion}) \times (\text{CH}_3\text{OH})$$

$$= k_{\text{est}} \times \frac{K'_{\text{base}}}{K''} \times (\text{Acet. Acid}) \times (\text{H}) \times (\text{CH}_3\text{OH})$$

In the presence of acid:

$$V_{\text{est(HCl)}} = k_{\text{est}} \times \frac{K'_{\text{base}}}{K''} \times (\text{Acet. Acid}) \times (\text{H}') \times (\text{CH}_3\text{OH})$$

We find again that the change in the velocity of esterification demanded by the application of this theory is simply proportionate to the change in concentration of the hydrogen ions — which agrees with experience.

When equilibrium is established between the two reversible reactions in the absence of hydrochloric acid we have

$$V_{\text{sap}} = V_{\text{est}}, \text{ or}$$

$$k_{\text{sap}} \times \frac{K_{\text{base}}}{K'} \times (\text{Ester}) \times (\text{H}_2\text{O}) \times (\text{H}) =$$

$$k_{\text{est}} \times \frac{K'_{\text{base}}}{K''} \times (\text{Acet. Acid}) \times (\text{CH}_3\text{OH}) \times (\text{H})$$

An inspection of the equations shows that we also have then:

$$V_{\text{sap(HCl)}} = V_{\text{est(HCl)}}$$

since according to the equation just given

$$k_{\text{sap}} \times \frac{K_{\text{base}}}{K'} \times (\text{Ester}) \times (\text{H}') \times (\text{H}_2\text{O})$$

must equal $k_{\text{est}} \times \frac{K'_{\text{base}}}{K''} \times (\text{Acet. Acid}) \times (\text{CH}_3\text{OH}) \times (\text{H}')$

In other words the addition of the catalyzing acid will not affect the ultimate condition of equilibrium between ester, water, acid, and alcohol.

We find thus the theory that acids may act as catalytic agents simply through salt or ion formation, as proved by the experiments with the imido-esters and the rearranging amino carbonates, leads by the rigorous application of our laws of dynamics also directly to the very facts in regard to the catalysis of methyl acetate which have long been known as vital results of experimental observation. The three important characteristic features of the catalysis — a velocity proportionate to the concentration of the hydrogen ions, the catalyzer apparently acting only by its presence and not changing the final condition of equilibrium, all are in perfect agreement with this simple conception of the manner in which the catalyzer produces its apparently marvelous result. The future must determine how many of the catalytic actions which are of such fundamental importance in the economy of organic life will be capable of explanations equally simple and quantitative in their ultimate terms, however much these terms may vary in details.

PRESENT PROBLEMS OF ORGANIC CHEMISTRY

BY WILLIAM ALBERT NOYES

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There is a strong tendency on the part of some chemists, at the present time, to claim that chemical science in the true sense includes only such portions of our knowledge as can be stated in accurate mathematical terms. One distinguished representative of this school of chemistry has said, "It is not in the province of science to explain phenomena," and another has written, "It is not a part of its ultimate object [*i. e.*, of natural science] to acquire knowledge in regard to mentally conceived existences, such as the atoms of matter, or the particles of luminiferous ether, which are of such a magnitude and character as to lie far beyond the limits of human conception." I think that nearly all of those now actively engaged in working over the problems of organic chemistry would dissent strongly from these statements. Long experience in dealing with the cumulative, non-mathematical evidence upon which our knowledge of chemical structure is founded has led to a very firm conviction that human knowledge is not bounded by the limits of sense-perception. We are inclined rather to the view that, while there are, undoubtedly, many things which will always remain beyond any direct cognizance of our senses, yet, so far as these have a real existence, we may in the end secure, regarding them, very practical and positive knowledge. It is impossible to conceive that those theories with regard to structure which have guided the work of thousands of chemists for the last fifty years do not in some measure express the actual truth with regard to atoms and their relation to each other in organic compounds.

Let us follow, for a few moments, in very brief outline, the steps which have led to the present standpoint. So far as the matters which interest us most are concerned, there was practically no knowledge of organic chemistry before the nineteenth century. The first steps were, of course, the preparation of pure substances and the development of accurate methods of analysis. In both of these fields Liebig was the great master. The formulæ which were calculated were, at first, of little value except to check the accuracy of the analyses and as a simple expression for empirical composition. I need not dwell on the confusion which existed throughout the first half of the century because there was no agreement as to the basis for molecular weights or atomic weights, nor upon the large part played by the study of organic compounds in finally clarifying the view of chemists upon these matters. Yet, in spite of this confusion, two discoveries of fundamental importance date from this period: (1) That the empirical composition alone does not fix the nature of a compound, *i. e.*, the fact of isomerism; (2) that certain groups of atoms may remain together in passing from one compound to another through a whole series. The first fact furnishes one of the strongest reasons why an empirical formula for an organic compound is not enough; and the second fact furnishes the most important experimental basis at the foundation of our structural formulæ.

The studies of this period furnished a knowledge of the empirical composition of many natural products and of the products obtained from these by oxidation, reduction, and the action of various agents. But while some might, perhaps, be inclined to look upon this mass of empirical knowledge as the most valuable acquisition of that time and to think that the theories in vogue were so imperfect or erroneous as to be of no value, such a view is certainly superficial. There were plenty of chemists in that day, too, who were ready to decry theories which seemed to them worthless, and it is interesting to read to-day what the great Laurent said upon this matter. He wrote in 1837:[1] "If I could believe that the purpose of my work was only to find a few new compounds or that it would end in my being able to say that there is an atom more or less in this compound or that, I would give it up on the spot. Only the desire of finding an explanation for some phenomena and of proposing some more or less general theories can give me the courage to follow a course in which I have found so little encouragement and where I have met with so many obstacles to overcome." Any one who has followed the story of how the older theories of radicals paved the way for the theory of types and of how the typical formulæ were so easily transformed into structural formulæ when the fact of valence was once grasped, cannot fail to see that the larger and fuller view is an outgrowth from the earlier theories. And we must acknowledge that Laurent was right and that the theories upon which he was working were of vastly more importance than the mass of empirical facts which furnished him with their scaffolding.

Do not misunderstand me. There were two theories of radicals at that time — one which devised radicals in the study which should accord with the electro-chemical theories held at the time and which

[1] *Ann. d. Chem.* (Liebig), 22, 143.

did not attempt to secure evidence of their existence from the conduct of the compounds containing them, another which kept in much closer touch with the facts discovered in the laboratory. It was only the latter theory which contributed much to the growth of our knowledge. A theory which cannot secure for itself a sound experimental basis is, of course, of only ephemeral value.

These, then, are the steps which have led to our present standpoint in organic chemistry: The discovery of isomerism, the discovery of radicals, the older radical theory, the theory of types, the establishment of true molecular weights, the discovery of the fact of valence, the determination of structure.

I think that all workers in organic chemistry will accept the following as a conservative statement of our present knowledge: (1) That in organic compounds, at least, each atom is attached *directly* to only a limited, small number of other atoms; (2) that in the sense of the order of the successive direct attachments the structure of a very large number of compounds is known with a degree of probability that amounts to practical certainty.

This brings me to the task which has been set, an attempt to outline the problems which lie before us in the further development of our science.

In the first place, there is still much to be done to extend our knowledge of compounds found in nature. This field is much less cultivated, relatively, than was the case sixty years ago. There has been good reason for this because of the problems of absorbing interest which have arisen in the preparation and study of new compounds and in the extension of our knowledge of old ones. But there must still remain many compounds to discover among both animal and vegetable products. On this side organic chemistry resembles the descriptive sciences of botany, zoölogy, and mineralogy. And just as botanists think it worth their while to secure as complete a description as possible of the plants to be found on the earth, so it lies in our province to isolate and identify the carbon compounds of the animal and vegetable worlds — with the difference that in our case each compound, new or old, may be the starting-point for the preparation of an almost endless number of others. But here most of us recognize that unless a compound has some further interest than that it is new it is not worth the time taken in its preparation. I am afraid, however, as we look over the pages of our journals, there is too much evidence that not every one lives up to this view. Our ever-increasing army of nascent doctors must needs have something to do, and it is so easy to make new compounds, and so difficult to find something new of larger scope and really worth the doing.

There still remains much to do in the determination of the structure of compounds which have long been known. The study of a single compound often involves an incredible amount of work. Baeyer worked with indigo for fifteen years before his labors were crowned with a successful synthesis, and twenty years more and the work of very many chemists were needed before the scientific achievement could become a commercial success.

It was nearly twenty-five years after the first structural formula was proposed for camphor before Bredt was fortunate enough to suggest the true arrangement of its atoms, and it was ten years longer, and required in all the work of more than fifty chemists, before Bredt's suggestion was confirmed by Komppa's beautiful synthesis.

More than thirty formulæ were proposed for camphor, and those who think little of organic chemistry have some reason if they say that we jump at conclusions too hastily and propose too many formulæ that are mere guesses. Some might even say that the last formula is not worth much, but those who have followed the matter know that step by step we have arrived at an almost positive certainty even in this complex problem.

The final solution of a problem with regard to the structure of a compound of natural origin is not usually considered to have been satisfactorily attained until its synthesis has been effected. Those who have attempted work of this character know that months or even years of work are frequently spent to obtain the synthesis of a single compound. In spite of the wealth of methods at our command, — a wealth so great that it is often very difficult to select between several which are equally unpromising, — it is evident that these methods of synthesis need improvement at many points. Not only do we need new and better methods, but many old methods require further study to disclose why they succeed in some cases and fail in others, and to secure a fuller knowledge of secondary reactions which often occur. As recent remarkable achievements in this field of synthetic methods may be mentioned the brilliant results obtained by Grignard with magnesium compounds, Bouveault's elegant new solution of the old problem of transforming an acid into the corresponding alcohol, and Scheuble's reduction of the amides of bibasic acids to the corresponding glycols.

Work along the lines suggested needs to be done in order to fill out and complete our knowledge in a systematic way, and occasionally work along such lines is rewarded by results of epoch-making significance, as when Gomberg discovered triphenylmethyl in his endeavor to prepare hexaphenylethane. Such work is not likely, however, to greatly advance our insight into the real nature of carbon compounds, and we all feel that there are far more fundamental problems which demand attention.

As outlined above, the theories of valence and of structure now universally accepted imply a certain amount of knowledge of the arrangement of atoms in space. So far as the original and fundamental conceptions are concerned, however, this knowledge is quite vague. The much more definite conception proposed by van't Hoff, and in a somewhat different manner by Le Bel, is, of course, familiar to you all. In discussing any hypothesis it is always important to have clearly before us the facts upon which it is based. As I have already hinted, I believe that the theory of valence and the theory of structure in the sense of a sequence of atoms within the molecule are supported by our knowledge of such a vast accumulation of consistently interrelated phenomena that we are justified in believing that we have positive knowledge with regard to the structure of the molecules of organic compounds. I am as ready as any one to demand that every theory, no matter how old or how universally accepted, shall be continually brought back to the test of agreement with experimental facts, but I am not willing to admit that we may not, in the end, acquire positive knowledge by the process of inductive reasoning.

Assuming, then, the fact of a knowledge of the sequence of atoms in organic compounds, we have this basis for van't Hoff's hypothesis: (1) When four unlike atoms or groups are combined with a single carbon atom, optical activity results in such a manner that there may always be found two compounds having identical sequence of the atoms within the molecule, and exactly equal rotary power, but of opposite signs. (2) That when two adjacent carbon atoms are combined each with three unlike groups, two compounds may result which, while optically inactive and having the same sequence of atoms, still differ in physical properties. An illustration of this is found in racemic and mesotartaric acids. (3) Rings containing five and six atoms are formed with especial ease, those containing three, four, and seven atoms less readily, and rings containing more than seven atoms are scarcely known. (4) Derivatives of cyclopropane, cyclobutane, cyclopentane, and cyclohexane having two substituents combined with different carbon atoms often exist in two isomeric forms in which the sequence of the atoms is the same. (5) Derivatives of ethylene often exhibit a similar isomerism.

Assuming as true that we have acquired a knowledge of the sequence of atoms in carbon compounds, the facts which I have enumerated lead almost inevitably to the corollary that the four atoms attached to a given carbon atom are arranged in approximate symmetry around the centre of that atom for their position of most stable equilibrium. The relation between this conclusion and the theory of the sequence of atoms in carbon compounds, or what is ordinarily understood as structure, is very similar to the relation between the atomic theory and Avogadro's law. If we accept the atomic theory, there seems to be no rational escape from the acceptance of Avogadro's law. In a similar manner, if we accept the theory of the sequence of atoms in carbon compounds, there seems no reasonable possibility other than that van't Hoff's hypothesis is true in its broad outlines.

I hope I may be pardoned here for a brief digression. I am aware that Franz Wald [1] believes that he can give a satisfactory explanation of the laws of fixed and multiple proportion and of combining weights without the aid of the atomic theory, and that Professor Ostwald in his recent Faraday lecture [2] has accepted and expanded the same thought. I will say frankly that their reasoning does not appear to me conclusive. Ostwald defines a chemical individual as "a body which can form hylotropic phases within a finite range of temperature and pressure," [3] and deduces from this the fact that a given hylotropic phase must have a fixed composition. He appears to forget that the existence of these hylotropic phases implies that the properties of matter are discontinuous, or, in other words, that there is a finite number of hylotropic bodies, one of the facts for which the atomic theory gives an explanation.

There is another characteristic, too, of a chemical compound which all chemists will agree is at least as important as that it shall consist of a "hylotropic phase." This is that the compound must not only have a fixed composition, but this composition must bear a definite relation to those numerical quantities which represent the proportion in which each element of which it is composed always combines with other elements. I need hardly add that these numerical quantities are so deeply seated in the properties of matter that, having adopted a unit, all chemists are absolutely agreed in selecting one and only one such quantity for each of the well-known elements.

In attempting to deduce this law of combining weights Ostwald assumes that three elements form the compounds AB, AC, BC, and ABC, and adds, "There shall be but one compound of every [each] kind." With this assumption, his reasoning may be sound, but I fail to see how it applies when we find ten thousand compounds ABC instead of one. The case which he supposes is so far theoretical that I have been unable to find an actual case where the compound ABC can be formed, by the union both of AB with C and of AC with B.[4] But I have taken too much time with a matter which is aside

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[1] *Ztschr. Phys. Chem.*, 24, 633, 1897.

[2] *J. Chem. Soc.* (London), 35, 506.

[3] *Ibid.*, p. 515.

[4] It is quite possible that such an illustration may be found, but, in any case, Professor Ostwald's deduction cannot be made to apply to those cases in which the compound ABC does not exist, nor to those cases where the compound ABC cannot, even theoretically, be supposed to consist in turn of a known compound AB combined with C and of another known compound AC combined with B. Such cases are common because of the fact of valence. In its simplest form the law of combining weights is quite independent of the existence of the compound ABC and may be stated thus: If the composition of two compounds AB and BC

from my main purpose. Before leaving this topic I must add, however, that I have used the phrase "Avogadro's law" advisedly, in spite of the fashion set by some chemists of calling it Avogadro's hypothesis.[1]

I remarked, a few moments ago, that the facts which have been outlined almost compel us to the acceptance of van't Hoff's hypothesis in some form. It is of the utmost importance for us to recognize, however, that we are here at the very confines of our present knowledge, and that we must, at every step, bring ourselves back to the rigorous test of experimental fact. In accepting the hypothesis we are not compelled to consider molecules as set pieces of mechanism; on the contrary, there is strong reason for thinking that the positions assumed by the atoms are positions of dynamic and not of static equilibrium. While there have been many speculations in the matter, we have no strong reason for assuming, as yet, any definite shape for the carbon atom, nor even that there are within it definite points of attraction for other atoms. All that seems to be thoroughly established is that for their position of most stable equilibrium the four atoms or groups attached to a given carbon atom are arranged in approximate symmetry around its centre. I say *approximate* symmetry because the existence of compounds containing rings of three and four carbon atoms demonstrates that the symmetry is not always absolute, and makes it probable that in cases where the four atoms or groups are unlike the symmetry is also imperfect. So far as I am aware, no fact inconsistent with this fundamental conception is known, while very many facts about optically active and cyclic compounds find in this conception the only satisfactory explanation which has thus far been given. It is true, also, that many facts with regard to optically active compounds indicate that when one group is exchanged for another the exact configuration is often retained, or, in other words, the entering group takes the same position with

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has been determined, the composition of a series of compounds between A and *C* can be predicted and a compound which does not belong to this series has never been discovered. A still more general statement of the law, and one which includes, by implication, all of those facts which are used in the selection of atomic weights, is given above. In that form it is more properly called the law of atomic weights.

