SCIENCE

Vol. LIX JANUARY 18, 1924 No. 1516

CONTENTS

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS

Lancaster, Pa. Garrison, N. Y.

New York City: Grand Central Terminal.

Annual Subscription, $6.00. Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

Entered as second-class matter July 18, 1923, at the Post Office at Lancaster, Pa., under the Act of March 3, 1879.

SOME ASPECTS OF MODERN SPECTROSCOPY[1]

SEVENTEEN years ago, at the meeting in New York, some of us had the pleasure of listening to an address entitled "Fact and theory in spectroscopy," given to this section by its retiring chairman, Professor Henry Crew. It included a comprehensive and enlightening survey of atomic theory and of the requirements imposed upon any successful atomic model by the facts of spectroscopy known at that time. In the light of more recent work on this subject, it may be interesting to look at this same field, and consider in part the contributions of spectroscopy to atomic theory in this interval.

Your first reaction to such a proposal is perhaps a very natural fear that the territory to be covered is so vast that you must suffer an exhausting experience in being dragged over the whole of it, or be whisked about from point to point at a speed that will not allow you to enjoy the comforts of leisurely travel. Let me say at once that we shall view but a small corner of this domain, and, since I am to choose the route, it shall be from a standpoint with which until quite recently comparatively few were acquainted, but which nowadays is starred in the atomic Baedeker, and has suddenly achieved an enormous popularity.

It is with a certain sense of satisfaction that the experimental spectroscopists may legitimately regard their labors in the recent past. Twenty-five years ago there were those who said that the spectra of all the elements had been "done" by Kayser and Runge, and that there remained in this field nothing more attractive to seek than the next decimal place in wave-lengths. In spite of such pessimism, important advances began to be made, of which a few might be mentioned at this point. These years brought us the best part of the work of that gifted and brave spirit, Walter Ritz, whose early death was a very real loss to science. He gave us his famous combination principle, which first demonstrated the importance of spectroscopic "terms," now translated into energies by the Bohr theory. Then came a steady growth in our knowledge of the series structure in the simpler spectra, including the interpretation of the "spark" spectrum as that due to the ionized atom, and the

[1] Address of the vice-president and chairman of Section B—Physics—American Association for the Advancement of Science, Cincinnati, Ohio.

discovery by Fowler that this was also a series spectrum. A masterly series of researches by Paschen disclosed the extent and importance of the infra-red region, and (with Runge and Back) laid down a foundation of fact in regard to the Zeeman effect. Perhaps the most remarkable single piece of work in practical spectroscopy was Paschen's astonishing analysis of the spectrum of *Ne*, showing that in all probability all spectra were series spectra, though complex, and indicating the path forward in this tangled field. A steady improvement in technique and the invention of new sources of light have brought us to our present much improved situation. Nevertheless, it would now be quite reasonable to say that we are even yet at the verge of an untrodden field, with many of the most important facts in regard to the spectra of the elements still unknown.

The study of spectra possesses an unmistakable charm. We renew annually through our students that thrill that once came to each of us when we saw for the first time the spectrum of a luminous gas. What an enticing puzzle it presented! Here in the study of these vibrations was a chance to view the actions of an atom itself, to catch it in the very act of the performance of its most secret rites. Surely, we used to say, from the study of these vibrations we may attack the problem of atomic structure on purely mechanical principles, just as a blind listener might seek to deduce the fundamental structure of a musical instrument from the tones which it emitted. It was no simple problem, for there were many atoms whose known gamut of vibrations would put a complete orchestra to shame in its variety, if not in its range. Professor Crew left us after his address with a feeling that this problem was far from its solution. One great principle, which was then accepted by all, is stated by him:—"The hypothetical radiant atom must not in its behavior, except as a very last resort, contradict any of the established principles of physical science, be they mechanical, electrical or chemical." It was impossible to see how any of the models then proposed could be satisfactory on this basis.

