[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

A FORCE, APPARENTLY DUE TO MASS, ACTING ON AN ELECTRON, AND THE NON-IDENTITY OF ISOTOPES IN SPECTRA AND OTHER PROPERTIES.

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Both electrostatic and gravitational forces follow an inverse square law, and the constants are such that the gravitational force is only 4.1×10^{-40} times the electrostatic,[1] when one of the masses consists wholly of positive, and the other of negative electrons. The smallness of such a gravitational force would seem to indicate that when an electron in the outer part of an atom vibrates under the restraining force due to the attraction of the positive charge on the nucleus of the atom (modified by the effects of the adjacent negative electrons), its vibration will depend wholly upon the charge and not at all upon the mass of the nucleus, insofar as experimental methods are able to decide. It need not, then, be surprising that Bohr's first equation[2] for the possible frequencies emitted by the simplest atoms, such as hydrogen and helium, contained no term which took account of the mass of the nucleus. However, Fowler, in a discussion in *Nature*,[3] pointed out that certain of the formulas which had been used did not give accurately the lines found by him, and this led Bohr to show that the deviations could be accounted for by the introduction of a term for the mass of the central nucleus. Thus the Bohr equation[4] became

$$\nu = \frac{2\pi^2 e^2 E^2\, mM}{h^3\,(M + m)}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where ν is the frequency of the emitted light, e and E, and m and M, are the charge and mass of the electron and the nucleus, respectively. It is clear that this equation does not assume the existence of any force due to the mutual action of the masses of the positive and the negative electron, since the mass term is introduced for the purpose of correcting for the displacement of the nucleus from the center of gravity of the system, negative electronucleus, with a change in the mass of the nucleus.

Five years ago it occurred to one of the writers that the best test of the effect of mass as independent of a net charge, in attracting a negative electron, could be made by the use of isotopes, such as those of lead, for the net positive charge on the nuclei of isotopes is the same, but the mass is

[1] Richardson, "The Electron Theory of Matter," p. 590. Cambridge University Press, 1914.

[2] *Phil. Mag.*, 26, 10 (1913).

[3] *Nature*, 92, 95 (1913).

[4] *Ibid.*, 92, 231 (1913).

different. It seemed, however, both from the standpoint of theory and of past experimental experience, that there was little chance for the discovery of such an effect, since the Bohr theory predicted a difference between the wave length of the principal line in the spectrum of ordinary lead and of that derived from radium (radium G), of only 0.00005 Ångstrom, which is too small a difference to detect by the use of even the eschelons and gratings which give the highest dispersion. In addition to this prediction of theory, there was the fact that at least 7 careful experimental investigations had all resulted in the conclusion that the spectra of isotopes are *identical*. These investigations were as follows: those of Russell and Rossi,[1] and of Exner and Haschek,[2] using thorium and ionium; that of Aston[3] on the isotopes of neon; that of Soddy and Hyman[4] on lead from thorium and ordinary lead, and finally those of Richards and Lembert,[5] Hönigschmidt and St. Horivitz,[6] and of Merton,[7] on Radium G and ordinary lead. Merton used a grating, and finally a Fabry and Perot étalon, and concluded from his work with the latter that there is no difference in wave length as great as 0.003 Å. for the line λ4058 in the spectrum of ordinary lead and of radium G.

The Nature of Isotopes.

Isotopes are atomic species whose atoms contain the same number of planetary electrons, and, as is evidenced by the great likeness in their spectra, these electrons must form a system of almost, but, probably not quite, identical configuration. The net positive charge on the nuclei of isotopic atoms is the same, but either the stability or else the mass of the nuclei are different. In the radioactive series, isotopes derived from the same ancestor, either uranium or thorium, if they differ at all in mass, have nuclei which differ by an α-particle (the nucleus of a helium atom) and by 2 electrons, which may be called cementing electrons. If η is taken as the symbol of the hydrogen nucleus—the positive electron—and β as that of the negative electron, then the α-particle is $(\eta_4{}^+\beta_2{}^-)^{++}$. The α-particle together with the 2 cementing electrons which unite it to the rest of the nucleus, may be said to have the formula $((\eta_4{}^+\beta_4{}^-)$, which will be described by the term "helio group," and this has a zero net charge. That is, isotopes of different masses, if derived from the same ancestor, have nuclei which differ by one or two helio groups. Isotopes which are derived from different ancestors (uranium and thorium) have nuclei which differ by the group $(\eta_2{}^+\beta_2{}^-)$, which may be called the mu (μ) group,

[1] *Proc. Roy. Soc.* (*London*), **87**, 478 (1912).

[2] *Sitz. Akad. Wiss., Wien* (*Abt. IIa*), **121**, 175 (1912).

[3] *Brit. Assoc. Meeting*, **1913**, p. 403.