[1] Two reasons may be given for this usage. My own view is that we have, by a process of inductive reasoning, acquired such positive knowledge of the existence of atoms and molecules that the expression "Avogadro's law" is fully justified. But even if we admit the contention of those who think that the atomic theory must always remain an unproved hypothesis, it is possible to frame a definition of the word molecule which would be merely a generalized statement of those empirical facts which lie at the basis of our atomic and molecular theories. Such a generalized, empirical definition must, of course, be very complex, but it would not include the concept of discrete particles. Yet it will be still true of these empirically defined molecules that equal volumes of gases contain equal numbers under the same conditions of temperature and pressure. For instance, the term gram-molecule may be considered as a purely empirical generalization, and it is true that a gram-molecule of one gas occupies the same volume as a gram-molecule of any other. But this is, in essence, Avogadro's law.

regard to the other three atoms or groups as was held by the group which was displaced. The manner in which it has been possible to work out, consistently, the complex relations between a considerable number of sugars, gives a very strong experimental basis for this statement. On the other hand, it is well known that such reactions often give racemic mixtures, which indicates that a shifting of groups with regard to a central carbon atom takes place much more easily than the shifting of a group from one carbon atom to another, at least in saturated compounds. There are also a number of extremely interesting cases where a reaction gives rise to the optical antipode. Thus Walden has shown[1] that l-chlorsuccinnic acid is converted by silver oxide into l-malic acid, while potassium hydroxide converts it into the dextro-rotatory acid. It is evident that in one case or the other there has been a shifting of the groups. Again Ascham [2] has shown that when d-camphoric acid is heated with hydrochloric and acetic acids it may be about half converted into l-isocamphoric acid, and that the latter suffers a similar transformation. This case is more complicated, as a "cis" and "trans" isomerism of cyclic compounds is involved as well as the optical difference. Not many cases of this character are known, at present, but such cases certainly deserve further study and must be reckoned with in considering the question we have before us. Le Bel [3] has already pointed out the theoretical significance of Walden's work.

While we may feel that we have comparatively sure ground in the application of the theory of van 't Hoff and Le Bel to optically active and to cyclic compounds, the case is quite different when we come to the consideration of what are commonly known as "double" and "triple" unions. Professor Michael has done a very great service to chemistry in showing that the supposition of a more or less definite tetrahedral shape for the carbon atom and of "favored" configurations often leads to conclusions which are at variance with the facts. Philips [4] and Blanchard [5] and myself have found a case in which the addition of hydrobromic acid to an unsaturated compound produces an optically active body which evidently has the same configuration as the amino and hydroxy acids from which the unsaturated body is formed by the loss of ammonia or of water. We have here, apparently, a potential asymmetry occasioned by the double union which it is difficult to reconcile with the prevailing conception of such unions. This case is complicated by the presence of a second asymmetric carbon atom in the molecule and is worthy of further study. Rabe and

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[1] *Ber. d. Chem. Ges.* 32, 1855 (1899).
[2] *Ibid.* 27, 2004.
[3] *J. Chim. Phys.* 2, 344 (1904).
[4] *Am. Chem. J.* 24, 428.
[5] *Ibid.* 26, 281; 27, 428.

Billmann[1] have recently described a similar case, but very few instances of this kind are known.

Pfeiffer[2] has recently suggested a new interpretation of van 't Hoff's hypothesis as applied to unsaturated compounds. Pfeiffer assumes that unsaturated compounds retain essentially the same configuration as the saturated compounds, from which they are derived. On this side his interpretation is closely related to the old theory of free valences, which, if I understand him correctly, is favored by Professor Michael. Pfeiffer also brings his interpretation into a close relationship to Werner's theory of inorganic metallic compounds. The most serious objection to the theory is that it supposes the existence either of trivalent carbon atoms or of free valences, in ethylene and its derivatives, an objection which has appeared to most chemists very strong in the past. Pfeiffer points out, it is true, that since the discovery of triphenylmethyl we can no longer deny the possible existence of a trivalent carbon atom.[3] It would seem, however, that the great difference between the intense chemical activity of triphenylmethyl and the comparative inactivity of ethylene demonstrates that, if the latter does in reality have free valences, the fact that there are two such valences reduces the activity of each enormously. The inactivity of carbon monoxide may be significant in this connection.

A more serious objection to Pfeiffer's hypothesis lies in the fact that he supposes so slight a difference in the configuration of fumaric and of racemic acids that it is difficult to see why the former as well as the latter might not be split into a pair of optically active bodies.

We must admit, then, that we have, at present, no satisfactory theory of double and triple unions, and that we have here a problem which demands a large amount of further work before it is solved. When the solution is reached we shall probably gain a new insight into the perennial question of the structure of benzene, and our knowledge of tautomerism will cease to be, as it is at present, almost purely empirical. It is possible, perhaps probable, that Thiele's "conjugated double unions" will contribute toward the solution.

While I have no comprehensive theory with regard to double unions to advance, I will, with a good deal of hesitation, venture to express some thoughts with regard to the combination of atoms in general

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[1] *Ann. d. Chem.* (Liebig), 332, 25.

[2] *Ztschr. Phys. Chem.* 43, 40.

[3] The fact that triphenylmethyl exists as a doubled molecule in solution should not, I think, lead us to discard the monomolecular formula for it any more than we consider that acetic acid has, in the ordinary sense of structure, a doubled molecule because it exists as a doubled molecule in solution in benzene or in the state of vapor just above its boiling-point, nor because it forms acid salts. In these cases the chemical evidence appears to be more important and more conclusive than the physical. It is probable that the doubled physical molecule is the result of forces which do not produce a stable structure in the ordinary sense.

which have some bearing on this question. We are all familiar with Faraday's law, that, if a current of electricity is passed through a number of cells filled with solutions of different electrolytes and arranged in series, exactly equivalent amounts of the various components will be liberated at the electrodes in the successive cells. The beautiful experiments of Professor T. W. Richards have demonstrated that we are dealing here with a law which is true for different solvents and over a wide range of temperature; and also that the law is true with a degree of absolute accuracy which is of the same order as the laws of the combination of elements by weight. We are compelled, then, to believe that there is associated with each valence of an ion as it is transported through a solution, or at least as it separates at an electrode, a quantity of electricity which is invariable and independent of the nature of the ion. In other words, we have here a natural electrical unit which can be defined in its relation to atomic weights with a degree of accuracy which seems to be limited only by the refinement of our manipulations.

It is not always recognized as clearly as it should be that this unit quantity of electricity which is associated with one valence of any ion is not a unit of electrical energy. If it were, the same energy would be required to decompose the equivalent quantity of one electrolyte as of every other, which is manifestly not true. While the same current causes the separation of equivalent quantities in the different cells, the differences of potential, and so the amounts of energy required for the separation, vary greatly. It is evident then that when we say that a unit quantity of electricity is associated with each valence of every ion, we do not use the term *quantity* in the sense of quantity of electrical energy. Instead of this, when this conception of a unit quantity of electricity is examined, it will be seen that it is a conception of something whose properties are those of matter rather than those of energy. The facts appear to be consistent with the idea that the unit quantity of electricity of which we are speaking is of a material nature, and you have doubtless already perceived that I have the theory of electrons in mind. The ingenious experiments of J. J. Thomson have given us considerable reason for thinking that the negative electrons are capable of an independent existence and have also given a probable estimate of their mass, which is small in comparison with the mass of the hydrogen atom.

It has been customary to think of the unit charge of electricity as being involved only in those reactions which occur in solution. If, however, we accept the theory of electrons, it is evident that the electrons must be present in the molecule of an electrolyte, no matter in what manner it is formed. It is but a step further to the conclusion that the electrons are involved in every combination or separation of atoms, and, indeed, may be the chief factor in chemical combination.

Professor Kahlenberg [1] has shown that a practically instantaneous reaction takes place between hydrochloric acid and copper oleate in a solution in dry benzene, although the solution does not conduct an electric current and there is no evidence of the dissociation of either the copper oleate or of the hydrochloric acid. Professor Kahlenberg points out very justly that there is no apparent difference between these reactions and those which take place in aqueous solutions, where we have much independent evidence of the existence of ions. He draws the conclusion that no ions exist in either case. It would seem that we are equally justified in supposing that a substance not already in the form of ions may separate into them under the influence of a second substance with which it can react.

Some time ago Mr. Lyon and myself [2] showed that the primary reaction between chlorine and ammonia gives nitrogen tri-chloride, nitrogen, and hydrochloric acid, and that these products are formed in such proportion as to lead to the conclusion that three molecules of ammonia react simultaneously with six molecules of chlorine. It was pointed out at the time that the simplest explanation of this result is to be found in supposing that chlorine atoms separate during the reaction into positive and negative ions, while the ammonia separates partly into positive nitrogen and negative hydrogen and partly into negative nitrogen and positive hydrogen.[3] This hypothesis has met with some approval,[4] but has also received the criticism that such a dissociation as is supposed would result in the spontaneous decomposition of ammonia into nitrogen and hydrogen.[5]

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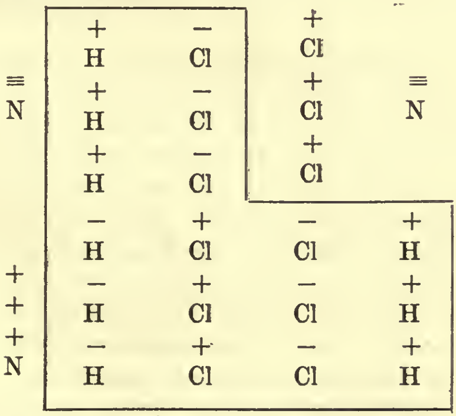
[1] *J. Phys. Chem.* 6, 1.

[2] *J. Am. Chem. Soc.* 23, 460.

[3] This was represented graphically thus:



[4] Stieglitz, *J. Chem. Soc.* 23, 707.

[5] *Ztschr. Phys. Chem.* 41, 378.

This criticism loses its force if we suppose that the separation into ions takes place only under the immediate influence of the chlorine with which the ammonia reacts. It has been pointed out by many different authors [1] that a separation of atoms from each other must occur either before or at the same time that they enter into combination with other atoms. The only part essentially new in the hypothesis proposed is that this separation is into positive and negative parts and that the same atom may be sometimes positive and sometimes negative. The idea of a dissociation which occurs under the influence of a reacting substance appears to be implied in a part of Professor Nef's discussion of methylene dissociation, but it is not always clear whether he has in mind chiefly a dissociation of this sort or one which is independent of the interaction of different compounds.

The thought that the same atom may be at one time positive and at another time negative is related to the older electrochemical theory which supposed water to be positive in acids and negative in bases.

We assume, then, that in every combination of atoms each union involves an attraction between the positive and negative electrons which are associated with the two atoms that unite. In saying this I do not lose sight of the fact that such a thing as attraction *per se,* in the sense that one body can influence another at a distance without an intervening medium, is apparently inconceivable. I think of the attraction as probably caused by some motion of the electrons which enables them to act on each other through the aid of the ether. It is convenient, however, to speak of this effect as an attraction, since our conception of its real nature is, of necessity, very vague. One advantage of the idea that the attraction of the electrons is of a kinetic nature is that we may conceive of the same electron as becoming positive or negative, according to the nature of its motion.

The common conception, at present, is that an atom which has lost an electron becomes positive, while either the electron in its independent existence or the atom to which it is attached becomes negative. So far as I am aware, it has not been pointed out that this view leads to the conclusion that the same atom must, under different conditions, have a different weight. Thus a bivalent copper atom which has lost two electrons must weigh less than a univalent copper atom, which has lost only a single electron. It is true that our methods of determining atomic weights are scarcely accurate enough to detect differences of this order. The suggestion which is made is that the electrons of two atoms which are united have motions which correspond to positive and negative charges, respectively, and that when the atoms separate these motions may be retained, or lost as

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[1] See Erlenmeyer, Jr., *Ann. Chem.* (Liebig), 316, 50.

in the case of a mercury atom which is uncombined, or that the motions may be reversed. In accordance with the hypothesis outlined above, we must assume that when two atoms separate either one may become positive; dependent partly on their nature, partly on the nature of the reacting substance. The conception here proposed is that of something very similar to the action of the pole of a magnet, which may attract another pole of the opposite kind, or induce the formation of a pole of the opposite kind, or it may reverse the polarity of another magnet.[1] This is, perhaps, simpler than to suppose the transfer of an electron from one atom to another in those cases where the electrical charges of the atoms are reversed in the ionization. A very accurate determination of the atomic weight of cupric copper as compared with that of cuprous copper might possibly decide between the two hypotheses.

It should be noted that the hypothesis that the electrical charges associated with the atoms are of a kinetic nature, and that these charges may be transferred without gain or loss of matter, is quite independent of the first hypothesis, which is that the atoms are ionized when they separate from each other and that the same atom may become either positive or negative.

In following farther the thought of the attraction between electrons as the cause of chemical combination, we must suppose that in addition to the effect of this attraction in holding together the atoms which are immediately attached, there is a residual effect upon other atoms within the molecule. This gives a rational explanation of the very great difference in the stability of the union between carbon atoms in different compounds as, for instance, the instability of acetic acid in comparison with butyric acid, occasioned by the substitution of an oxygen atom for two hydrogen atoms of the latter. The study of organic compounds has given us a knowledge of a large number of cases of this sort, and our text-books contain many empirical rules about them, but there have been few, if any, attempts to give for such facts any rational explanation.

In considering double unions three explanations suggest themselves: (1) We may suppose with Pfeiffer that such unions are in reality single unions and free valences. In this case the presence in adjacent carbon atoms of positive and negative electrons which are uncombined would reduce the attraction of each for the electrons of another molecule, thus explaining why two free valences are so much less active than a single one. (2) We may suppose that the carbon atoms are in reality doubly united, but that, owing to the localization of

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[1] This is, of course, only an analogy and must not be pressed too far; just as the electrical charges of atoms or ions conduct themselves very differently from those of masses. The latter divide themselves between two bodies in contact; the former may be transferred *completely* from one ion to another.

the electrons in definite parts of the carbon atoms, the four electrons involved cannot approach as near to each other as is the case in a single union. This is Baeyer's theory of strain, and is much better in accord than is the theory of free valences with the fact that cyclopropane and propylene appear to be about equally unsaturated, as evidenced by their heats of combustion and by their conduct toward bromine. On the other hand, it seems to lead logically to conclusions with regard to the addition of bromine to triple unions, which Professor Michael has shown are contrary to the facts. (3) Without a condition of strain, we may suppose that the presence of both a positive and a negative electron in each of the atoms united by the double union causes a lessening of the attraction of the electrons. This would result in such a union being less stable than a single union. The second and third views appear, at present, most in accord with the facts — possibly the truth lies in some combination of the two.

Whatever view we may take, it is noteworthy that double unions are usually formed by the loss of a positive and negative atom or group from adjacent carbon atoms, as hydrogen and hydroxyl or hydrogen and bromine. It is also true that in many double unions one of the carbon atoms is more positive than the other, causing the addition of halogen acids in a definite manner which may be predicted in accordance with Michael's "positive negative law." Applying this thought to conjugated double unions, we see that of the four atoms involved the two central ones are likely to be positive and negative respectively and neutralize each other's attraction for outside atoms, while an intensified attraction for outside atoms would be found in the exterior atoms. The effect may be analogous to that of the attractive forces of a magnet which exhibit themselves chiefly at the ends.

But I have permitted myself to wander much farther in the field of speculation than was my first intention — farther than is at all profitable, I fear, for these questions furnish, at present, few points for experimental study, and speculations divorced from experiment have usually been profitless. I should be very sorry if what has been said should give encouragement to such speculations. On the other hand, I have a very firm conviction that we should not be content with rounding out organic chemistry as a descriptive science, nor even with adding to the number of empirical rules which enable us to predict certain classes of phenomena. We must, instead, place before ourselves the much higher ideal of gaining a clear insight into the nature of atoms and molecules and of the forces or motions which are the real reason for the phenomena which we study. When we consider the progress which has been made and the knowledge of structure we now possess, which would have appeared sixty years ago to lie beyond the limits of possible acquirement, it is not presumptuous to think that a more complete knowledge of these questions will at some time be gained. This fuller knowledge will take account, too, of many lines of work upon which I have no time to dwell, such as the question of changing atomic volume to which Professors Richards and Traube have directed our attention, and the knowledge of heats of combustion, of molecular refraction and dispersion, of color, viscosity, dielectric constants, and other physical properties. The future must give to us a new theory, or a development of old ones, which shall include all of these phenomena in one comprehensive view.

SHORT PAPER

Professor Oswald Schreiner, of the United States Department of Agriculture, read a short paper on "A Study of the Sesquiterpene Class of Hydrocarbons."

SECTION C — PHYSICAL CHEMISTRY

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(*Hall* 16, *September* 22, 10 *a. m.*)

CHAIRMAN: PROFESSOR WILDER D. BANCROFT, Cornell University.
SPEAKERS: PROFESSOR J. H. VAN 'T HOFF, University of Berlin.
PROFESSOR ARTHUR A. NOYES, Massachusetts Institute of Technology.
SECRETARY: MR. W. R. WHITNEY, Schenectady, N. Y.

THE Chairman of the Section of Physical Chemistry was Professor Wilder D. Bancroft, of Cornell University, who opened the work of the Section with the following remarks:

"Twenty years ago physical chemistry was not recognized as a subdivision of chemistry. To-day nearly every larger university in this country has a chair of physical chemistry, and we have our regular place on the Programme along with inorganic and organic chemistry. In fact, Professor Clarke in his address rather implied that physical chemistry now dominates the whole of chemistry. Certain it is that physical chemists are much in demand at this Congress and that to hear them all you must go to many Sections. Van 't Hoff is to speak to you here this morning, Arrhenius delivers an address the next hour before the Section of Geophysics, Ostwald is to speak this afternoon as a philosopher, while Sir William Ramsay was one of the chief speakers yesterday before the Section of Inorganic Chemistry.

"In addition to the two longer addresses, our Programme includes shorter papers on the chemical affinity between solvent and solute, on the chemistry of liquid ammonia, on transference in acetic acid solutions, and on the application of physical chemistry to agriculture. The first address is on the history of physical chemistry by the man who made that history possible, Professor van 't Hoff of Berlin."