There are always among us conservatives and radicals. The former, with a wide vision over the past, continually remind us of the difficulties into which we shall fall if we abandon those principles that have already been shown to be useful. The latter are acutely sensitive to the dilemmas furnished by the present, and are willing to rush in where the conservatives fear to tread, and adopt any new hypotheses that appear likely to bring us a step forward. No moving machine is complete without motor and brakes; the motor calls for motion at all costs, the brakes for caution, or even complete stagnation. It is illegal to drive without brakes, but impossible to progress without a motor. Let us not therefore waste time trying to assign praise or blame to the conservatives or to the liberals in this matter. The fact is that, as far as progress in atomic theory went, our machine appeared to be stalled with the brakes jammed, until it occurred to Bohr, perhaps "as a very last resort," to postulate that there were processes going on in a radiating atom for which we have no mechanical models.

According to his theory, as you all know, we must assume a series of stationary states in the atom differing from one another in their energy content, and such that when the atom changes from one to another, a quantity of energy is liberated in the form of monochromatic radiation, whose frequency is proportional to the change of energy involved. It is to be noted that this theory gives us no definite idea of how the energy is emitted, how it happens to take the form of monochromatic radiation, apparently with all the properties of wave-motion, why its frequency follows the curious quantum law; nor have we as yet a definite idea of what the circumstances are which cause the atom to change from one stationary state to another. These and other features of the picture are left blank, to be filled in later on.

There are those who say that man is too finite an animal ever to be able to comprehend all the mysteries of nature. Perhaps in atomic theory we ought to postulate some fundamental thing or state of affairs and agree not to attempt to conceive of what lies beyond. Most of us will, I think, object to this abandonment of the chase so long as there are complexities unsolved. We demand ultimate simplicity on the part of nature. Theories which are complex and elaborate are not likely to be long-lived and fruitful. The charm of the Bohr theory is the simplicity which it has introduced into spectroscopy; but so long as the picture it gives us of the atom is complex and full of apparent miracles, the search for simpler conceptions will surely continue. Open processes, openly arrived at, are as desirable here as in politics, and perhaps as unlikely to be attained.

Bohr has shown it to be profitable to regard the stationary states as planetary orbits in which the electron revolves, at least in the case of the simplest atoms, according to mechanical laws, and the change from one of these states to another requires the electron to leave one orbit and fall into some other in a manner that would be most unbecoming of a member of a solar system. Perhaps it would be better to describe the process as one of complete disappearance in one orbit, and reappearance in the new one, for there is no clew as to the whereabouts or the actions of the electron during the change.

I need not here recount the brilliant successes of this theory: the quantitative calculation of the spectrum of hydrogen, the theory of the fine-structure of the lines in the spectrum of ionized helium, of the Stark and Zeeman effects, and of many matters connected with X-rays. Sommerfeld's masterly book on atomic structure shows to what an extraordinary extent the theory has widened our horizon. After one swallows the bitter medicine composing its fundamental postulates, it is evident that one feels immeasurably better. An ordinary spectrum appears in an altogether new light, with its complexities very greatly reduced in number, being those only of the various energy levels. Many of these can be explained by bringing in precession in the electronic orbits and taking account of changes of mass due to motion according to the theory of relativity.

I should like to apply the brakes for a moment, to help overcome a slightly dizzy feeling, and gaze upon the structure which is here presented. Consider, for example, the relatively simple atom of magnesium. Two of its electrons are coupled closely to the nucleus and presumably describing small orbits about it. Outside of these lie eight more, in orbits oriented in space with a sort of cubical symmetry; and beyond these again are two others, describing rather elliptical orbits, penetrating during each voyage around the nucleus into the internal tangle composed of the rest of the orbits, and being thrown thereby into a processional sort of motion whereby the same path is not exactly followed in successive revolutions. A radiant magnesium atom has had one of its outer electrons removed by some accident to a more distant orbit from which it returns to its normal position by one or more discontinuous jumps, a gradual return being supposed not to be possible.

This model is a beautiful product of the human imagination, a piece of scientific poetry of the highest art. Moreover, it has achieved such marked success that it must in many important respects be true and correct. Under these circumstances any criticism of the theory must be cautiously made, and with full acknowledgment of the fact that purely destructive criticism has but little value in itself. Nevertheless, it is interesting to consider certain aspects of this atomic model that seem to be somewhat incomplete.