[4] *J. Chem. Soc.*, **105**, 1402 (1914).

[5] THIS JOURNAL, **36**, 1329 (1914).

[6] *Sitz. Akad. Wiss., Wien* (*Abt. IIa*), **123**, Dec. (1914).

[7] *Proc. Roy. Soc.* (*London*), **91**, 198 (1914).

by the difference between a mu and a helio group or by both a mu and a helio group. Among the light atoms the only known isotopes, those of neon discovered by Thomson, and those of chlorine, presumably separated by Harkins and Broeker,[1] and with atomic weights 35 and 37 as determined by the positive ray method by Aston,[2] differ by the mu group. It is probable too, that the isotopes of magnesium and silicon, claimed by Harkins to exist (provided the most recent atomic weights, 24.3 for magnesium and 28.1 for silicon are sufficiently exact), differ also by the mu group.

In addition to the groups specified above, there is another, which, like the α-group without its cementing electrons, does not by itself give rise to the existence of an isotope, since its net charge is one positive. This is either the λ^{+++} group, (lithium nucleus group) or the nu (ν^{+}) group. Which of these is the primary group cannot well be decided at the present time. If it is the ν or $(\eta_3{}^{+}\beta_2{}^{-})^{+}$ group, then λ is equivalent to $\alpha\nu$. For the sake of simplicity the latter representation will be chosen. It is evident that isotopes might be formed by the addition of one ν group, together with one cementing electron. This would be equivalent in the sense of composition, to the inclusion of a group $\nu\beta$, or $\eta_3{}^{+}\beta_2{}^{-}\beta^{-}$, but does not imply that the third negative electron is directly associated with the other two. Isotopes might also be formed by the inclusion of one positive and one negative electron ($\eta^{+}\beta^{-}$), though members of this last class have not been discovered, nor have those which contain the $\eta_3{}^{+}\beta_2{}^{-}\beta^{-}$ electron addition, but the latter may, and probably will, be discovered later in the range between atomic numbers 28 and 82.

The formula of lead from radium (radium G) is, according to Harkins,[3] $(\alpha_{51}{}^{++}\beta_{20}{}^{-}\mu)^{82+}e'_{78}e_4$, where e represents an electron in the valence shell, and e' a planetary electron in an inner shell. That of lead from thorite, of atomic weight 208, is $(\alpha_{52}{}^{++}\beta_{22}{}^{-})^{82+}e'_{78}e_4$. Ordinary lead is either a mixture of these two isotopes, or it is an individual of the formula $(\alpha_{50}{}^{++}\lambda^{+++}\beta^{-}{}_{21})^{82}$ $e'_{78}e_4$ or $(\alpha_{51}{}^{++}\nu^{+}\beta_{21}{}^{-})e'_{78}e_4$. These last two are simply two different symbolic expressions for the same composition. The atomic weight evidence is slightly in favor of the idea that it is a mixture of the two isotopes. Also, ordinary lead is much more stable than is to be expected in general for an atom of such high nuclear charge whose nucleus contains an *odd* number of *negative* electrons, since relative instability usually accompanies the presence of an odd number of negative electrons. If ordinary lead is an individual isotope, then each of its nuclei contains one positive and one negative electron in excess of those contained in the lead from radium, and, in any case, this is the average difference.

[1] *Phys. Rev.*, **15**, 74 (1920); *Science, N. S.*, **51**, 289–91 (1920); *Nature*, **105**, 230–1 (1920).

[2] *Nature*, **104**, 392 (1919).

[3] *Phys. Rev.*, **15**, 73–94 (1920).

The Spectra of Isotopes.

The use of the conception of gravitational fields in an atom may be elucidated in the future by the newer relativity theory of Einstein, but such applications of the theory have not, as yet, been made. Since the gravitational fields upon which experiments are carried out are due to a large scale phenomenon, and to the resultant effect of 2 or more bodies which are practically neutral electrically, the effect of the addition of a neutral mass to the nucleus of an atom upon the vibration of an electron, a very small scale phenomenon, cannot be accurately predicted from the ordinary law of gravitation, which, as stated in the first paragraph, leads to the idea that such an effect is entirely negligible.