THE RELATIONS OF PHYSICAL CHEMISTRY TO PHYSICS AND CHEMISTRY

BY JACOBUS HENRICUS VAN 'T HOFF

[**Jacobus Henricus van 't Hoff,** Member of the Academy of Sciences, Berlin; Ordinary Honorary Professor, University of Berlin, Germany. **b.** August 30, 1852, Rotterdam. Ph.D. Polytechnic School, Delft; M.D. University of Utrecht; LL.D. University of Chicago; *ibid.* Harvard University. Honorary course, Griefswald and Utrecht. Tutor in Clinics, Veterinary School, Utrecht, 1876–78; Professor in Chemistry, Mineralogy and Geology, University of Amsterdam, 1878–96. Member of various societies in Amsterdam, Bologna, Christiania, Delft, Erlangen, Frankfurt, Göttingen. Batavia, Copenhagen, Lund, Mexico, New York, Philadelphia, Rotterdam, St. Petersburg, Turin, Utrecht, Vienna, Venice, Washington.]

According to the Programme, I have to consider the "General Principles and Fundamental Conceptions which connect Physical Chemistry with the Related Sciences, reviewing in this way the development of the science in question itself."

Let me begin by defining physical chemistry as the science devoted to the introduction of physical knowledge into chemistry, with the aim of being useful to the latter. On this basis I can limit my task to the relations of physical chemistry to the two sciences it unites, chemistry and physics.

But even if I limit myself to these relations, which are not the only two,[1] I wish to restrict myself yet more, in order, in the spirit of this Congress, to call your attention to broad views. So I shall follow up only two lines, in answering two questions regarding two fundamental problems in chemistry: (1) What has physical chemistry done for our ideas concerning matter? (2) What has it done for our ideas concerning affinity?

The small table which I have the honor to put before you will enable us to answer these questions by appeal to the scientific development of our science, which also I have to review:

I. *Ideas concerning Matter*

(1) Lavoisier, Dalton (1808).
(2) Gay-Lussac, Avogadro (1811).
(3) Dulong, Petit, Mitscherlich (1820).
(4) Faraday (1832).
(5) Bunsen, Kirchhoff (1861).
(6) Periodic System (1869).

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[1] In Chicago I devoted to this subject eight lectures, which have since appeared in the Decennial Publications under the title 'Physical Chemistry in the Service of the Sciences,' Chicago, 1903.

(7) Pasteur (1853), Stereochemistry (1874).
(8) Raoult, Arrhenius (1886–87).
(9) Radioactivity (Becquerel, Curies).

II. *Ideas concerning Affinity*

(1) Berthollet, Guldberg, Waage (1867).
(2) Berzelius, Helmholtz (1887).
(3) Mitscherlich, Spring (1904).
(4) Deville, Debray, Berthelot.
(5) Thomson, Berthelot (1865).
(6) Horstmann, Gibbs, Helmholtz.

I. *Physical Chemistry and our Ideas concerning Matter*

The Concepts of Atoms and Molecules. Regarded as a whole, we may say that the initial application of physical knowledge for the purpose of developing our ideas of matter consisted chiefly in the employment of physical methods and instruments in the study of the properties of matter. This stood foremost in physical chemistry in the first period of its existence.

Reviewing the history of chemistry, we must acknowledge that one of the first fundamental steps was made by the study of the physical property of weight, and the introduction of a physical instrument, the balance, for this purpose. It was, in large part, on this basis that Lavoisier was the great innovator of chemistry; and it was due solely to the following of chemical change with the balance that chemistry got its fundamental laws of constant weight and of constant and multiple proportions. These were summarized by Dalton in the fruitful though hypothetical conception of atoms, which, as is well known to you all, asserts that every element exists in the form of small unchangeable particles, identical for a given element, but differing with the latter.

As the study of weight led to the idea of atoms, so the study of another physical property, that of volume and density, led to our idea of molecules. These molecules, which might be described as constellations of atoms, were a necessity with Dalton's conception; but, in a binary compound, for instance, they might consist of two atoms or of twenty. Now, it hardly needs to be recalled that Gay-Lussac, and especially Avogadro, in following the volume relations of gases in chemical action, drew the conclusion that the molecules of gases occupy equal volumes under identical conditions. Thenceforward we had a reliable method for determining the relative weights of such molecules.

As the study of the physical properties weight and volume led to the concepts of atoms and molecules, so sharply defined that the relative weights of these entities form the fundamental constants of chemistry, so a further study of physical properties has led to broad generalizations concerning the nature of atoms and molecules, which we shall now outline.

Properties of Atoms. As to atoms, I would call your attention to four peculiarities which seem to me of fundamental importance. First, Dulong and Petit found that the physical property called heat capacity is nearly the same for different atoms, *i. e.*, that the quantity of heat requisite to produce a given rise of temperature does not vary greatly for atomic quantities, for 7 parts of lithium and for 240 parts of uranium.

Second, Faraday, in studying the electrical conductivity of electrolytes, *e. g.*, of aqueous solutions of salts, found that the quantity of electricity which atoms can transport varies as the whole numbers, — from one in potassium to two in zinc. This fundamental property, which gives the sharpest expression to our notion of valency, was brought by Helmholtz into a very clear form by the assumption that electricity as well as matter consists of atoms, either negative or positive, and that material atoms are able to combine with them, — potassium with one of the positive kind, zinc with two, chlorine with a negative one, — and so transport them in electrolysis.

The third great step was made by the study of light, a physical property again. Bunsen and Kirchhoff found that, heated in the gaseous state, every atom emits a definite set of light-waves, producing a characteristic line-spectrum which is yet the sharpest test of the kind of atoms one is dealing with, and which so became the most fruitful guide in the detection of new kinds.

The last generalization that I have to mention, and which we owe to Newlands, Mendeléeff, and Lothar Meyer, includes physical properties in general, and asserts that they vary with increasing atomic weight in a periodic way. This shows itself most sharply in the atomic volume, which passes through maximum values in lithium (7), sodium (23), potassium (39), rubidium (85), and cæsium (133). A corresponding periodicity is observed in other properties, as, for example, that of combining with electrical atoms, or valency, which in the said elements passes through unity. Analogous behavior is exhibited by the melting-points and boiling-points, which for these metals are exceptionally low.

If my programme did not to a certain extent exclude quite recent investigations, confining me to a view of past history, I should like to consider one more physical property, that of radioactivity, which also seems to be a property of atoms. I can only insist on the fact that it was physical properties again, the making the air conductive for electricity, and the spectrum, which revealed radium.

Properties of Molecules. Turning to molecules, I have three predominant generalizations to outline. The first is Mitscherlich's discovery of the fact that analogous molecular constitution corresponds to analogous outer crystalline form, to so-called isomorphism. Let me add that there is hardly any more satisfactory proof of the soundness of our concept of the internal structure of matter than, *e. g.*, the identity of the crystalline forms of the alums, which we consider to have corresponding internal structure.

A second step, to a certain extent a similar one, was made by Pasteur when he deduced disymmetry of molecular constitution from disymmetry in behavior, optically as well as crystallographically. For instance, the dextrorotatory ordinary tartaric acid and its lævorotatory antipode showed this disymmetry both in optical rotation and in the particular so-called enantiomorphous crystalline form. The molecules were supposed to have analogous structures differing from each other as the right hand from the left. As is well known, it was only later that the probable molecular structure was sharply defined, and stereochemistry was founded.

The third great step was the opening of a way to determine the molecular weights of dissolved substances. It was chiefly the application of Avogadro's law to osmotic pressures, in connection with Raoult's measurements of freezing-points and vapor-pressures, that opened the way. We may now assert that the liquid state is not characterized by high molecular complexity. But the great innovation, introduced by Arrhenius and immediately brought into relation with the achievement in question, was the admission of the existence of ions in electrolytes — for example, the presence of negatively charged chlorine atoms and positively charged sodium atoms in an ordinary salt solution. Once more it was a physical property, the electrical conductivity, that led to this extremely fruitful supposition.

Conclusion. If, after this short summary of its properties, we try to look into the nature of matter, we conclude that matter is not continuous, but that there are centres of action which seem to have an eternal existence, changing only in the place that they occupy — these are the atoms. They keep together in some way and form the molecule; how, it is pretty hard to say. The planetary constellation, with ordinary attraction and centrifugal force in equilibrium, is excluded by the consideration that at the absolute zero there is no movement at all. The repulsive force that we want might be of electrical nature; and so we come to our combination of material and electrical atoms. There is indeed something fascinating here, and when we admit for carbon that it may unite to four equally charged electrical atoms and hold them by a force of the nature of elasticity, we have at once a possible equilibrium and the tetrahedral grouping. My only difficulty is that an uncharged atom of carbon, coming into contact with the ions just described, would take away half the electric charge, and so the valency of any element might be reduced to unity. The latest supposition, that matter is built up of electricity alone, lies again beyond the scope of this address.

Let me now turn to the second part of my subject, and touch upon the problem of affinity; indeed, the action that keeps atoms together must be closely related to affinity.

II. *Physical Chemistry and our Notions concerning Affinity*

While physical chemistry, in the first period of its development, was chiefly devoted to the study of the physical properties of matter, the second and present period is characterized by the predominant place of the problem of affinity.

This change in the general aspect of our science goes hand in hand with a different way of working: in the development of our ideas of matter, physical chemistry introduced physical methods and instruments for the study of physical properties; in the development of our ideas of affinity, physical chemistry has introduced physical principles.

Affinity considered as Force. The first line of thought considered affinity as a force, and in this direction it was natural to think of the Newtonian attraction as the chemical agent. So it was that Berthollet, and with far more success Guldberg and Waage, applied the laws of mass-action to problems of affinity, formulating a relation still known as the mass-law, according to which affinity is proportional to the weight in the unit of volume.

Now, as we all know, affinity is of a specific nature, and does not depend on weight merely; on the contrary, the least heavy elements are generally the most active. So Berzelius built up his system founded on the notion that elements have a specific electrical character, either positive or negative, and, in combining, act by electrical attraction. In this direction Helmholtz made a further step in taking into account the quantitative side. Considering the electrical charges involved in Faraday's law, he pointed out as very important that the attraction due, for instance, to the negative charge in chlorine and the positive one in hydrogen far exceeds the gravitational attraction of the masses. Yet a satisfying notion of affinity was not obtained in this way.

Affinity measured as Work. A second line of thought took into consideration not the force but the work that affinity represents; and it seemed a decisive step when Thomson and Berthelot declared that the heat developed in chemical change corresponds to the work that affinity can produce. Indeed, it was in this way that in many cases an *a priori* calculation of the heat development of a reaction permitted prediction of the direction in which the process would proceed, the direction being that of the evolution of heat. Yet this principle, however weighty, is not absolutely reliable. The chemical actions that produce cold, as that of hydrochloric acid on sodium sulphate, are objections not to be overcome.

The step really leading to a clear and unobjectionable notion of affinity was made in the study of the so-called reversible chemical changes. This reversible character perhaps needs some explanation, easily to be provided by an illustration. Kill a chicken and prepare chicken soup; it would then be very difficult to get your chicken again. This is because preparing chicken soup is not reversible. On the contrary, let water evaporate or freeze; it will be easy to reproduce the water.

Now, at first sight, chemical change does not seem reversible; and indeed it often is not, as in the explosion of gunpowder. But investigations of Berthelot and Péan de St. Gilles on the mutual action of acids and alcohols, and those of Deville and Debray on high temperature action, which even splits up water, have shown that many chemical changes can be reversed. Indeed, we have types corresponding absolutely to evaporation, as the loss of water-vapor from hydrates: and others corresponding as well to freezing and melting, as the splitting of double salts into their components at definite temperatures. *e. g.*, copper calcium acetate at 77° C. Also in analogy with physical phenomena, we have in these reversible chemical changes the possibility of equilibrium, the two chemically different forms of matter coexisting, as do water and its vapor at a maximum pressure.

Such a reversal of chemical change can take place under the influence of temperature, of electricity, of light, of pressure. And the easiest way to arrive at a measure of affinity is presented in the last case, as was foreseen by Mitscherlich. Let us take gypsum as an example. Burnt commercial gypsum, mixed with water, will combine with the water. We know that this chemical change can produce pressure, and that it may be prevented by sufficient pressure and be reversed by it, as Spring succeeded in pressing out sulphuric acid from sodium bisulphate. And it is possible in such cases exactly to determine the limiting pressure, such that a higher one presses out the sulphuric acid while a lower one is overpowered by the affinity action. If the chemical change takes place under a pressure only slightly less than that which would prevent it, thus practically taking place under the limiting pressure, we get out of affinity the greatest quantity of work that it can possibly produce; and this quantity is the same whatever the nature of the opposing action, be it electricity, light, or anything else. Therefore, in this maximum work we have a sound measure of affinity.

It was a very happy coincidence indeed, that this conception of affinity made possible the application of a physical principle known as the second law of thermodynamics. This principle may be formulated in different ways. For my purpose let me say that it limits the possibility of natural processes to the occurrence of those in which a difference of intensity is diminished. If there is a difference of pressure in two parts of a gas, a movement will occur producing equality; if there is a difference of temperature, heat will be transported so as to produce equality once more. It is curious that such simple necessities, which we all feel as such, can be converted into far-reaching sharply formulated equations, as was done by Carnot and Clausius. These principles were first applied in chemistry by Horstmann. Then, by successive application to chemical problems by Massieu, Gibbs, Helmholtz, and others, was won a system of relations touching the problem of affinity, to which I can give only brief attention:

(1) Affinity may be defined as the maximum quantity of work that a chemical change can produce. Equilibrium ensues when this quantity is zero.

(2) The mass-law can be obtained in a well-founded and somewhat modified form, restricted to dilute gases and solutions.

(3) The Thomson-Berthelot principle assumes a modified form in the rule that a fall of temperature induces the formation of that which develops heat. It is, for instance, in accordance with this rule that at ordinary temperatures water is stable in comparison with detonating gas, and that at high temperatures this relation is reversed, as it was found by Deville to be.

(4) Lastly, we have the phase rule, indicating, for example, in what cases chemical phenomena will be comparable with melting and freezing, and in what cases they will be comparable with evaporation and condensation.

Most curious of all, we can treat problems of affinity in an absolutely trustworthy way, so that our calculations furnish a check upon experiment, without admitting anything concerning the nature of affinity or of the matter wherein the affinity is supposed to reside.

THE PHYSICAL PROPERTIES OF AQUEOUS SALT SOLUTIONS IN RELATION TO THE IONIC THEORY.

BY ARTHUR A. NOYES

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It is generally recognized that the further progress of physical science will be greatly facilitated by a better systematization of the knowledge already accumulated, and this is true in an especially high degree of the newly developed branch of science in which this Section is directly interested. It has therefore seemed to me that the most valuable contribution that I could make toward the solution of the present problems of physical chemistry in correspondence with the aims of this Congress would be a formulation of the present status of some of our knowledge relating to important classes of phenomena which are being actively investigated, but which have not yet received a final interpretation. It was my original hope to discuss several such classes of phenomena; but the effort involved in the collation and criticism of the available data connected with the problem which was first studied forced me to confine my attention to that alone. This problem concerns *the physical properties of aqueous salt solutions in relation to the ionic theory.* This is the subject which I shall attempt to present to you: I hope that its importance and the greater definiteness that can be given to its treatment may compensate for the somewhat limited scope of this paper.

Permit me to say in advance that I have studied this subject primarily from an empirical standpoint, and that it will be my aim to present to you a series of generalized statements of the experimental results, formulated in such a way as to show their relation to the important hypotheses connected with the ionic theory. Unfortunately, it will not be possible in this address to reproduce, or even fully refer to, the data upon which these conclusions are based — a defect serious in a work of this kind, which will be remedied in a subsequent publication. I shall, however, try to show the general character of the evidence for each conclusion and the degree of accuracy within which it has been confirmed. I wish to add that I have been most ably assisted in the preparation of the material upon which this paper is based by Dr. J. W. Brown and Dr. M. S. Sherrill, of the Massachusetts Institute of Technology.

The principles to be first presented have reference to two of the main hypotheses which are commonly employed in quantitative applications of the ionic theory. One of these hypotheses is that *the migration-velocities of the ions of a salt do not vary appreciably with its concentration, at least up to a moderate concentration; and consequently, that the degree of ionization is equal to the ratio of the equivalent conductivity at the concentration in question to the limiting value of the equivalent conductivity at zero concentration* — a ratio which I will hereafter call simply the conductivity-ratio. The other hypothesis is that *ions, and also the un-ionized molecules accompanying them, produce an osmotic pressure substantially equal to the pressure exerted by the same number of gaseous molecules at the same temperature, at least up to a moderate concentration;* an hypothesis which may be more briefly expressed by the statement that the osmotic pressure-constant for dissolved electrolytes is identical with the gas-constant. It is evident that with the help of this hypothesis we can calculate, either from measurements of osmotic pressure or from those of any other property which is thermodynamically related to osmotic pressure, the number of mols in the solution resulting from one formula weight of salt, that is, the quantity which van 't Hoff has represented by the letter i. From the latter, provided the ionization is not complicated by the formation of complex molecules or ions, the degree of ionization is readily derived.

The first of these hypotheses cannot be independently tested, because no direct method of determining the change of migration-velocity with the concentration is known. But the following principle, which has an important significance with reference to the *relative* influence of concentration on the velocities of different ions, has been established by measurements of the concentration-changes at the electrodes attending the electrolysis of salt solutions.