Much thought is now being expended on the problem of harmonizing this planetary type of atom model with the more or less static model proposed some years ago by G. N. Lewis and so conspicuously useful in the study of chemical phenomena. In an interesting book on Valence which has just appeared, Lewis himself indicates a way in which this can be done. He would like us to regard the electron's position as given by the orbit as a whole, rather than by the actual instantaneous position of the electron itself in that orbit. He points out, further, that in Bohr's model one electron in revolution is apparently unable to act upon another with the force which one would expect it to exert if the two happen to come near one another, but that we shall have to suppose, if I understand him correctly, that the action of the electron takes place from its average position rather than its position at any instant. This sounds very much like regarding the electron, at least while we are considering its perturbing effect, as though it were spread uniformly over the whole circumference of its orbit, in other words, as an elliptically-shaped ring. Such electrons might then be thought of, except for their magnetic effects, as static, and the important differences between the two points of view begin to show signs of disappearing. On the other hand, many objections may be brought forward against the conception of ring electrons as large and curious as these would have to be. The results of experiments on scattering, the phenomena of radioactivity and of ionization seem difficult to account for on this view.

It seems to be necessary, as Lewis points out, to suppose that the electrons in revolution generate magnetic fields in the familiar way. It is by no means evident that a single electron must produce effects of the same sort that myriads of electrons are observed to give. We are, perhaps, prone to push analogy too far. The beautiful experiments of Stern and Gerlach, however, in which silver atoms disclosed their magnetic moments, give a sense of reality to atomic magnetic fields that they did not possess before. These fields must have an important part to play in orienting the electron orbits with respect to each other, which seems not to have yet been very fully considered. Also, a conservatively-minded person finds it odd to have to retain the magnetic field produced by a revolving electron, while denying the existence of any radiation emitted by it in a steady state. A ring electron is again indicated as the only easy way of harmonizing these two ideas.

There is evidence of an important property of the electron of which but little account seems to have been taken in Bohr's theory. I refer to the tendency, at least in the presence of an atomic nucleus, for the electrons to form in pairs. Lewis mentions several indications of this sort; the stability of the helium atom suggests itself as an example. Other bits of evidence pointing in this same direction will be mentioned presently. As Lewis shows, a magnetic field associated with each electron gives us a very convenient way of pairing them off, after the manner of two magnets, which, when free to move, make as intimate a combination as possible by coming close together. If the magnetic properties of an atom reside largely in its outer electrons, as there seems now to be some reason to believe, it is not apparent how Bohr's atom model makes any use of this pairing action. Of course, the nature of the electron itself must be closely studied in the hope that it will yield the cause of this remarkable effect.

We must not forget how incomplete our knowledge still is of the electron. Sir Oliver Lodge has recently suggested the possibility that light may generate electrons. One might put in the same category the suggestion that "excited" electrons in atoms may be different from normal ones; or that they may cease to be indivisible when engaged in radiating. However that may be, we may safely pin our hopes upon the electron, in the expectation that when its nature is better known we shall at the same time have a clew as to the nature of radiation, and the reason for quanta of energy. Speculations on these matters in the present state of our knowledge may well be a waste of time, but in the long run something important is likely to result from such an exercise of the imagination.

We need badly some picture of how the vibratory features in radiation are produced. A quantum of energy emitted appears as a train of waves. Apparently no one is yet able to do without these waves. Certainly no teacher who has to present to his students the phenomena of interference and polarization and their simple explanation on the wave-theory will be willing to abandon this idea without a struggle, no matter how badly it may fit with the facts of photoelectricity, etc. But there is no mechanism in our atomic model which appears to vibrate, and some would prefer to leave us no medium in which the vibrations might travel. Can the electron orbits be made to serve? The frequency of revolution looks promising, agreeing as it does in extreme cases with the frequency of the emitted radiation. Certainly it seems painful to conceive, as C. G. Darwin puts it, of an electron with a knowledge of the future, so that while leaping from one orbit to another it determines in advance the frequency with which it would be appropriate to radiate, taking into account its final destination. This is less physics than metaphysics.