The transference number, or ratio of the conductivity of one ion to the sum of the conductivities of both ions, is constant within one per cent, between the concentrations of $\frac{1}{200}$ *and* $\frac{1}{10}$ *normal, for all salts thus far accurately investigated, except lithium chloride, the halides of bivalent metals, and cadmium sulphate.*

This principle holds true, according to the results of various investigators, in the case of potassium and sodium chlorides, hydrochloric and nitric acids, silver nitrate, barium nitrate, potassium sulphate, and copper sulphate — thus in the case of salts of the three different ionic types, which I will speak of as the uni-univalent, the uni-bivalent, and the bi-bivalent types, in correspondence with the valences of the two ions composing the salt.

Two conclusions are to be drawn from this result. The first is, that complex ions are not present in important quantity in the solutions of these salts. And the second is, that the migration-velocities of the two ions of a salt vary by the same percentage amount, if they vary at all, with changes in its concentration. It is scarcely admissible, however, to regard this last fact even as an indication that the hypothesis of constant migration-velocities is correct; for any change in the character of the liquid medium might well affect the velocities of different ions not far from equally.

Important evidence in regard to this hypothesis and that stating that ions and the un-ionized molecules associated with them have a normal osmotic pressure is, however, furnished by the agreement of the ionization values derived, on the one hand, from the conductivity-ratio, and, on the other, from the properties thermodynamically related to osmotic pressure. Three of these properties have been measured with sufficient accuracy with certain electrolytes to make the results of significance, namely, the freezing-point lowering, the electromotive force of concentration-cells, and the heat of solution in relation to change of solubility with the temperature. Under the assumption that osmotic pressure and gaseous pressure are equal under identical conditions, a relation between each of these properties and the degree of ionization of an electrolyte can be derived with the help of the second law of energetics. Then, either this ionization value may be directly compared with the conductivity-ratio, or, assuming provisionally that the latter is a correct measure of ionization, the magnitude of the property in question may be calculated, and the result compared with that obtained by direct measurement. In the case of the freezing-point lowering, I have adopted the first of these methods. For the five salts for which both reliable freezing-point determinations and accurate conductivity-measurements at 0° exist, the ionization values corresponding to both of these properties have been computed. Especial attention was given to the selection of the best value of the freezing-point lowering constant and to the extrapolation of the conductivity for zero concentration, the details of which cannot be here described. The results may be summarized as follows:

In case of the two uni-univalent salts and the three uni-bivalent salts hitherto carefully investigated, the ionization values derived from freezing-point lowering do not differ from those derived from conductivity, between the concentrations of $\frac{1}{200}$ *and* $\frac{1}{4}$ *normal, by more than* 2 *or* 3 *per cent.*

The five salts referred to are potassium and sodium chlorides, potassium and sodium sulphates, and barium chloride. The two sets of values for potassium chloride, for which an abundant experimental material exists, exhibit no pronounced or systematic differences; but for the other four salts the freezing-point leads to values which are in general from two to three per cent higher at all concentrations than the conductivity-ratio. The fact that these differences do not, as a rule, increase with increasing concentration indicates that they may be due to some constant experimental error, or to an error in the extrapolated conductivity value.

Accurate measurements have been made by Jahn of the electromotive force of concentration-cells consisting of two silver or mercury electrodes covered with silver chloride or mercurous chloride, one of which is immersed in a weak solution and the other in a strong solution of sodium or potassium chloride. These measured values were compared by him with those calculated from the thermodynamic relation between electromotive force and the concentrations and degrees of ionization of the salt in the cell. Unfortunately, however, the thermodynamic relation employed involved the assumption that the ionization varies with the concentration in accordance with the Mass-Action Law — an assumption which is known not to be true of the ionization values derived from conductivity. The assumption is, therefore, an irrational one — one by which the question at issue is prejudged. What should be done in calculating the electromotive force so as to determine whether the conductivity-ratio gives ionization values consistent with the measured electromotive forces is evidently to assume that the ionization changes with the concentration in the way that the conductivity indicates that it does. Arrhenius recognized this error and partially corrected for it by a method of approximation. I have repeated the calculations by an exact thermodynamic formula based on an empirical law expressing the change of the conductivity-ratio with the concentration, to which I will refer later. The results are summed up in the statement that, *when the conductivity-ratio is assumed to represent the degree of ionization of the salt, the calculated values of the electromotive force of concentration-cells exceed the measured ones by only about one per cent in the case of potassium and sodium chloride between the concentrations of* $\frac{1}{600}$ *and* $\frac{1}{20}$ *normal.* The measured electromotive force corresponds to an ionization value at the latter concentration about one per cent less than the conductivity-ratio.

The thermodynamic relation involving heat of solution has been accurately tested with only one salt — potassium perchlorate; but since it is a different salt from those used in the other experiments, and since its concentration was fairly high — $\frac{1}{8}$ normal — the result is of interest. It was found that the *measured heat of solution was less by only* 1.1 *per cent than that calculated under the assumption that the conductivity-ratio is equal to the degree of ionization.* The measured heat of solution corresponds to an ionization value $2\frac{1}{2}$ per cent lower than the conductivity-ratio.

With respect to these small deviations of the results obtained by the three methods of comparison, it is important to note that they lie in opposite directions, the freezing-point lowering corresponding to larger values of the ionization, and the measured electromotive forces and heat of solution to smaller ones than the conductivity-ratio. This fact makes it almost certain that they are due to experimental errors. Nevertheless, further exact measurements of all these properties are highly desirable.

From a theoretical standpoint these three methods are based on the same hypotheses — namely, that the osmotic pressure-constant for ions and un-ionized molecules is identical with the gas-constant; that the conductivity-ratio is a correct measure of ionization, and that complex molecules or ions are not present in the solution. The concordance of the results furnishes, therefore, a strong confirmation of the correctness of these fundamental hypotheses. The only alternative conclusion is that an error in one of these hypotheses is compensated by an error of opposite effect in one of the others; but it seems very improbable that such a compensation could occur in the case of so many salts of different chemical nature and different types through the range of concentration ($\frac{1}{200}$ to $\frac{1}{4}$ normal) for which the agreement of the experimental results has been shown to hold true. It is certainly more consistent with the modern methods of science to adopt these simpler hypotheses, which are in full accord with the considerable number of facts thus far known, than deliberately to introduce more complicated assumptions for which there is at present no experimental warrant.

The combination of these hypotheses with the experimental values of the quantities involved at varying concentrations makes necessary the further conclusion that the *degree of ionization of salts, whether derived from the conductivity-ratio or from thermodynamic relations involving the equality of the osmotic pressure-constant and the gas-constant, does not vary with the concentration even approximately in accordance with the Law of Chemical Mass-Action.*

This empirical consequence of the fundamental hypotheses of the ionic theory has led several investigators to raise a theoretical objection to them, it being contended that the laws of thermodynamics require that the validity of these hypotheses involves that of the Mass-Action Law itself. This apparent inconsistency between the inductive and deductive conclusions makes it probable that some unproved, erroneous assumption is tacitly involved in the theoretical derivation. That there is, in fact, a possible alternative, which has, I believe, been previously overlooked in the thermodynamic discussions, will be evident from the following considerations. The thermodynamic relations between ionization and freezing-point, electromotive force, or heat of solution, involve only the assumption that the work done in reversibly separating water from a solution at constant concentration is equal to that done in producing the same volume-change in a gas, which implies, of course, that the ions and un-ionized molecules have in the presence of each other normal osmotic pressures. On the other hand, the derivation of the Mass-Action Law equation is based on cyclical processes which necessarily involve the separate introduction and removal of the un-ionized molecules and of the ions into or from solutions of different concentrations, and it further involves the assumption that this introduction or removal of molecules or ions can be effected by the application of an external pressure equal to that osmotic pressure which each of them possesses in the mixture; that is, the possibility is ignored that the separation of the molecules from the ions may itself give rise to some new force, and may involve, consequently, another quantity of work than that corresponding to the osmotic pressure. The ionic theory would evidently predict a result of this kind if an attempt were made to separate the positive ions from the negative, even though their osmotic pressures when present together were perfectly normal; and it is quite conceivable, even though the reason for it be not apparent, that the separation of the un-ionized molecules from the ions, with which they may be in electrical as well as chemical equilibrium, should involve an abnormal quantity of work. The assertion that the validity of the osmotic-pressure principle necessarily implies that of the Mass-Action Law is therefore unwarranted from a deductive standpoint; while the inductive evidence, pointing strongly as it does to the substantial correctness of the former principle and the complete inadequacy of the latter one, makes it highly probable that the *separation of un-ionized molecules from ions does involve the expenditure of other work than that corresponding to their osmotic pressures.*

Since the ionization does not change with the concentration in accordance with the Mass-Action Law, it is natural to inquire what the law of its change is. This matter has been investigated from an empirical standpoint by several investigators with the help of the conductivity data. The results justify the statement of the following principles:

The un-ionized fraction of a salt as determined from the conductivity-ratio is proportional to the cube root of its total concentration, or to that of its ion-concentration, between $\frac{1}{2000}$ and $\frac{1}{10}$ *normal, in the case of both uni-univalent and uni-multivalent salts.* That is, $1-\gamma=Kc_{\frac{1}{3}}$, or $1-\gamma=K(c\gamma)^{\frac{1}{3}}$, where γ is the degree of ionization, c the concentration and K a constant. The first of these functions was proposed by Kohlrausch, the second by Barmwater. Owing to the relatively small variation of the ionization, these two functions cannot differ much as to their constancy, but on the whole the experimental data indicate that the second function is somewhat more constant. The average deviations of the actual measurements from the values corresponding to this function are $\frac{1}{4}$ per cent in the case of ten uni-univalent salts, $\frac{1}{3}$ per cent in the case of nine uni-bivalent salts, and also $\frac{1}{3}$ per cent in the case of three uni-tri- and uni-quadrivalent salts. The maximum deviations are two or three times as great. It is of interest to note that the strong mineral acids, hydrochloric and nitric, behave like salts in this respect. These functions have been shown to apply to potassium and sodium chlorides through a range of temperature extending from 18° to 306°. They do not apply at all closely to such salts of the bi-bivalent type as magnesium and copper sulphates, perhaps owing to appreciable hydrolysis. Nor do they represent satisfactorily the experimental data for any kind of salts at the very low concentrations lying between $\frac{1}{100000}$ and $\frac{1}{2000}$ normal, nor at concentrations higher than $\frac{1}{5}$ normal.

The experimental results are also well expressed by the statement that *in the case both of uni-univalent and uni-bivalent salts, between the concentrations of* $\frac{1}{10000}$ *and* $\frac{1}{5}$ *normal, the concentration of the un-ionized molecules is proportional to the concentration of the ions raised to a constant power, varying somewhat with the salt and the temperature, but as a rule only between the limits of* 1.43 *and* 1.56. That is, $c\,(1-\gamma) = K(c\gamma)^n$, where $n > 1.43$ and < 1.56.

This general function was first applied by Storch and was afterward further discussed by Euler and Bancroft. It has the advantage over the previous ones that it represents the data with accuracy even up to the highest dilutions, and therefore can be used for obtaining the limiting conductivity at zero concentration.

The applicability to the salts of different types of either of these principles governing the change of ionization with the concentration leads to the important conclusion that *the form of the concentration function is independent of the number of ions into which the molecules of the salt dissociate.* This remarkable fact, though previously recognized, has not been sufficiently emphasized, and it has been often ignored in discussions of the cause of the deviation of the ionization of salts from the requirements of the Mass-Action Law. It seems to me to show almost conclusively that chemical mass-action has no appreciable influence in determining the equilibrium between ions and un-ionized molecules. How complete the contradiction with the Mass-Action Law is may be illustrated by citing the specific facts that for di-ionic, tri-ionic, and tetra-ionic salts this law requires that the concentration of the un-ionized molecules be proportional to the square, the cube, and the fourth power, respectively, of the concentration of the ions; while the experimental data show that it is approximately proportional to the $\frac{3}{2}$ power of that concentration, whatever may be the type of salt.

Having seen in what manner the degree of ionization varies when the concentrations of both ions of the salt are simultaneously varied by dilution, it is of interest to determine the effect of changing the concentration of either ion separately. A study of the conductivity and the freezing-point of mixtures of two salts having one ion in common throws much light upon this question, for the following simple principle has been found to represent this phenomenon: *The conductivity and the freezing-point lowering of a mixture of salts having one ion in common are those calculated under the assumption that the degree of ionization of each salt is that which it would have if present alone at such an equivalent concentration that the concentration of either of its ions were equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture.*

This somewhat complicated statement may be illustrated by the following example: Suppose that a mixed solution is 0.1 normal with respect to sodium chloride and 0.2 normal with respect to sodium sulphate, and that it is 0.18 normal with reference to the positive or negative ions of these salts. The principle then requires that the ionization of either of these salts in the mixture be the same as it is in water alone when its ion-concentration is 0.18 normal.

This principle in regard to the conductivity of mixtures, which has been definitely stated by Arrhenius, is shown by the existing data to hold true, almost, if not quite, within the small experimental error of the determinations both for mixtures of salts of the same type and for those of salts of different types up to a concentration of at least ½ normal. Experiments confirming this principle have been made upon eight pairs of uni-univalent salts by Arrhenius, Manson, and Barmwater. In addition, the principle has been shown by several Canadian investigators, Archibald, McKay, and Barnes, to hold true for mixtures of potassium and sodium sulphates, potassium and copper or magnesium sulphates (up to 0.1 normal), potassium sulphate and chloride, barium and sodium chlorides, and zinc and copper sulphates — thus for almost every possible typical combination of uni-uni-, uni-bi-, and bi-bivalent salts. That the same principle is true of the freezing-point lowering is shown by the measurements of Archibald with mixtures of potassium and sodium sulphate. This proves that the phenomenon really has reference to the degree of ionization and that it does not arise from a possible variation in the migration-velocities of the ions.

Of especial interest is the relation of this principle to the validity of the Mass-Action Law. Almost all investigators of the conductivity of mixtures have concluded, from the fact that upon mixing solutions of equal ion-concentration there is no change in ionization, that the results do conform to this law. Yet it is scarcely conceivable that this law can apply to mixtures of salts in which the concentration of one ion is varied while maintaining that of the other constant, in view of the fact that it is known not to hold true for the variations of the concentrations of both ions produced by dilution. And in reality this conclusion, if regarded as a general expression of the facts, is entirely unwarranted. It is true that for certain typical combinations of salts — those for which from one molecule of each salt results by ionization not more than one ion of the kind not common to the salts — the principle here stated does coincide with the requirement of the Mass-Action Law. But for combinations not so characterized the Mass-Action Law predicts, as is readily seen upon formulating the equations, a conductivity of the mixture widely divergent from that actually found, and, therefore, from that expressed by the principle under consideration. This last statement applies, for example, to the mixtures before referred to of potassium sulphate with sodium sulphate, and of potassium sulphate with copper or magnesium sulphate, the first of which have been studied both with respect to their conductivity and freezing-point. The Law of Chemical Mass-Action here again shows itself entirely inapplicable to the phenomena connected with the ionization of salts. The opinion of some investigators that the deviations from this law indicated by the conductivity were only apparent, and that they were attributable to variations in the migration-velocity, has arisen, no doubt, from the fact that they have confined their attention to di-ionic salts, and have failed to recognize, on the one hand, the striking divergences from it exhibited by tri-ionic salts, and, on the other, the substantial correspondence of the conductivity and freezing-point results.

Combining this principle in regard to the ionization of mixed salts in solution with the empirical concentration law of Storch for single salts, we are led to the conclusion that the ratio of the concentration of the un-ionized part to the product of the concentrations of the two ions (but in the case of tri-ionic salts *not* raised to a power corresponding to the requirements of the Mass-Action Law) is a function of the sum of the equivalent concentrations of all the ions in the solution and of that alone.[1] This ratio is, moreover, roughly inversely proportional to the square root of the total ion-concentration.

The correctness of this principle is further demonstrated by the fact that with its aid the conductivity of a mixture of two salts without a common ion can be computed from their separate conductivities. This is shown by the conductivity measurements, made by Archibald and more recently by Sherrill, upon mixtures of potassium chloride and sodium sulphate, or of sodium chloride and potassium sulphate. Up to at least 0.2 normal concentration, the agreement between the observed and calculated values is within 0.5 per cent. On the other

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[1] This is expressed mathematically by the following equation in which c_1 and c_2 represent the equivalent concentrations of the two salts, and γ_1 and γ_2 their degrees of ionization in the presence of each other:

$$\frac{c_1\gamma_1(c_1\gamma_1+c_2\gamma_2)}{c_1(1-\gamma_1)}=K_1(c_1\gamma_1+c_2\gamma_2)^{n-1}$$

hand, the divergence of the observed values from the requirement of the Mass-Action Law amounts to many per cent.

It seems appropriate at once to supplement these principles in regard to the form of the concentration function by a statement of two general rules which have been found to express the magnitude of the ionization of salts of different types. These rules, unlike the preceding principles, are only crude approximations; but, nevertheless, they prove of some assistance in rough applications of the ionic theory, and undoubtedly possess an important theoretical significance not yet recognized. They may be stated as follows: (1) *the decrease of ionization with increasing concentration is roughly constant in the case of different salts of the same type;* and (2) *the un-ionized fraction at any definite molal concentration is roughly proportional to the product of the valences of the two ions in the case of salts of different types.* Thus, at 0.1 normal concentration the mean value of the degree of ionization for 17 uni-univalent salts measured at 18° is 83.3 per cent, the average deviation of the separate values from this mean is 2.1 per cent, and the maximum deviation of any of them is 5.4 per cent, of the mean value; while for fourteen uni-bivalent salts the mean value is 69.8 per cent, the average deviation 5 per cent of this, and the maximum deviation about 10 per cent of it. The un-ionized fraction in $\frac{1}{20}$ molal solution is 13½ per cent for these univalent salts; 30 per cent, or about twice as great, for the uni-bivalent salts; and 60 per cent, or about four times as great, for the three bi-bivalent salts investigated (zinc, magnesium, and copper sulphates). The salts of mercury and cadmium are pronounced exceptions to the rule.

Far more extensive material for testing these rules is furnished by the measurements made at 25° between the concentrations of $\frac{1}{32}$ and $\frac{1}{1024}$ normal. In the case of the uni-univalent salts, data exist at this temperature and these concentrations for thirty-six inorganic salts, about sixty-five sodium salts of organic acids, and about an equal number of hydrochlorates of organic bases. A consideration of all these data shows that, with only three or four exceptions not of a pronounced character, the values of the degree of ionization of all these salts in $\frac{1}{32}$ normal solution lie between the limits of 84 and 90 per cent and are fairly uniformly distributed throughout this range of 6 per cent. For sixty-seven uni-bivalent salts the corresponding limits of the ionization values are 72 and 81 per cent, while for only four such salts do the values lie beyond these limits. For the six uni-trivalent salts investigated the range is from 67 to 76 per cent; for the three uni-quadrivalent salts from 59 to 63 per cent, and for twelve bi-bivalent salts from 49 to 63 per cent, while three such salts show more considerable variations. The values of the un-ionized fraction corresponding to the mean of these two limits for the different types of salts at the same equivalent concentration increase somewhat more slowly than the product of the valences of the ions. The proportionality becomes a fairly close one, however, when the salts are compared at the same molal instead of the same equivalent concentration. Thus, with the help of the Kohlrausch concentration function, it is calculated from the preceding values that the un-ionized fractions in $\frac{1}{32}$ molal solution are as follows:

13 per cent for the uni-univalent salts,
29½ per cent for the uni-bivalent salts,
41 per cent for the uni-trivalent salts,
62 per cent for the uni-quadrivalent salts,
55 per cent for the bi-bivalent salts, —

which are seen to be approximately the required multiples of the constant factor 14.

Before leaving this subject it should be stated that the results conform, on the whole, about equally well to the rule that *the decrease of equivalent conductivity* (*instead of ionization*) *is roughly constant for salts of the same type;* and when the comparison is made at the same equivalent concentration, distinctly better to the rule that the *decrease of equivalent conductivity is proportional to the product of the valences of the ions for salts of different types.* When compared at the same *molal* concentration, however, this rule does not apply. These rules were originally stated by Ostwald. They differ not inconsiderably from those expressing the change in ionization — namely, to an extent corresponding to the variations of the conductivities at extreme dilution. The deviations are so irregular, however, that, from an empirical standpoint, the choice between the two pairs of rules is arbitrary. In either form these rules seem to justify the inference that the degree of ionization of salts, unlike that of the organic acids and bases, is not primarily a specific chemical property determined by chemical affinity, but that it is determined, at least in the main, by the magnitude of the electric charges on the ions.

The establishment of the principle in regard to the ionization of a mixture of salts has a direct bearing on the phenomenon of the effect of one salt on the solubility of another with a common ion. It has been usually assumed that in a (not too concentrated) saturated solution the un-ionized molecules of the salt always have the same concentration; and, secondly, that the product of the *ion*-concentrations (each raised to a power corresponding to the number resulting from one molecule) also retains the same value. And the experimental results in several cases have been shown to accord fairly well with these two hypotheses. Yet their simultaneous validity is quite inconsistent with the principle in regard to the ionization in mixtures. In fact, when considered in the light of this principle, the existing data lead to the conclusion that the former hypothesis is not even approximately true, and that the latter one, at any rate in cases where the ionization is far from complete, is affected by a considerable error. One example may be cited: when thallous chloride and bromate, each of which alone has a solubility of about $\frac{1}{40}$ normal in water at 40°, are simultaneously present as solid phases, the solubility of each is reduced by the other to an extent which shows that the concentration of the un-ionized molecules is diminished by about 15 per cent and that the product of the ion-concentrations is increased by about 5 per cent. This case is a typical one; but what the quantitative law of the influence in question is, can be determined only by a further study of the phenomenon. In the case of tri-ionic salts, the ion-concentration product is even approximately constant, only when the square — not when the first power — of the concentration of the univalent ion is employed. This has been shown by experiments with lead iodide in the presence of potassium iodide, with lead chloride in that of other chlorides, and with calcium hydroxide in that of ammonium chloride.

I will close by calling your attention to a remarkable principle in regard to the properties of salt solutions, of a character quite distinct from those thus far considered. That many properties of dilute salt solutions can be expressed as the sum of values assigned once for all to the constituent radicals or ions was long ago recognized, and has often been cited as a corollary from the ionic theory. That this additivity of properties persists up to fairly high concentrations is a fact, however, that has received scant consideration, owing to its apparent lack of relationship to that theory. This fact is shown strikingly in the case of certain highly specific optical properties which are ordinarily found to be dependent in a high degree on molecular structure. Thus, the experimental data fully warrant the statement of the principle that *the optical activity and the color of salts in solution, when referred to equivalent quantities, are independent of the concentration and therefore of the degree of ionization of the salts, and are additive with respect to the properties of the constituent ions even up to concentrations where a large proportion of the salt is in the un-ionized state.* Abundant data might be cited in support of this principle, especially with reference to optical activity. But I can only illustrate the character of the evidence by presenting a few of the results obtained by Walden with the salts of *a*-brom-camphor-sulphonic acid. In $\frac{1}{30}$ normal solution he found the following values of the molal rotatory power:

Lithium salt	275	Acid itself	273
Sodium salt	272	Beryllium salt	274
Potassium salt	273	Zinc salt	272
Thallium salt	273	Barium salt	272

The values are seen to be substantially identical, although the conductivity shows the acid to have an un-ionized fraction of 7 per cent, the salts of the univalent metals one of 16 per cent, and those of the bivalent metals one of 30 per cent, and although the un-ionized molecules present contain in some cases the elements hydrogen, lithium, and beryllium of very small atomic weights, and in two others the elements thallium and barium of large atomic weights.

If there were not other evidence to the contrary, the existence of this general principle, which is also applicable to many other properties, would almost warrant the conclusion that the salts are completely ionized up to the concentration in question, and that the decrease in conductivity is due merely to a change in migration-velocity. But, in view of the apparently conclusive evidence against such an hypothesis, we can only conclude that the form of union represented by the un-ionized molecules of salts differs essentially from ordinary chemical combination, it being so much less intimate that the ions still exhibit their characteristic properties, in so far as these are not dependent upon their existence as separate aggregates.

These, then, are the empirical principles to which a critical analysis of the experimental data leads. Upon these principles must be based the rational, theoretical explanation of the phenomena in question. The discovery of that explanation constitutes one of the most important of the present problems of physical chemistry.

SHORT PAPERS

Dr. Frank K. Cameron, of the United States Department of Agriculture, presented a paper on "The Application of Physical Chemistry to Agricultural Chemistry," in which he stated that there was some difficulty in approaching this subject, for the reason that what constitutes agricultural chemistry cannot be clearly defined, and the boundary lines between it and other branches of applied chemistry are not always evident. Much of biological chemistry and much of geological chemistry along lines on which notable achievements have been made by the applications of the principles and methods which in recent years have come to be called physical chemistry, could with propriety be claimed also for agricultural chemistry. One finds agricultural chemists engaged in the examination of drugs, fertilizers, leathers, and tannins, etc., as well as in the examination of foods or soils. Important applications of physical chemistry are to be found along many of these lines which might be claimed for the agricultural chemist, but disputed as belonging to the field of the industrial chemist or others. The manufacture of nitric acid by electrochemical methods, while a problem of industrial chemistry, is important mainly because of the use of nitrates in agriculture. But confining one's self strictly to the work professedly done in the immediate interest of agriculture or farm practices, there is much evidence to be found of the increasing influence of physical chemistry.

A valuable and interesting paper followed on the close relation and applications of physical chemistry to the science of agriculture, and the speaker concluded by saying that "The problems presented by agricultural chemistry do not commend themselves to the investigator who is interested in chemistry alone for its own sake. They are generally complex and not well suited to the elucidation or illustration of hypotheses in pure chemistry. The pecuniary rewards which agricultural chemistry offers are not sufficient in comparison with other fields to tempt the man trained in physical chemistry who wishes to use his equipment to this end. But to the man who has the training and who cares not so much that his problems be pure science as that they may be undertaken in a scientific spirit and with scientific methods, the application of physical chemistry to agriculture offers many opportunities. He can have the satisfaction of not only doing good scientific work but directly helping an industry of ultimate importance to all his race and of immediate importance to the numerically largest class of the race."

Professor Henry Snyder, of the University of Minnesota, read a paper on "The Digestibility of Bread."

Professor Louis Kahlenberg, of the University of Wisconsin, read a paper "On the Relation between the Processes of Solution, Chemical Action, and Osmosis."

GOLDEN AGE OF THE MEDICI

Photogravure of a Painting by Andreas Müller

While the Medici family were distinguished for cruelty, some of them, notably the queen of Henry IV, were no less famous for their patronage of learning. The artist has admirably illustrated the spirit of that age by grouping the most famous literati of Europe in the Park Monceaux, each being a portrait, while the assemblage is presided over by Marie de Medici, who is awarding tributes to those who have contributed to the glory of literature. The conception is grand, and the execution most excellent.


VERGILIUS

SECTION D—PHYSIOLOGICAL CHEMISTRY

SECTION D — PHYSIOLOGICAL CHEMISTRY

(*Hall* 16, *September* 22, 3 *p. m.*)

CHAIRMAN: PROFESSOR WILBUR O. ATWATER, Wesleyan University.
SPEAKERS: PROFESSOR O. COHNHEIM, University of Heidelberg.
PROFESSOR RUSSELL H. CHITTENDEN, Yale University.
SECRETARY: DR. C. L. ALSBERG, Harvard University.

PROBLEMS IN NUTRITION

BY OTTO COHNHEIM

(*Translated from the German by Prof. J. L. R. Morgan, Columbia University*)

[**Otto Cohnheim,** Special Professor of Physiology, University of Heidelberg; Assistant Physiological Institute. b. May 30, 1873, Breslau, Germany. Graduate Physician, Heidelberg, 1896; M.D. *ibid.* 1896; Privat-Docent, *ibid.* 1898; Zoölogical Station, Naples, 1900–02; Pawlow's Institute, St. Petersburg, 1902. Author of *Chemistry of Albuminous Substances*; *Physiology of Alpinism*; and many articles on biology and physiological chemistry.]

THE object of the papers read here is not so much the consideration of any one restricted branch of science as it is the discussion of those broader fields which lie between and are intimately connected with several branches of science. In accord with this I propose to speak on a subject belonging primarily to the physiology of nutrition, but one which at the same time has very great politico-economic importance. To-day, as the result of the great progress which has been made in the physiology of nutrition, we can in general give a definite answer to the question as to the extent of the agreement between the actually observed dietary of an individual or group of individuals, and the conclusions obtained theoretically. At any rate to-day we can account physiologically for, and regard as physiologically necessary, a whole series of phenomena which in the past could only be accepted as empirical facts. The physiological consideration of race-dietary, on the other hand, will show how it happened that social considerations for decades have directed and restricted physiological progress.

The food of man, as is well known, is composed of proteids, fats, and carbohydrates. In most food-stuffs we have all three classes of substances; only sugar and butter belong solely to one class, the former being a carbohydrate, the latter a fat. The proteids assume a particularly important position owing to the fact that our bodies themselves are composed to a very large extent of proteinaceous material and hence can only be built up by proteids. The major portion of the proteids we absorb are derived from bread and meat. The foods richest in proteids are meat, fish, eggs, cheese, milk, etc.; in short, those foods having an animal origin. The older physiology considered the material composition of the food as the essential characteristic, although even Liebig recognized metabolism as a process of combustion, and it is the work of the Voit school which has caused the calorimetrical value of food to attain its present central position. By its combustion, the nutriment absorbed supplies the energy which is required by the human body for its various purposes. The value of a food, then, can be expressed by the amount of energy it can produce, and this value can be stated clearly and accurately in the ordinary terms of energy, *i. e.*, in units of heat, or calories. As the result of years of work by various investigators it has been found that the individual foods can be almost completely represented by their calorimetrical values. Rubner, Zuntz, and Atwater, by differing methods, have all come to the same conclusion, viz. that for purposes of heat and muscular action, *i. e.*, for its principal requirements, proteids, fats, and carbohydrates, the organism can employ vegetable and animal foods equally well. That the civilized nations of Europe and America employ bread and meat as the principal source, while the Indians and Chinese use rice exclusively, and the Esquimos fat, is not due to any difference in physiological organization, or to differing needs of the body, but simply to the more or less easy attainment of the substances, fruitfulness of the soil, and other secondary circumstances.

The law of the calorimetrical equivalency of all food-stuffs has but one notable exception. So far as investigation has been carried out it has been found that the dietary of any man or race always contains a certain and apparently similar amount of proteinaceous material. The kind of material seemingly has little influence, but about 100 gr. of protein is found with great constancy in the daily food of the individual. In the food of a powerful man, who exerts a fairly large amount of muscular effort, Voit found 118 gr. of proteids per day, and he assumes this as a basis for the dietary of a soldier. Weaker men, doing less muscular work, require, according to Voit, a smaller quantity of proteids. For the poorly nourished, and also for those who are incapable of any intense effort, the hand-loom weavers of Zittau, the poor of Naples, and the poorest negroes of Alabama, von Rechenberg, Manfredi, and Atwater have found much lower amounts. During comparatively short laboratory experiments, Munk, Hirschfeld, Kumagawa, and especially Sivén have found considerably smaller quantities. For well-nourished men, during long periods, Chittenden, only, found less proteids; otherwise, physiological investigation, as well as the experience of daily life, has shown that it is not well to consume less than 100 gr. of proteids per day.

This amount, indeed, is rarely exceeded, for Chittenden has shown that even the diet of well-to-do Americans, which appears to us as the richest in proteids, scarcely ever exceeds 100 gr. of proteids a day, and the investigation of the freely-chosen fare of the most various individuals leads to the same result.

The question as to the need of the human body for 100 gr. of proteinaceous material per day has often been raised; and even to-day cannot be answered with certainty. During the last years, however, we have learned of a series of reasons which may serve to throw some light upon the subject.

That the growing organism requires proteids is self-evident, for in this way only can it obtain the materials of which it is composed. We know further, however, that the adult organism continually repairs and increases its organs and consequently also requires proteids. According to Zuntz a man increases his muscles when he does unaccustomed work (for example, when he learns a new sport) or even by increased exertion upon his usual work. Bunge attributes a considerable requirement of proteids in adults to the loss of organ-proteids in the sperm of man, and to menstruation, pregnancy, and lactation in woman. And later years have disclosed the genetic relations of many decomposition-products of the proteids with carbohydrates, with substances of the bile, and others, which are necessary, at any rate for a time, to neutralize poisons, or which are essential for the intermediate metabolism; and these relations appear to render desirable at least the presence of a copious supply of proteinaceous material.

A second reason is more difficult to grasp. Even the first metabolic experiments of Voit showed that although the proteids possess no higher nutritive (fuel) value than the carbohydrates, and a very much smaller nutritive (fuel) value than the fats, they burn very much more rapidly; and this has since been repeatedly confirmed. When the supply of proteids in the food is increased above the actual need of the body, the fats and carbohydrates are stored up, and the proteids are burned to a very much greater extent. The relations between the cells of our bodies and the substances absorbed as nutriment can best be illustrated by an analogy. For the neutralization of an alkali any acid may be employed; but when several acids of differing strength are present together, the strongest one will be partially saturated before the others even begin to react. In the same way protoplasm can supply its need with all three nutritive substances; but when all three are present at once the proteids burn first. With a large excess of the other two, however, the action of their masses becomes evident, exactly as in the illustration with the acids, and they protect the proteids from combustion. In the absence of fats and carbohydrates, the body readily goes into such a state that its own proteids are attacked, *i. e.*, it consumes itself. This is probably the most important reason why a definite minimum amount of proteids is essential in a small total amount of nutriment. That further differences exist among the individual organs themselves is still to be proven, but at present it appears quite probable.

A third ground has been disclosed during the past few years by the work of the great Russian investigator, Pawlow. We know from this that the nervous connection of the digestive system with the sense organs of the head determines the enjoyment of the food, and hence regulates the choice of that. We know further from Pawlow, Weinland, and Starling that this connection is not fixed once for all, but varies according to the needs of the time. When any such relation is observed we must always conclude that it is adapted to an end, for otherwise it would have disappeared within a short time. Pure proteids are tasteless and odorless, and also fail to act upon the sensitive nerves of the stomach and intestine; in all natural foods, on the other hand, the proteids are always associated with the pleasant-tasting constituents of nutriment, and those which stimulate digestion. For us, just as for the carnivorous animals investigated by Pawlow, the substances richest in proteids are always the most pleasant to the taste, and those which arouse the appetite the most. The foods which are poorer in proteids, as rice and potatoes, stimulate the digestion less and consequently are more difficultly digestible. A food-stuff free from proteids has already been shown in animal experiments to be impossible as a diet, and even in experiments with substances which are poor in proteids Sivén and Röhl encountered insurmountable difficulties owing to the tastelessness of the material.