Let us not give up the hope that our present atomic model will be somewhat simplified and that one may some day be found that will fit the facts without invoking the aid of so many non-mechanical processes. It is perhaps in this connection a little cheering to note that whenever established mechanical principles are useful in explaining the behavior of electrons in atoms, they are freely used. There is in the correspondence principle an admission that they lead us to the neighborhood of the truth, if not exactly to the truth itself.

Releasing the brakes now, for a moment, we can not fail to admit that the adoption of so much that violates classical mechanics has brought us very considerably forward and that, since we must progress at all costs, this may after all be the only possible way.

Leaving now the game of atom-building, let us gaze again upon those humble toilers, the experimental spectroscopists, who have all this time been busily grubbing about in the terra firma of observation, and have after all succeeded in raising from their labors the very considerable crop of facts upon which the theory has been nourished. Recently their numbers have been swelled by the addition of many workers, and many of the highest ability. As a result, important advances in our understanding of the structure of spectra are appearing now each month. The discovery of multiplets by Catalan has inspired a number of courageous souls to attack the more complex spectra, and it will not now be long before such as Fe, Mn, Ti, etc., must yield their secrets. The working rules for the structure of complex Zeeman patterns given us by Landé add enormously to the value of this phenomenon in furnishing us with a key to the structure of spectra.

In addition to such major attacks, minor sallies have been made against the lesser difficulties, some of which have disclosed matters of interest in connection with atomic theory. One of these, in which H. N. Russell and I have been interested, has been concerned with those curious groups of six lines which occur in the spectra of Be, Mg, Ca, etc., and have become known among spectroscopists as the pp′ groups. These are formed, in the language of the Bohr atom, by an electron jumping to the lowest of the triplet p levels, or orbits (which are involved in the production of the strongest triplets in the spectrum), from some other triple levels which appear to have no connection with the series structure of the spectrum.

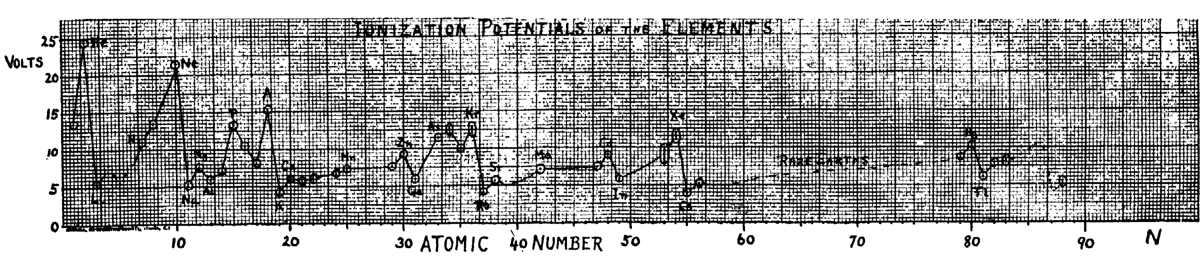

FIG. 1.

We are now able to show, through the recent discovery of three new groups of this sort in the Ca spectrum, that these groups belong in a spectrum series of their own, but that the "terms" (numbers proportional to the energy in each level) of some of them are negative. This means that more energy is emitted, when these jumps occur, than the electron possesses. The simplest source for this extra energy seems to lie in the other electron, hitherto supposed to be inactive during this process. We have merely to suppose that the second electron also makes an appropriate leap and supplies the deficiency of energy. This involves a nice degree of cooperation between the two electrons, whereby the atom as a whole loses a quantum of energy due to changes in two of its parts simultaneously. Such team work has appeared before in the emission of band spectra from molecules, but seems hitherto not to have been supposed to be associated with atoms. Perhaps another and a better explanation may be found; but, in any case, the occurrence of such lines as these with great intensity indicates that the event which produces them is a common one.