Even though we do not as yet know all the reasons, it is at any rate obvious that, for long periods of time and for normal nutrition, Voit has discovered the correct condition, viz., that an amount of proteids equal to 100 gr. per day is essential, or at any rate can be designated as desirable.

Since in consequence of the special internal organization of the human body, and because it is the minimum amount used by all men, this amount of proteids is independent of the form of nourishment absorbed, and independent of the habits of life. Even as early as 1860 and 1866 Voit showed that the protein consumption of those doing hard work is not greater than of those who do none; and this result has been confirmed many times. The American physiologist, Atwater, has made an especial study of this question, using his respiration calorimeter. As the average of numerous experiments, carried out with the greatest exactness, he found that the subject of experiment, whether resting or working, decomposed the same amount of proteids, even when the production of calories by the work rose to double or more. Indeed, the decomposition of proteids can even be decreased by muscular activity, for the larger total of nutriment consumed prevents the decomposition of the proteids of the body.

The total amount of nutriment of a man is almost exclusively determined by the muscular work he performs. The mental work has nothing to do with nutrition; whether the brain is used intensely, or whether it is retained as inactive as is possible, as far as we know to-day, does not seem to affect the requirement of energy by the body, nor its requirement of food. The amount of energy required by the individual to sustain his bodily temperature differs but slightly, for the differences in external temperature are nearly compensated by the wonderfully acting heat regulation of our bodies, and the artificial heat regulation by our clothes and dwellings. The influence of muscular activity is very much greater. A man resting quietly in a warm room requires from 1500–1700 calories per day; while one working in the laboratory, or sitting, produces from 2100–2400 calories. For light hand labor this is increased to 2800, while for laborers, Liebig and others have observed from 4000–6000 calories, and Atwater and Wood found up to 8000 calories for the lumbermen of Maine. As the average of all his experiments, Atwater found 2270 calories for quiescent, and 4550 calories for hard-working people, *i. e.*, exactly double the value.

Although the total number of calories varies according to the work, the amount of proteids for all men remains approximately equal, and from this we can draw an important conclusion. The food of those not doing physical work must be relatively richer in proteids, for an equal absolute amount of proteids must be contained in a smaller total amount of food. The foods richest in proteids are meat and the other products of the animal kingdom, and it is evident that the diet must be the richer in meat, the less physical work done by the person. An illustrative example will make this quite clear. A laborer does hard physical work, and consequently requires a diet which produces 5000 calories per day. Consuming only bread, potatoes, and other vegetable products, he would obtain 100 gr. of proteids and even more without trouble. Let us assume that he moves to a city and changes his occupation, living a sedentary life. For this he would require but 2500 calories, and retaining the quality of his dietary he would have to do one of two things. Either he must eat the previous quantity, which would be impossible for any length of time, for the body could not use such an excessive amount, or he must decrease it to one half, whereby he would obtain the requisite number of calories, but with them only 50 gr. of proteids. To nourish himself properly, then, he will have to decrease his allowance of food to one half, and add to it 50 gr. of proteids, *i. e.*, about 250 gr. of meat. This example, of course, is extreme, and will not often be observed with such distinctness. The principle, however, is always to be observed. The food of those belonging to the well-to-do classes, *i. e.*, of those who do no hard physical work, in all countries contains the most meat. This, however, is no luxury, but is based upon physiological grounds. Comparing different countries, or different classes in the same country, we always obtain the following result. To the degree that pure hand labor is replaced by the work of the head, and that of overseeing machines, to that same degree is the consumption of meat increased. This is shown most obviously, however, by the comparison of the country population with that of the city. The modern mill-hand lives, it is true, by the work of his hands, but that work is quite different from that done by the farm laborer. The overseeing and directing of the complicated machines, as every other form of skilled labor, requires attention, intelligence and dexterity, but does not require the muscular exertion necessary for mowing, threshing, and the felling of trees. With the difference in activity there must also be a difference in the quantity and kind of food. The people in a city in general eat less in total amount, but this food is qualitatively different, *i. e.*, must consist of substances relatively rich in proteids, as meat and other animal products.

From the politico-economical, as well as from the medical, point of view the smaller amount of food consumed by the mill-hand, as compared to that of the farm laborer, is regarded as a sign of degeneration. This is obviously untrue, for there is no general standard of nutrition which is applicable, or even desirable, for all men. The nutriment, with respect to quantity, is dependent solely upon the amount of muscular work done. On the other hand, the increased consumption of meat, eggs, and other foods, agreeable to the taste because rich in proteids, has been attributed to the greediness of the urban population. Nothing could be more false. It is just for this large class that the enjoyment of meat and other foods rich in proteids is a physiological postulate; and for the other large class making up the urban population, merchants, officials, clerks, etc., this is true in even a more striking degree, for the physical work necessary in such occupations is still smaller in amount, and their food must consequently be even richer in proteids.

It is not for me to draw further conclusions from the physiological principle that the food of the urban population should contain less vegetable and more animal substance. I must rather consider the influence of these relations upon physiology itself. The classes not doing severe physical work are the higher and better-to-do, and, since they are great meat-eaters, it is but too easy to conclude that in general meat-eaters are the most valuable and best. This opinion is very rife in lay circles, and even physiology has not long been free from it. The great Liebig, the founder of the doctrine of scientific nutrition, held that meat is the only active form of food (for muscular activity), and ascribed to it a very high nutritive value. Liebig's theory was disproved 44 years ago by Voit and soon afterward by Fick and Wislicenius. But even to-day there are physiologists who hold fast to the Liebig doctrine, and indeed the relics of it are still to be found everywhere in physiology and medicine. The tenacity of life of this old error would be difficult to explain, were it not apparently supported by the daily experience that the well-to-do eat meat, eggs, etc., while the day laborers satisfy themselves with bread and potatoes.

From the difference in the diet of those who do severe muscular work and those who do none, there is a further conclusion to be drawn. The only indigestible constituent of human food is cellulose. Cellulose, being contained only in vegetable food, forms but a small constituent of the diet of the man doing little physical work. According to von Knieriem cellulose is of great importance in the process of digestion, for as indigestible, solid substance it stimulates the activity of the intestine. While carnivorous animals, with their short muscular intestine, do not require it, graminivorous animals, with their long, coiled, weak intestine, cannot do without it for any length of time. Man, in the organization of his digestive apparatus, stands midway between these two extremes, and while cellulose is not absolutely essential to him, its absence sometimes causes a motoric atrophy of the intestine which results in chronic constipation and its consequences. The connection between constipation and sedentary occupations has long been recognized, but people have been too prone to attempt to explain it mechanically, whereas the connecting link in reality is the dietary of the man leading the sedentary life. In his daily life such a man does but little physical work, and consequently in general eats little, and especially little of the vegetable food poor in proteids but rich in cellulose. We hear nothing of digestive troubles of the people living in the country, while city people, especially the well-to-do, suffer severely from them. In England and America, judging from the wide advertisement of purgatives, the trouble is much more common than in Germany; but in both lands the rye bread, which is comparatively rich in cellulose, is replaced by fine wheat bread, which is much poorer in cellulose, and the substitution of animal products for bread is also more common than with us.

The vegetarians have been agreed on this point for a long time. They observed how many digestive and other troubles are common to the dwellers in cities (*i. e.*, where few live like the vegetarian peasant), and all without knowledge of the physiological grounds held up the peasant as the ideal for the citizen. But what is correct for the peasant, who must produce 4000–5000 calories, is not correct for those who require but 2300 calories or less. He obtains, then, as explained above, too little of proteids, or aids himself by his fondness for the vegetables rich in proteids, but at the same time poor in cellulose, and hence fails utterly to attain his end.

It would be more correct if the transition to the vegetable diet is combined with a treatment which will increase the need of substance, as has been done from non-scientific sides and without knowledge of the physiological principle.

The only rational cure for the disturbances which can ultimately be traced to the lack of muscular activity is to devote one's self to this muscular work outside of one's daily occupation, as is possible by aid of the various sports. It is no accident, but rather a necessary physiological phenomenon, that the need of active sports has always developed wherever there is a class of society made up of those doing no intense physical work. Indeed, we can readily follow this in history; when the citizens of the Greek cities devoted themselves to athletic sports, when the knights of the Middle Ages jousted, there was always an aristocracy who did no manual labor. The home of our modern sports is England, the oldest industrial country. In Germany the first steps in the direction of sports were made at the universities, where thousands of young men did mental work. The scope of the sport of to-day is very much broader, however, for its followers include merchants and the workers in the various industries. Sports lead directly to a change in the food requirements of the individual; every bicyclist, every mountain climber knows that on his trips he can eat things which do not appeal to him at all when at home. I must be content here to restrict myself to these indications disclosing the scientific principles of this subject, which is apparently so far removed from our point of departure. By unwearying work the physiology of nutrition has established a scientific experimental foundation upon which other sciences may now build.

THE PRESENT PROBLEMS OF PHYSIOLOGICAL CHEMISTRY

BY RUSSELL HENRY CHITTENDEN

[Russell Henry Chittenden, LL.D. Sc.D., Director and Treasurer of the Sheffield Scientific School, Yale University, and Professor of Physiological Chemistry. b. February 18, 1856, New Haven, Connecticut. Ph.B. and Ph.D. Yale University; Special course, Heidelberg University. President of the American Physiological Society, 1895–1904; President of the American Society of Naturalists, 1893. Member of the Connecticut Academy of Arts and Sciences; National Academy of Sciences; American Philosophical Society. Author of many papers on physiological subjects published in American and foreign journals.]

In considering a proper presentation of the subject assigned me, I am impressed with the influence which a man's own field of work and his own line of thought will naturally exercise upon his point of view. It may be questioned whether his judgment can be wholly trusted, whether he will not in fact, unconsciously it may be, give a dwarfed or one-sided presentation of the subject from a natural habit of looking at things in their bearing upon the line of work and thought in which he himself is personally most interested. While this may not be wholly undesirable, of still greater advantage will be a brief but judicious presentation of all the more important problems that confront the physiological chemist of the present day; but whether this can be done satisfactorily in the time allotted is very questionable. However, the effort will be made to emphasize, so far as the time will allow, what to the writer seem the more significant and far-reaching problems in physiological chemistry that call for speedy solution.

Of fundamental importance is the question, what is the exact chemical constitution of proteid matter? The basis of all cell-life, the most complex molecule that enters into the structure of the living organism, proteid or albuminous material holds a peculiar position. A labile molecule, it is easily prone to change, and its many decomposition-products confront us on all sides in our study of life's processes. Yet to-day, in spite of all that has been accomplished, even with the brilliant work of Kossel and Emil Fischer, we still lack adequate knowledge of all the groups and radicles that are combined in this atomic complex.

In the study of metabolism and nutrition, both in health and in disease, in our conception of the anabolic processes of life, in our theories regarding the chemical relationships of the varied katabolites floating about through the organism, and in many other connections, we need for our guidance a full knowledge of the chemical nature of this most important class of substances. Thanks to the work of many brilliant investigators, our knowledge is progressing and broadening, but we still lack that comprehensive understanding of the inner structure of the molecule that would serve to illuminate our field of vision and give us a clear conception of the chemical constitution of this group of physiologically important ground substances in living protoplasm.

As is well known, the proteid bodies constitute a group of widely divergent substances. Of these, the basic protamines are undoubtedly the simplest and lowest in the scale, and it is quite probable, as suggested by Kossel, that these substances constitute the nuclei of all proteids. The protamines differ somewhat among themselves, but as a group they are characterized by their high content of diamino-acids, especially arginin. Thus, salmin yields on decomposition 84 per cent of arginin, clupein 82 per cent, cyclopterin 62 per cent, and sturin 58 per cent.[1] Sturin also contains 13 per cent of histidin and 12 per cent of lysin, while the other protamines appear to contain no diamino-acids aside from arginin. Further, the protamines contain diamido-valerianic acid, monoamido-valerianic acid, tyrosin or p-oxyphenyl-amidopropionic acid, skatolaminoacetic acid, a-pyrrolidincarbonic acid and serin.[2] Salmin [3] has also been shown to contain alanin, leucin, probably also phenylalanin and aspartic acid.

If we pass from the simplest of the proteid bodies to the most complex, as the nucleins, we find present in the latter not only arginin, lysin, and histidin, but, in addition, such bodies as thymin, the purin bases, leucin, aspartic, and glutamic acids, two sulphur-containing groups, furfurol-forming groups, pyrrolidincarbonic acid, a skatol-forming group, phosphoric acid, amidovalerianic acid, a levulinic acid-forming group, glycosamine, pentose, uracil, and probably phenylamido-propionic acid.[4] In the histon from the nucleohiston of the thymus, we find in addition to the hexone bases and the monoamido-acids characteristic of the ordinary albuminous bodies such substances as glycocoll, cystin, and alanin.

These statements, brief and incomplete though they are, will serve to illustrate the complexity of the proteid molecule, and at the same time they indicate the close genetic relationship which unquestionably exists between the varied members of this large group of substances. There is no doubt that Kossel and his co-workers, in their efforts to unravel the constitution of the protamines, are pursuing a wise course in paving the way for a comprehension of the exact nature of the more

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[1] Kossel and his students. See Kossel and Dakin, *Ueber Salmin und Clupein, Zeitschrift für physiologische Chemie*, Band 41, p. 407.

[2] Kossel und Dakin, *Beiträge zum System der einfachsten Eiweisskörper, Zeitschrift für physiologische Chemie*, Band 40, p. 565.

[3] Abderhalden, *Die Monoaminosäuren des Salmins, Zeitschrift für physiologische Chemie*, Band 41, p. 55.

[4] See Kossel, *Über den gegenwärtigen Stand der Eiweiss Chemie, Berichte der Deutschen Chem. Gesellschaft*, Jahrgang 34, p. 3214.

complicated proteids. There is no doubt that the protamines of one type or another are integral parts of every proteid molecule, and when their chemical constitution is made quite clear, much will have been accomplished toward a fuller understanding of the more complicated forms.

It needs no imagination to foresee what a full knowledge of the chemical constitution of all types of proteid matter will mean for the physiologist and physiological chemist. Much that is now cloudy and uncertain in our understanding of cell and tissue metabolism, in our comprehension of nutritive changes in general, of digestive proteolysis and of intracellular autolysis, will become clear as crystal. The problem, however, is not a simple one, but is exceedingly complex, for it is to be remembered that just as the individual proteids differ from each other in superficial reactions and characteristics, so do they undoubtedly differ in their inner structure. Hence, we must expect to find variations in the make-up of the individual molecules, and it is one of the most important problems of to-day to ascertain the nature of these chemical variations, to recognize the individual groups that give character to the molecules, and to learn how these groups are bound together to make the typical proteid of this and that tissue or organ. The solution of this problem promises much for the advancement of physiological chemistry, but it holds out the promise of even more for the good of physiology in general, since there is bound up in the chemical structure of the proteid molecules a full and complete explanation of tissue changes, and of many metabolic phenomena which to-day are as sealed volumes.

The development of our knowledge regarding the cell as a physiological unit has led to a fuller recognition of the importance of discriminating between the primary and secondary cell constituents. As a result, the physiological chemist has come to realize the necessity of more exact knowledge as to the nature and distribution of the primary components of cells, because of the bearing this knowledge may have upon the general question of how far the lines of chemical decomposition characteristic of each group of cells are dependent upon the character of the anabolic processes by which that particular cell protoplasm is formed, and how far the peculiar katabolic or retrogressive changes of that group of cells are due to outside influences, exerted by specific nerve fibres, or by the character of the blood and lymph stream. The physiological chemist would know whether the secret of glandular secretion, of tissue changes, of metabolic activity, is to be found in the particular forms of protoplasm that enter into the structure of the component cells, whether it is associated in any way with some inherent quality of the primary cell constituents.

There is something marvelous in the unerring certainty with which a given group of cells performs its work, never deviating a hair's breadth from the beaten course, and turning out year after year a definite line of products for the specific purpose in view. Why is it that the epithelial cells of the salivary glands always manufacture mucinogen and ptyalin; the gastric gland cells pepsinogen, renninogen, and hydrochloric acid; the cells of the pancreas trypsinogen and steapsin; the hepatic cells bilirubin, biliverdin, and the specific bile acids; the cells of the thyroid iodothyrin, and the cells of the adrenals epinephrin? Essentially the same blood and lymph bathe all these cells with a like nutritive pabulum, and yet each group of cells performs its own line of work, never going astray, in health, and never even temporarily producing a product which rightfully belongs to the other class of cells. Are we to suppose that all these varied products are manufactured from the same cell protoplasm, from a common stock, that each one owes its origin to some particular force controlled by extracellular influences, each group of cells being made to manufacture a given product out of the same mother substance? Or, on the other hand, are we to assume that each group of cells, as it is developed, has as a birthright the quality of producing from its particular protoplasm a certain line of products, simply because of the peculiar chemical nature or constitution of that protoplasm?

In other words, do all the intricacies of cellular activity depend primarily upon the character of the anabolic processes by which that protoplasm is built up out of the food-materials by which the cells are nourished? It may be just as difficult to explain why and how the cells are able to manufacture a specific protoplasm out of a common pabulum, but the main problem which confronts us is surely capable of being solved. We need to know how far the primary cell constituents of different groups of cells, of the different organs and tissues, are similar to or unlike each other. If it is shown that the primary cell constituents differ for each glandular organ and tissue, that each group of individualized cells has a protoplasm characterized by some specific feature, then we shall have reason to believe that the anabolic processes are as much, if not more, responsible for individuality of function than the katabolic processes. We may conceive of all protoplasm being built, so to speak, on a certain general plan of structure, but with side-chains of varying nature, and that these side-chains determine in a measure the character of the katabolic or alteration products that result from the natural activity of the cell protoplasm. In other words, if this conception be true, it is the chemical constitution of the cell protoplasm that is primarily responsible for the character of the changes that take place in all active tissues and organs. The extent of oxygenation as influenced by the circulating blood, the direct and indirect influence of various nerve fibres, etc., may all act as modifying agents, but only to the degree of accelerating or inhibiting the rhythmical process which travels along a certain definite channel because of the peculiar chemical nature of the cell protoplasm. Once started, the process of katabolism takes a definite course, with formation invariably of the same products, because that particular cell protoplasm, owing to its peculiar make-up, tends to break down along certain definite lines of cleavage, as it were, and so the products split off are always the same.

We already have considerable knowledge which tends to indicate that the cells of individual organs and tissues have a certain individuality as regards their primary components, notably in the nucleo-proteids present, but our knowledge is by no means complete enough to permit of broad generalization. The problem is an interesting one, and permits of a definite answer by the application of thorough and persistent investigation.

As an allied question, more or less in harmony with what has just been said, reference may be made to the part which ferments and enzymes possibly play in initiating and carrying forward tissue changes, as well as the metabolic changes that occur in glandular organs. Ferments have come into such prominence of late years as responsible agents for so many transformations that we may well query whether their influence does not extend far beyond the limits originally assigned to their field of activity. The discovery of oxidases and the part which these agents may play in tissue changes, the undoubted existence of ferments in such glands as the thymus, suprarenal, spleen, etc., by which the recently studied autolytic changes in these glands are produced, raise the question whether ferments or enzymes are not far more largely responsible for the many transformations that take place in active tissues than has been hitherto supposed. Consider for a moment the peculiar products which result from the self-digestion (autolysis) of many of the glands so far studied. Note how the nucleo-proteid of the thymus, for example, breaks down, yielding xanthin and a little hypoxanthin, together with uracil, but no guanin, adenin, or thymin.[1] How the adrenal nucleo-proteid likewise yields by autolysis considerable xanthin, but only traces at the most of the other alloxuric bases (Jones). By the self-digestion of the spleen, guanin as well as hypoxanthin is conspicuous, but it is a noticeable fact that in the autolysis of the thymus, for example, there is no appreciable amount of leucin to be detected, thus indicating that the above autolytic changes are not due to any ordinary proteolytic enzyme, but to some peculiar enzyme which acts directly and solely upon the nucleo-proteids, splitting off certain of the contained alloxuric groups. In harmony with this view, Jones has just announced the presence in the pancreas, thymus, and adrenals, of an enzyme to which he gives the name of guanase, which has the power of

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[1] Jones, *Ueber die Selbstverdanung von Nucleoproteiden, Zeitschrift für physiologische Chemie,* Band 42, p. 35.

transforming guanin into xanthin. The same investigator also claims the presence in the spleen of a related enzyme, called adenase, which transforms adenin into hypoxanthin. The inference is that in many glands and tissues there are specific enzymes, as yet undiscovered, which may be responsible for at least some of the transformations known to occur there.

That autolysis may be a possible explanation of the process of animal metabolism has been suggested by Levene [1] and also by Wells.[2] It has been clearly indicated by such able workers as Salkowski, Jacoby, and others, that practically all animal cells contain within themselves ferments or enzymes that are capable, under suitable conditions, of digesting or breaking down the cell-contents by a process similar to ordinary proteolysis, and it may perhaps be assumed that all active cells carry forward their ordinary metabolic processes by the agency of these intracellular ferments. Moreover, it is not inconceivable that ferments or enzymes of several kinds may exist side by side in a given group of cells, just as they are known to exist in the pancreas, by which we might infer the possibility of a series of transformations taking place at essentially the same time, through the harmonious action of a row of enzymes physiologically quite distinct.

Further, the recently discovered reversible action of enzymes, on which we have at command so much valuable work, suggests the possibility of a maintenance of cell-equilibrium through this peculiarity of action, thus affording a tangible explanation of the means by which intracellular nitrogenous or proteid equilibrium is maintained, the various cells of the body building up or breaking down the proteid matter of their own tissues as circumstances require. If these ideas are true, then our conception of ferment action must be considerably broadened, and we have before us the possibility of explaining many of the phenomena of tissue metabolism by the action and interaction of intracellular enzymes. This is a problem well worthy of broader study, with a view to the elucidation of the general laws that govern tissue changes in general. In this connection we also have suggested the possibility of interaction of another kind, viz., that interdependence of one tissue or gland upon another for the full development of its functional activity, as illustrated by the part played by the enterokinase of the intestinal glands in the development of an active trypsin from the zymogen of the pancreatic cells, and by the action of the internal secretion of the pancreas upon the inert constituents of the muscle to develop in the latter an active glycolytic enzyme. How far this general principle extends in the metabolic phenomena of the body is entirely problematical, but merits careful study. Here, then, we

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[1] *Die Endprodukte der Selbsiverdauung tierischer Organe, Zeitschrift für physiologische Chemie*, Band 41, p. 393.

[2] *On the Relation of Autolysis to Proteid Metabolism, Amer. Journal of Physiology*, vol. 11, p. 351.

have an added field of inquiry, worthy of careful consideration, if we are to possess a clear understanding of nature's processes.

Between the animal and the vegetable cell certain sharp lines of distinction are frequently drawn. Physiologists are wont to believe that the processes characteristic of the cells of animal tissues and organs are essentially destructive, *i. e.*, that they are principally katabolic, while in vegetable tissues, on the other hand, constructive processes are very conspicuous. In no way is this better illustrated than in the prevalent opinions regarding the parts played by the two classes of cells in the metabolism of proteid matter. We are accustomed to think that all proteid matter has its primary origin in the synthetical power of the vegetable cell, aided by its contained chlorophyll and the beneficent action of the sun's rays. The animal cell, on the other hand, can merely transform and reconstruct the various proteids furnished by the vegetable world, being without power to manufacture proteid matter *de novo* out of the simple groups and radicles which the vegetable cell utilizes so rapidly. In ordinary proteid katabolism, the various nitrogenous decomposition-products are presumably all converted into urea and allied substances adapted for excretion. If, however, there is reversible ferment or enzyme action in the animal body, why may there not also be power to utilize, in some measure at least, the crystalline nitrogenous bases and amido-acids so abundantly formed in trypsin proteolysis, for the construction of fresh proteid matter? One may well query, considering the vigor of the proteolytic action of the enzymes poured into the alimentary tract, whether all these nitrogenous waste products represent just so much lost energy in their production and a further loss of energy in their immediate excretion from the body. In harmony with the "luxus consumption" theory we may assume wisdom and ultimate gain in this speedy decomposition of excessive proteid foods in the alimentary tract, but the argument is not very convincing. Why may not animal cells, or the animal body as a whole, build up proteid matter out of simple nitrogenous compounds analogous to the action of plant cells? Loew[1] has indeed experimented in this direction and states that the biuret-free end-products resulting from the proteolysis of ordinary food albumin can be utilized by the animal body for the maintenance of nitrogenous equilibrium, etc., equally well with the common proteid food-stuffs. His conclusions, however, have been called in question by other investigators, notably by Lesser,[2] whose experimental data failed to confirm the above conclusion.

The problem, however, is an exceedingly important one. If the animal body has no power of utilizing the varied nitrogenous com-

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[1] *Ueber Eiweissynthese im Thierkörper, Archiv für exper. Pharmakol. u. Pathol.*, Band 48, p. 303.

[2] *Ueber Stoffwechselversuche mit den Endprodukten peptischer und tryptischer Eiweissverdauung, Zeitschr. für Biologie*, Band 45, p. 497.

pounds of simple constitution formed in the gastro-intestinal tract by the digestive enzymes; if there is a complete lack of ability to construct new proteid matter out of these simple decomposition-products, then surely we must inquire what is the real purpose of their formation. It is true that, with the limitations of our present knowledge, it is difficult to see why, if digestive proteolysis has for its sole object the conversion of the proteid foods into forms suitable for absorption, there should be any considerable breaking-down of proteid beyond the proteose or peptone stage, since the latter bodies would seem to be most easily adaptable for transformation into the proteids of blood lymph and tissue. On the other hand, it is well known that the proteid of the food is possessed of a physiological and chemical nature quite different from that of the proteid in the blood and tissues of the feeding animal, and it is quite conceivable that a synthetical process might be essential — in some degree — for the manufacture of the specific proteids called for by the blood and tissues of that particular species or individual. The question is one that demands careful consideration and thorough investigation, for it touches upon a chapter in nutrition on which we have at present very little satisfactory or convincing knowledge.

In this connection we may call attention to another problem, somewhat far-reaching, but suggested by one of the preceding paragraphs, viz., the possible physiological action of the many katabolites, or decomposition-products resulting from tissue-changes throughout the animal body. In vegetable tissues, many of the nitrogenous products common to these structures are endowed with marked physiological power, as witness the vegetable alkaloids and the non-nitrogenous bodies like salicin, digitalin, picrotoxin, etc. Years ago, physiologists recognized that some of these nitrogenous bodies present in animal tissues did have a distinctly toxic action when introduced directly into the circulation, and hence they were frequently called animal alkaloids, but our knowledge upon these points is exceedingly obscure and indefinite. When we take into consideration the large number of nitrogenous products formed and present in the various tissues and organs of the body, products of proteolysis and of tissue-changes; when we consider how these products circulate through the organism, in blood and lymph; how they come in more or less immediate contact with the different cells of the body prior to their decomposition or elimination, we cannot avoid being impressed with the part they may play in stimulating and modifying tissue or other changes.

The significance of this suggestion is made all the more potent by the knowledge recently acquired concerning several of the internal secretions of the body and the powerful physiological influence exerted by their components. Where can be found a more active physiological agent than the blood-pressure-raising constituent of the adrenals, the epinephrin? Where is there a more active agent in modifying the nutritional processes of the body than the iodine-containing constituent of the thyroid, the iodothyrin? These may truly be counted as representing a type of substances manufactured or secreted primarily for the physiological effect they are capable of exerting; but what about the host of other substances present in the body, many of them simple products of katabolism? May they not have some marked physiological property that if known would serve as a sufficient excuse for their formation? Or, may they not possess some hidden or obscure property which if once understood would make clear a secondary or subsidiary function of no small import for the maintenance of physiological equilibrium, or for the welfare of the body? Many suggestions and some facts present themselves illustrating how direct and indirect influences may be exerted, all pointing toward the harmonious action and interdependence in function of many of the substances formed in the body. Some, however, undoubtedly have more or less of a toxic action, especially when formed in excessive or undue amounts. Thus, the alloxuric bases seemingly cause fever when injected into the circulation or taken *per os*,[1] and according to the recent observations of Mandel[2] there is a very striking relationship between the quantity of alloxuric bases eliminated in the urine and the temperature of the body in cases of aseptic fevers, indicating that these substances, with possibly other incomplete products of tissue-metabolism, are important factors in the production of febrile temperature. We may confidently expect that a thorough study of the physiological action of all the varied katabolic products formed in the body will result in a decided expansion of our knowledge regarding the part these substances may play in normal and abnormal metabolism, and in nutrition in general.

Just here, reference may be made to the many problems in the broad field of nutrition that confront the physiological chemist of the present day. The maintenance of life on a sound physiological basis is one of the practical problems in physiological chemistry, and its solution is not yet attained. We need fuller knowledge regarding the part played by the different nitrogenous food-stuffs, the relative physiological value of animal and vegetable proteid, the relative value of fats and carbohydrates as nutrients aside from their different calorific power, and, by no means least, a fuller and more accurate knowledge of the true physiological needs of the body for proteid foods. Our present dietetic standards are absolutely false and valueless. Our present conception of the physiological needs of the body is altogether faulty and distorted. Our ideas of the rate and extent of proteid metabol-

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[1] See Burian and Schur, *Archiv für die gesammte Physiologie*, Band 87, p. 239.

[2] *The Alloxuric Bases in Aseptic Fevers, Amer. Journal of Physiology*, vol. 10, p. 452.

ism necessary for the maintenance of health and strength are crude and inexact. We place the nitrogen requirement of the healthy man at an absurdly high level, apparently because observation has shown that man is disposed to consume an equivalent in proteid food per day. We need to ascertain by scientific experiment how far such standards are justified; to determine by definite analysis the amounts of nitrogen actually required to maintain nitrogen equilibrium and keep up bodily and mental vigor. Upon the physiological chemist of the present day rests the responsibility for the establishment of nutritive standards that will endure the test of scientific criticism, that will harmonize with daily experience, and that will prove to be physiologically correct.

Further, we need to know more concerning the relative decomposition within the body of the truly organized proteid matter of the tissues, and of the albuminous food-stuffs which, having been digested and absorbed, are in a sense a part of the tissues, but not thoroughly or completely incorporated as an integral part of the living cells. Does the urea of the daily excretion come primarily from the breaking-down of the organized proteid, or does it come preferably from the disintegration of the circulating proteid? We recall the famous experiments of Schöndorff, in which blood was made to circulate through the muscles and liver of well-nourished and fasting dogs, with the result that the urea of the blood was increased only when the blood circulated through the tissues of a well-nourished animal. It made no difference with the result whether the blood employed was from a well-fed or a fasting animal; the essential factor was the condition of the muscle tissue through which the blood was made to flow. Schöndorff drew the natural conclusion that the extent of proteid metabolism was dependent upon the nutritive condition of the cells of the tissue, upon the mass of the living cell-material, *i. e.*, upon the amount of morphotic proteid present, and that the proteid content of the intermediary fluids, as blood or lymph, was of no moment in determining the rate of urea formation.

We may well doubt, however, if all the urea formed daily under ordinary conditions of life comes solely from the breaking-down of the truly organized or morphotic proteid. It is more than probable that the urea has at least a twofold origin, and, if so, it is an important matter to be able to discriminate between that which comes from the breaking-down of the unorganized albumen, and that which is derived from the organized tissues. Unquestionably, the decomposition of organized proteid, the morphotic part of the living protoplasm, is quite different from that of the unorganized pabulum of the cell and surrounding media. Quite possibly, the influences controlling the two lines of metabolism are different; perhaps, there are even different kinds of nerve control.

Equally important is it for the physiologist to know more fully regarding the sources of the carbonic acid resulting from oxidation in the body. What proportion of the ever-varying output of this gaseous product of metabolism comes from the oxidation of organized tissue-material, and what from the oxidation of circulating carbohydrate and fat and unorganized material in general? We have learned, for example, that the excretion of carbonic acid runs more or less closely parallel with the degree of muscular activity, and we should possess the means of discriminating between the output from true tissue-oxidation and that which is derived from extracellular sources. A study of the excretion of carbonic acid by fasting individuals, under different conditions of life and activity, would be helpful in throwing light upon this question, and also in giving us a clearer idea of the minimal requirements of the body for non-nitrogenous foods to make good the loss of energy in heat-liberation, muscular work, etc. By such a study we might hope for added light upon that much-discussed problem, the source of the energy of muscular contraction. While most physiologists are certainly agreed that this energy comes preferably from the oxidation of non-nitrogenous matter, there remain many obscure points upon which we need enlightenment.

We likewise need fuller and more exact knowledge of the ways in which uric acid originates in the body, especially regarding its relationship to intracellular decomposition. Our present understanding of the twofold origin of this substance — endogenous and exogenous — is most helpful in making clear many formerly obscure points connected with the formation of this substance from the different classes of food-stuffs. To-day, however, we understand quite clearly the genetic relationship between the free and combined purin bases and uric acid, but we are still uncertain whether this substance is formed to some extent synthetically and whether when once formed it is all eliminated unchanged or undergoes oxidation, in part, into less harmful substances. In other words, we do not yet know how far the uric acid which is contained in the daily urine is a measure of the *production* of uric acid for the twenty-four hours. Uric acid and the alloxuric bases are such important substances, in their influence upon health and the general nutritive condition of the body, that it is extremely important for us to know more concerning their origin and their ultimate fate in the body. We may likewise inquire where uric acid is formed. Does it originate entirely in the liver, or are there other depots where it is produced and collected?

Turning our attention now in another direction, we may revert to the relationship between stereochemical configuration and physiological action as a fruitful subject for investigation. Many interesting facts have already been gleaned, and certain general rules or laws have been formulated, connecting given lines of physiological action with a definite chemical structure. Thus, it is well understood to-day, for example, that all substances which contain a nitro or nitroso group united with or bound to oxygen have the effect of dilating blood-vessels, while, on the other hand, substances which contain the same nitro or nitroso group joined to carbon have a quite different physiological action, being mostly blood-poisons. Further, nitrils, R. CN, tend to produce coma, while isonitrils, R. $N=C$, are much more toxic and tend to produce paralysis of the respiratory centre.[1] In other words, it is clearly manifest that certain definite groupings within the molecule are the cause of the physiological action of the molecule. At the same time, it is also known that in order to have the physiological action of a substance manifest, not only must it contain the necessary group or groupings, but there must likewise be present a second group which has the power of combining with and holding fast to the tissue upon which the physiological action manifests itself. Slight chemical alteration of a substance may, therefore, interfere with or nullify its ordinary physiological action without necessarily altering the physiologically active groups; but by simply changing these other groups through which the molecule ordinarily attaches itself, so that the latter can no longer adhere to the cell-substance or tissue-protoplasm, there occurs a consequent loss of physiological action.