Among the most remarkable consequences of the new theories have been the connection which they have given us between phenomena at first sight unrelated. Who could, for instance, have supposed a few years ago that we might now be getting definite ideas about specific heats and molecular moments of inertia from a study of the lines in band spectra? Let us pause a moment over another such matter, the ionization potentials of the elements. The Rutherford-Bohr atom gives us a definite picture of the process of ionization by impact with a wandering electron. Experiments to measure the potential through which the impinging electron must fall in order to ionize the atom were begun many years ago, and have been very successful. Certain difficulties present themselves, however, especially in making due allowance for the initial speeds of the electrons, and in some cases in determining in just what stage of ionization or dissociation the atom or molecule is left after the impact; and these have been the cause of undue variations among the observed values. Bohr's theory gave us an immediate connection between the most important series in the spectrum of an element and its ionization potential. According to this theory the electron must be removed from the atom by an impact before it or some other electron is recaptured and allowed to fall in to the lowest possible level, thus causing the emission of the spectrum lines. The energy eV given to the electron by a fall through the ionizing potential must be equal to $h\nu$ where ν is the frequency of the limit of the most important series in the spectrum, *i.e.*, the highest frequency that could be emitted by the atom. Now these series may be found by purely spectroscopic observations, and the calculated potential thus compared with that directly observed by bombarding atoms with accelerated electrons until they are ionized. The odds are in favor of the spectroscopic results. Witness their recent triumph in the case of He, where the discovery of the right series by Lyman disclosed an error of 0.8 volt in the hitherto accepted value.

Recently additional data on ionization potentials have been accumulating at such a rate that it now seems profitable to look for a moment at the curves

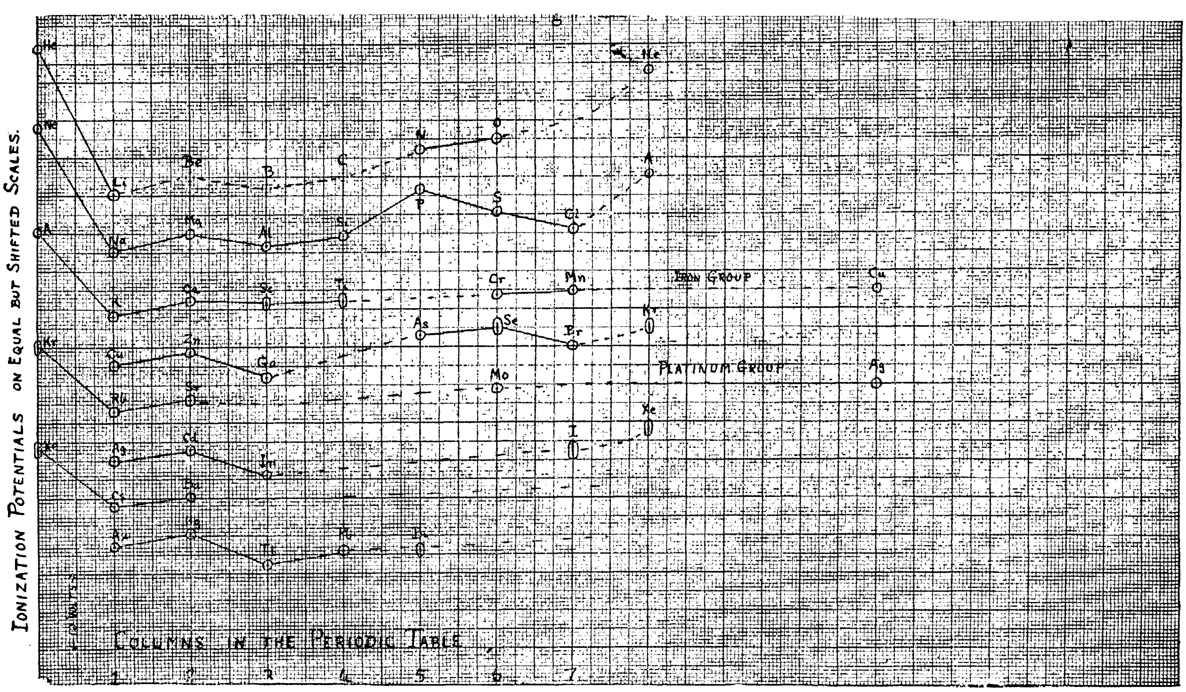

FIG. 2.

showing the variations of this quantity with the atomic number of the elements. No originality is claimed for this mode of presenting them; it has already been used by Catalan, and perhaps by others. As has happened so often before, it is in the air. Such a curve is presented in Fig. 1. In this figure you may be more conscious of the gaps than of the points that are filled in. Fig. 2 shows a grouping of the same points arranged according to the periodic table of the elements, *i.e.*, all the elements of the first column are shown at points whose abscissae are 1, the abscissae thus standing for the number of outer, or valency, electrons in the atom. The scale of volts (ordinates) has been kept the same throughout, but its origin shifted arbitrarily so as to prevent the curves from falling upon one another, and to bring out similarities in form.

Several conclusions can be drawn from these curves. First, of course, is shown the extraordinary stability of the inert gases, and next the ease with which the atom immediately following each one can part with its external electron. In passing from columns 1 to 2 one is struck by the parallelism of the lines, and the ionization potential of Be may be predicted from this diagram with what would seem to be a reasonably small error. Although the gaps prevent one from drawing any exact conclusions, it would appear that there is on the whole a rise of ionization potential with the number of external electrons between one alkali metal and the next inert gas, with, however, in several cases an alternation, giving a zig-zag appearance to the curve. If this alternation is real, it furnishes a bit of evidence to add to the many others already gathered in favor of the existence of a tendency for the electrons to form themselves into pairs, so that a third or a fifth is a distinct outsider. The very nature of the spectra points the same way, for in the Na family we have pair series which seem therefore to be characteristic of a single, rather free external electron; and we meet with these again in the Al family, probably also in N, and in ionized Ca(Ca^+), C^+, Si^{+++}, etc.

Certain points on the curves deserve a word more. The values for O and S are determined from spectroscopic observations (Hopfield and Birge) and are, therefore, probably very close. The value for N (Smyth) and P (Foote and Mohler) are from direct experiment and the irregularity which they introduce into the curves is suspicious. The difficulties involved in such experiments make it possible to hope that later observations will smooth out this part of the diagram. Spectroscopic indications would place the point for N somewhat above Smyth's value (say 12 volts or thereabouts), and his method of determination may perhaps be reconciled with such a change. The value for P is by analogy with recent work on N probably the ionization potential of the molecule rather than of the atom. One would not anticipate a value for the P atom which was higher than that for N. The points for Cr, Mn and Mo are from recent work by Catalan; for Au from Thorsen's recently discovered series; for Ti from unpublished work by Russell. In some of these cases the value is uncertain within a small range, indicated on the diagram. The points for A, Kr and Xe are from a very recent paper by Sponer, and that for Bi from a note just published by Foote and others in *Nature*. This same note indicates that the point for As should be placed a little lower. The point for Se is suspicious; one would expect a lower value for this element than for O and S.

The ionization potential of Si entered on this curve is intended to lie between 7 and 7.5 volts, with a probable value near 7.2. It is determined from observations on the spectrum, which show that there occurs in Si a persistent line at λ2881 bearing all the signs of being an "ultimate" line and the first member of the principal series of singlets of this element. The second member should lie in a region in which one suitable line occurs, and one only, at λ2124. A third line of this series has I think also been found. Mr. W. J. Cahill is working in the Jefferson laboratory on several of these spectra, and we hope to be able to confirm this new series shortly, as well as to give definite values to the points dotted in vaguely on the graph from spectroscopic indications for Be, B and C. Observations on these elements have disclosed a number of new lines that appear to belong to the normal atom. The present indications would fix the points near the situations suggested on the diagram, and it is interesting to note that if the value here predicted for C (7 to 8 volts) is confirmed, it indicates no very special strength in its tetrahedral structure as compared for instance with the great stability of groups of eight electrons. This point is of interest in connection with Bohr's discussion of the electron orbits.

It is of interest to note also that the long periods of 18 elements in the periodic table appear to involve very small changes of the values of the ionization potentials throughout the middle of their length, and the rare earths are not likely to have values that differ much from one another. One may check such speculations by reference to a number of other facts. Attention might be called, for instance, to the general distribution of the majority of the lines in the spectrum of an element, as an indication of its probable ionization potential. It is thus perfectly plain on inspection that the ionization potentials of Be, B and C must be fairly high, and that Fe, Ni and Co can not differ much from one another, and the values of their potentials must be moderate.