Another fact clearly understood is that two substances having the same nucleus and like side-chains, with an entirely similar grouping, may still be physiologically unlike, owing to a different arrangement in space. This is well illustrated by the dextro- and lævo-rotary tartaric acids, one of which is readily utilized by *Penicillium glaucum* as nutriment, while the other cannot be so consumed. Many other illustrations might be cited, especially with various types of organic poisons, all tending to show that physiological action is dependent upon the *arrangement* of the atoms or radicles in space, as well as upon the *nature* of the atoms or radicles. With these facts before us, we see many lines of inquiry presenting themselves, many problems demanding solution, with reference both to pharmacology and physiology.

Confining our attention more especially to physiological matters, we are certainly justified in considering the application of these principles to many of the substances conspicuous in the processes of the body. The work and suggestions of Pasteur and Emil Fischer have indicated certain possibilities regarding the nature and action of enzymes, not to be overlooked. Stereochemical configuration may be just as much responsible for enzyme action, for proteolysis, amylolysis, etc., as any other feature of the active molecule, and how far other lines of physiological action may be due to chemical structure and the configuration

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[1] See Fränkel *Ergebnisse der Physiologie, Dritter Jahrgang. Biochemie*, p. 291.

of the molecule, who can say? One's thoughts naturally turn to the living muscle plasma and the chemical changes that follow or accompany the advent of rigor mortis; to the circulating blood and lymph, and the transformations that occur when these fluids are withdrawn from the protecting influence of the endothelial lining of the living vessels; to the axis cylinder of the nerve-fibres and the changes that occur when the fibres are severed from their connection with the ganglionic cells. These and many other suggestions arise, all calling for a further study of the chemical constitution and stereochemical configuration of the molecules involved, since in the knowledge thus gained may be found the solution of many physiological processes now shrouded in mystery.

The reference just made to nerve-fibres and ganglionic cells suggests another problem in physiological chemistry, solution of which has long been deferred, viz., the exact chemical nature of nerve-tissue, and the character of the changes involved in the passage of a stimulus or nervous impulse through a nerve to its ending in the muscle or secreting cell. Further, what is the real purpose of the complex myelin surrounding the axis cylinder of medullated nerves, and the corresponding substance imbedded in the gray matter of the brain and cord? These are problems that have long waited solution, and yet they are vital to any clear understanding of the nutritive or other changes that take place in nerve-tissue, either in rest or in activity. Nerve-tissue is strikingly peculiar in its large content of phosphorized bodies of the lecithin type, cerebrosides and cholesterins. These substances, complex in nature and of large molecular structure, are all alike in having the physical properties of fats. Further, lecithin and the cerebrosides all contain fatty acid radicles in large amount, and in addition lecithin contains the radicle of glycero-phosphoric acid. Moreover, the cerebrosides contain a carbohydrate group yielding galactose on decomposition, so it is plain to see that the bodies which give character to the myelin material are highly nutritive substances with high calorific power. These facts might readily be taken as indicating that the function of the myelin is to nourish the more important axis cylinder, to furnish the necessary pabulum for growth and repair as well as to meet the daily demand for energy-yielding material.

While we may speculate, however, as to the part these peculiar substances play in the life of nerve-tissue, we really possess very little positive knowledge of their true purpose. Indeed, we do not know how these bodies actually exist in the living tissue, as is well evidenced by the utter lack of agreement among physiological chemists as to the entity of the so-called protagon. Whether this phosphorized substance, studied by so many investigators, exists as such in the living tissue, or whether it is simply an intimate mixture of lecithin, cerebrin, and one or more other substances, is not yet settled to the satisfaction of all concerned. Further, it is not at all impossible that the cerebrosides, as well as lecithin and possibly cholesterin, may exist in the living tissue combined with some one or more of the proteids present there. Our lack of knowledge is deplorable, and yet, in the words of Sir Michael Foster, this is one of the "master tissues" of the body. Surely, considering the preëminent position and controlling influence of this tissue, we may look for a speedy clearing away of the darkness that enshrouds our understanding of the exact chemical composition of nerve-tissue, and especially of the way these peculiar substances of the myelin material exist in the living tissue.

Again, we may ask ourselves what is the nature of the chemical changes that take place in nerve-tissue; in the ganglionic cells of the gray matter and in the axis cylinder of the nerve-fibres. When a muscle contracts there is a measurable chemical decomposition. The energy of muscular contraction comes from the breaking-down of non-nitrogenous components of the muscle, and perhaps in some measure from the decomposition of nitrogenous constituents. Further, there is a liberation of heat, a development of lactic acids, etc. When a stimulus is applied to a nerve, on the other hand, no such manifestations of chemical action are apparent. The muscle to which the nerve is attached contracts, the secreting cell pours forth the product of its activity, etc., but there is no noticeable change in the nerve itself, no recognizable liberation of heat, no change of reaction, no output of carbonic acid, that can be detected. Are we to conclude, then, that the axis cylinder of the nerve-fibre acts simply as a conducting agent without itself undergoing any change? Is it to be compared to an electric wire, with the surrounding myelin material, the substance of Schwan, serving as a convenient insulating or protective medium? If we are to accept this view, what are we to say regarding the non-medullated fibres? Do not they need an insulating material likewise? We can argue that the myelin substance is especially adapted for the nourishment of the nerve, that its high potential value renders it peculiarly suitable as a concentrated nutriment, and that its intimate contact with the neuraxis and with the ganglionic cells of gray matter proclaims its probable use in this direction. Moreover, if we follow this line of argument still further, we may be led to believe that the stimulation of a nerve, its power of conductivity, etc., are associated with chemical decompositions along its axis as marked in their way as those that occur in a contracting muscle-fibre. Truly, we have here a multitude of questions, for which at present no satisfactory answers are to be found. The problems are on the surface awaiting solution.

Finally, emphasis must be laid upon a series of problems in physiological chemistry, true solution of which will do much to explain natural and artificial immunity, the action of toxins and antitoxins, the bactericidal action of blood-sera, the effect of oxidizing enzymes, of animal and vegetable origin, upon toxins of various kinds, etc. Ehrlich's theories regarding the protection furnished by antitoxic and bactericidal sera, so elaborately devised, constitute a working hypothesis of great value, but we need much additional knowledge concerning the nature and action of the so-called complements and anticomplements, of amboceptors, of haptophor groups, of agglutinins, of precipitins, and of hemolysis. The physiological chemist studies with care the important and suggestive work being carried forward by the many brilliant investigators in pathology and bacteriology, with the feeling, however, that the true explanations for most of the phenomena in question are chemical, and that the actions and interactions involved are chemical ones, to be eventually made clear by a fuller chemical knowledge of the toxic and antitoxic substances themselves and of their alteration and combination under different physiological conditions.

The well-known natural immunity possessed by some animals toward certain diseases, together with the difficulty experienced by most micro-organisms in developing in the healthy body,— a difficulty which at once disappears when from any cause the tissues of the body lose their original vitality and vigor, — all point to the presence in the healthy body of certain general or specific substances which are directly deleterious to the micro-organisms. Such substances are obviously bactericidal, and it is equally plain that in the bodies of many species of animals there are specific antisubstances present which are lacking in other species, thereby explaining the natural immunity of the former towards certain diseases. As is well known, blood-serum possesses, as a rule, a bactericidal power upon most micro-organisms, and we have every reason to believe in the existence of specific substances in the serum which exert some influence upon the growth and development of micro-organisms, and also upon the toxic products they tend to elaborate. These protective substances — the alexins of Buchner — appear to be proteid in nature, resembling globulins, since they are precipitated from serum by the action of certain strong solutions of alkali salts, as sodium sulphate. We know, however, very little regarding their chemical nature aside from the fact that they are obviously very complex, although perhaps even this point is not quite certain. These protective substances are presumably elaborated by the leucocytes of the blood and lymph, cells rich in nuclein and nucleoproteid material. Doubtless, also, some of the gland-cells in the body have a corresponding action; statements which, if true, tend to emphasize the possible proteid nature of the protective substances.

While in a general way we may say that the natural immunity to certain bacteria possessed by some animals is due in large measure to an inhibition of the growth of the micro-organism, it must also be remembered that there is in many species a distinct immunity to the action of the poison which the specific micro-organism produces. This immunity depends either upon a destruction of the poison as by oxidation, upon a combination between the poison and some constituents of the active protoplasmic cells of the body, thereby rendering the poison inactive, or, lastly, upon some action of the specific protoplasmic cells of the body usually affected by the poison, by which the latter is unable to combine with the cells upon which it ordinarily acts. All these suggestions, however, imply chemical reactions of some kind, and obviously should be understood for a betterment of our knowledge upon this important matter.

Again, the specific immunity which shows itself after exposure to a given disease, so that a second infection becomes practically impossible, can be explained satisfactorily only on chemical grounds, viz., by the presence in the blood and lymph of certain protective or immunizing substances which presumably originate through chemical changes in the blood-serum, under the influence of the bacteria causing the disease. These are chemical substances, formed through chemical decompositions or alterations of normal constituents of the blood, and obviously we need to know more of their exact nature.

Following Ehrlich's views, specific antitoxins, bactericidal sera, etc., result from the overproduction of molecules in cells which are sensitive to the action of toxins and other bacterial products. Antitoxins so formed unite with toxins, and the so-called complementary bodies and the bactericidal anti-bodies combine with the bacterial cells, thus affording protection. These processes of alteration and combination, however, are presumably all chemical, involving either alteration of chemical structure, or direct combination of bodies chemically the opposite of each other. Further, the so-called haptophor groups of the toxin molecule are probably represented in fact by chemical groups or radicles, which owe their power of combination with corresponding groups of other cells to chemical affinity. Again, the complementary body, normally present in all healthy blood-sera and which is needed along with the specific anti-body for the destruction of bacterial cells, must owe its activity to the power of chemical combination. Hence, we have presented to us at every turn the question of the chemical nature of these various substances, toxin and antitoxin, complement, receptor, haptophor, etc., which are of such vital importance in the production and maintenance of immunity and protection. Surely this is one of the most important problems of the present day in the domain of physiological chemistry, and calls for both patience and skill of the highest order in its solution.

SHORT PAPER

Mr. Edward Mallinckrodt, Jr., of St. Louis, Missouri, read a paper to this Section on "The Diet, Physical Condition, and Mental Performance of Certain Students in Harvard University."

BIBLIOGRAPHY: DEPARTMENT OF CHEMISTRY

(Prepared for the Department by the courtesy of Professor James M. Crafts)

ANALYTICAL CHEMISTRY

Carnot, Traité d'analyse des substances minerales, 2 vols., 1898–1904.
Classen, Ausgewählte Methoden der analytischen Chemie, 2 vols., 1901–1903.
Crookes, Select Methods in Chemical Analysis, 1894.
Fresenius, Qualitative Chemical Analysis, 1897.
Quantitative Chemical Analysis, 1904, 2 vols.

PHYSICAL CHEMISTRY

Donnan, F. G.; Thermodynamics.
Findlay, A., The Phase Rule.
Kohlrausch and Holborn, Leitvermögen der Elektrolyte, 1898.
Landolt, Bornstein, and Meyerhoffer, Physikalisch-chemische Tabellen, 1905.
Lehfeldt, R. A., Electrochemistry.
Meller, J. W., Chemical Statics and Dynamics.
Nernst, W., Theoretische Chemie, 1904 (English translation by Lehfeldt).
Ostwald, W., Lehrbuch der allgemeinen Chemie, 3 vols., 1891–1902.
Ostwald, W., and Luther, R., Hand-und-Hülfsbuch physiko-chemischer Messugen, 1902.
Ramsay, W., Text-books of Physical Chemistry, 1904–05.
Rooseboom, B., Die heterogene Gleichgewichte, 1901, 1904.
Van 't Hoff, J. H., Vorlesungen über theoretische und physikalische Chemie, 1898–99 (English translation by Lehfeldt).
Young, S., Stochiometry.

TECHNICAL CHEMISTRY

Ahrens, Sammlung chemischer und chemisch-technische Vortrage, 9 vols., 1896–1905.
Dammer, Handbuch der Chemischen Technologie, 5 vols., 1895–98.
Davis, Handbook of Chemical Engineering, 2 vols., 1901–02.
Groves and Thorp, Chemical Technology, 4 vols., 1889–1903.
Ostwald, Electrochemie, 1896.
Stillman, Engineering Chemistry, 1897.
Thorpe, Dictionary of Applied Chemistry, 3 vols., 1890–93.
Wagner, Jahresbericht über der Leistungen der Chemischen Technologie, 1855–1905.
Jahrbuch der Electrochemie, 1895–1903.

GENERAL INORGANIC CHEMISTRY

Dammer, Handbuch der anorganischen Chemie, 4 vols., 1892–1903.
Graham-Otto, Ausführliches Lehrbuch der anorganischen Chemie, 8 vols 1885–89.
Mendelejeff, Principles of Chemistry, 2 vols., 1897.
Ostwald, Grundriss der Allgemeinen Chemie, 1899.
Roscoe and Schorlemmer, Treatise on Chemistry, 2 vols., 1895–98.

WATTS, Dictionary of Chemistry, 4 vols., 1888–94.

WURTZ, Dictionnaire de Chimie pure et appliqué, 3 vols.
1st Supplement, 2 vols.
2d Supplement, 5 vols., 1869–1905.

ORGANIC CHEMISTRY

ALLEN, A. H., Commercial Organic Analysis. 3d ed., 4 vols. in 8, 1898–1903.

BEILSTEIN, F. F., Handbuch der organischen Chemie. 3d ed., 4 vols., und 2 Erganzungsbande, 1893–1903.

GATTERMANN, L., Practical Methods of Chemical Analysis. Trans. by Shober. 6th ed., 1904.

LASSAR-COHN, Arbeitsmethoden für organisch-chemische Laboratorien. 3d ed., 1903.

MEYER, V., and JACOBSON, P., Lehrbuch der organischen Chemie, 2 vols. in 3, 1893–1903.

RICHTER, M. M., Lexikon der Kohlenstoff-Verbindungen. 2 vols. und 2 suppl. 1900–05.

SADTLER, S. P., Handbook of Industrial Organic Chemistry. 3d ed., 1900.

SCHULTZ, G., Chemie des Steinkohlentheers. 3d ed., 2 vols., 1900–01.

STOHMANN and KERL (EDS.), Muspratt-Handbuch der Technischen Chemie. 4th ed., 6 vols.

SPECIAL WORKS OF REFERENCE

(*Prepared for the paper on "History of Chemistry" by its author, Professor Frank W. Clarke*)

Bolton, H. Carrington, Select Bibliography of Chemistry, no. 850, Smithsonian Miscellaneous Collections, pp. 85–170; no. 1170, pp. 22–44; no. 1440, pp. 12–22.

Kopp, H., Geschichte der Chemie, 4 vols. Braunschweig, 1843–47.

Ladenburg, A., Lectures on the History of the Development of Chemistry since the Time of Lavoisier. Trans. from the German by Leonard Dobbin. Edinburgh and London.

Meyer, E. von, A History of Chemistry from the Earliest Times to the Present Day, etc. Trans. from the German by George McGowan. London, 1898.

Thomson, T., The History of Chemistry, 2 vols. London, 1830.

Tilden, W. A., A Short History of the Progress of Chemistry in Our Own Times. London, 1899.

Wurtz, A., Histoire des Doctrines Chimiques depuis Lavoisier, jusqu'à nos jours, Paris, 1869.
La Théorie Atomique, Paris, 1886.

SPECIAL WORKS OF REFERENCE

(Prepared for the Section of Physiological Chemistry by Professor O. Cohnheim)

Atwater, W. A., Ergebnisse der Physiologie, iii; Biochemie, 1904.

Atwater, W. A., and Benedikt, F. G., U. S. Dept. of Agriculture, Office of Experiment Stations, Bull. no. 136, 1903.

Knieriem, W. von, Zeitschr. f. Biologie, 21, 67, 1885.

Pawlow, J. P., Arbeit der Verdauungsdrüse n. Deutsch von Walther, Wiesbaden, 1898.

Rubner, M., Zeitschr. f. Biologie, 42, 261, 1901.
Handbuch der Ernahrungstherapie, Bd. i, p. 20, 1898.

Voit, C. v., Hermann's Handbuch der Physiologie, vi, 1, 1881.
Zeitschr. f. Biologie, 25, 232, 1889.

Zuntz, N., Archiv f. Anatomie und Physiologie, Physiologische Abteilung, p. 541, 1894, and p. 267, 1898.

Zuntz, N., und Schumburg, Physiologie des Marsches, Berlin, 1901.

Zuntz, N. (mit Heinemann, Frentzel, Reach, Caspari, Bornstein), Pflüger's Arch. 83, 1901.

ADDENDA PAGES

FOR LECTURE NOTES AND MEMORANDA OF
COLLATERAL READING