The study of the more complex spectra is yielding approximate values for ionization potentials in a few cases, and also a picture of the way in which the complexities of spectra increase in passing across the periodic table. With Professor Russell's kind permission I mention a conclusion to which he has recently come, to the effect that the complexities run as follows: in column I all lines are pairs; in II they are singlets or triplets; in III pairs or quadruplets; in IV singlets, triplets or quintuplets; and so forth in a regular manner alternating and increasing across the table. Analogy indicates that the fundamental lines will lie with the least of the complexities, and it is on this ground that the singlets in Si have been assumed to furnish the ionization potential of that element. There are interesting facts now available in regard to the way in which these complexities widen out or shrink in passing down the columns of the periodic table, or across them, or from one element in the normal state to the same in various stages of ionization, or from an ionized element to others containing the same numbers of external electrons (but different nuclei). The facts are unfortunately not quite well enough known to permit much analysis, and there is little theory as yet on these difficult relations.

Another spectroscopic aspect of the atomic problem is furnished by the new atoms created by the removal of one or more electrons. These are temporary atoms, but their spectral similarities (*e.g.*, Al^{++} and Mg^{+} with Na, Al^{+} with Mg, etc.) tell us something about their probable chemical properties, and their spectral series yield their ionization potentials. Their occurrence offers a number of attractive puzzles as yet almost untouched. They appear, for instance, to have the ability to form temporary compounds, whose existence may sometimes be proved from band spectra. Somewhat similar is the occurrence of molecules in *He* which are supposed to be formed by "excited" atoms, *i.e.*, those in which one electron is displaced from its innermost position to an outer orbit.

Much praise is due to Fowler and to Paschen for their recent work on the spectra of ionized Si and Al. Paschen found it possible to sort out in the spectra furnished by sparks and other sources those lines due to Al, to Al^{+} and to Al^{++}, and to show that they form systems of series requiring four times the universal series constant N for the atom Al^{+} and 9N for the series formulae of Al^{++}. Fowler found in Si^{+++} series requiring 16N, thus furnishing a striking confirmation of a prediction originally made by Bohr.

Finally, in the direction of very short wave lengths, experiment has recently blasted out new trails which will doubtless lead us to much that is of the greatest interest. The work of Lyman, Millikan and many others is disclosing the most important radiations of many atoms, and much more needs to be known, especially about series spectra in this region, to bring about a closer connection between optical and X-ray series in the lighter elements. This is probably, to quote a happy phrase of Professor Russell's, the heroic age of spectroscopy, and in the next few years we may hope to have laid a thoroughly sound foundation for future builders of atomic models. Not until then at least shall we have begun to emerge from the darkness of ignorance in which we are still plunged, or to have begun to deserve the name imposed somewhat prematurely upon our species—Homo sapiens.

F. A. SAUNDERS

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY

ON CERTAIN COURSES NOT LISTED IN THE MEDICAL CURRICULUM[1]

EDUCATION in medicine has changed greatly since the war. Practically all the good medical colleges have found it necessary to limit the numbers of their students on account of the increasing masses of men and women who seek admission to the various institutions of learning. This has made it possible for us here at Cornell to select only those who have the best educational and personal qualifications. This selection is difficult, but the dean and secretary have acquired great skill and we are becoming accustomed to increasingly enthusiastic reports from the teachers of the first-year classes. The medical college secures a much better group of students. The students secure, or should secure, a better understanding of their indebtedness towards the college. Each one of you is virtually receiving a scholarship of approximately one thousand dollars a year, since it costs the university this sum in excess of the tuition fees to furnish the education that the faculty believes to be essential. The expenditure of this sum was made possible through the generosity of the late Colonel Payne, who endowed our medical college. Your acceptance of its benefits entails on your part a serious realization of your obligations to the community. The community expects not only well-educated conscientious practitioners, but also devoted public servants. If in addition your class develops, as we expect it to develop, leaders in the science of medicine, we are more than repaid for the investment of money and the labor of teaching.

The year of 1923 marks a change in the policy of the Cornell University Medical College. The faculty has realized that the curriculum is overcrowded and has decided to reduce the number of hours of instruc-

[1] An address delivered to the medical students at the opening of the college year.