The details of the experimental work on the spectra of ordinary lead and a lead from radium of atomic weight 206.318, very kindly supplied by Professor T. W. Richards, were presented in 2 short notes[1] published 2 years ago. It was found that the wave length of the line λ4058 as obtained from the radio-lead was 0.0044 Å. greater than that from ordinary lead; that is, the difference in wave length found is *one-millionth of the total wave length*, or one-ten-thousandth of one per cent. *It is to be noted that this is an effect 100 times greater than that predicted by the theory of Bohr* and enormously greater than that predicted by the simple gravitational theory. This result was obtained in a most careful joint investigation carried out by Professor H. G. Gale and the writers. Sixteen comparison plates were taken, and a number of exposures were taken in which the spectra of 2 specimens of ordinary lead were compared. In every case, when the radio-lead and the ordinary lead were interchanged in their position with reference to the spectrograph, the shift in wave length followed the shift in position. The experimental work, carried out by the use of the Michelson 10-inch grating with a 30-foot Littrow mounting, used in the sixth order, was of such a character that there seemed to be no reasonable doubt of its correctness. There was certainly no doubt that the shift was real, since it could be easily seen. However, on account of the smallness of the wave length difference, and because it was nevertheless much greater than that predicted by Bohr's theory, it seemed best to defer our discussion of the meaning and importance of the result until it had been confirmed in a totally independent investigation. Recently[2] Merton has obtained such a confirmation, and finds that not only the direction, but also the magnitude of the shift obtained by him is the same within the limits of error, as that obtained by us. He did not use a grating, but a Fabry and Perot étalon. Our source of light was a Wali-Mohammed vacuum arc, Fig. 1, run at 0.04 mm. pressure, with a

[1] Harkins and Aronberg, *Proc. Nat. Acad. Sci.*, 3, 710–15 (1917). "Note on the Spectrum of the Isotopes of Lead," Aronberg, *Astrophys. J.*, 47, 96–103 (1918).

[2] *Proc. Roy. Soc.* (*London*), **96A**, 388–95 (1920).

current of 1.1 amperes and a voltage of 40. Merton used an arc produced between the lead and a piece of tungsten, and a current of one ampere at 100 volts, burning under a bell jar at a "fraction of a millimeter" of pressure. In our experiments the amperage and voltage were varied intentionally in some of the experiments, but without any noticeable effect upon the results. The shift in wave length found by Merton was 0.0050 Å. ± 0.0007 Å., while the average of 16 measurements as found by us was 0.0044 Å., an agreement within about twelve one-millionths of one per cent. of the total wave length which is not far from the experimental error. As stated, our radio-lead had an atomic weight equal to 206.312, while that of the lead used by Merton is not given in his paper. He found, also, a difference of 0.0022 Å. ± 0.0008 Å. between the wave length of ordinary and that of thorite lead, but the latter contained about 20% of ordinary lead, so its atomic weight is about 207.84. When it is considered that the difference in the atomic weights of the 2 forms of lead used by us is 0.89, while that between the thorite lead and ordinary lead used by Merton was about 0.6, it is seen that all of the measurements are in as good agreement as could be expected, *the electron in the heavier atom always showing the greater frequency, as would be predicted from theory if it is the additional mass in the nucleus which produces the effect.*

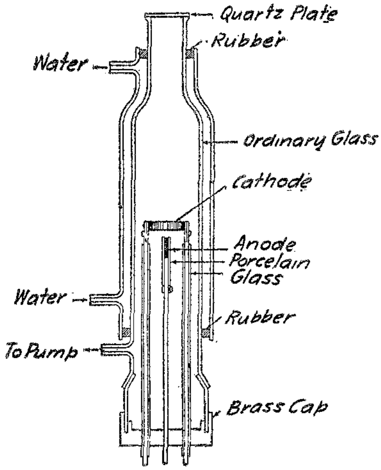

Fig. 1.

Thus there has been discovered an effect upon the vibration of an electron, the only apparent cause of which is the change in the mass of the nucleus of an atom, which must then be accompanied with a change in the force acting upon the electron, otherwise the vibration period of the latter would not be changed. The interest in this phenomenon lies in its close relationship to gravitation, and also in the fact that its magnitude far exceeds ordinary gravitation, which would seem to indicate that such small scale mass effects do not follow the same simple form of the law as large scale gravitational effects. It is possible that the effect discovered is due to the fact that the positive and negative electrons added to the nucleus, in the change from a lighter to a heavier lead, are not coincident in space, but this lack of coincidence is also present in the rest of the nucleus, and may also be related in some way to gravitational effects. Thus it is not unlikely that this newly-discovered effect is related in some way to the electromagnetic field in the atom, which is related in some unknown way to the large scale gravitational field.

The newer relativity assumes a proportionality between mass and weight, and by the results which it obtains, makes it seem probable that such a proportionality exists, but, on the other hand, the experimental tests of this relationship, though they have been carried out with great care and precision, as in the work of Eötvös, do not give as conclusive evidence as could be desired, since they have been carried out with materials of such a nature that the crucial test has not, as yet, been made, at least not with the attainable degree of accuracy. The newer theories of the constitution of the nucleus of the atom as worked out by Harkins,[1] suggest that for such a test one of the masses should consist wholly, or as largely as is possible, of hydrogen, while the other should contain no hydrogen, since the percentage change of mass which occurs in the formation of complex atoms is practically independent of the atom which is formed, provided hydrogen is taken as the material for their formation. Thus when hydrogen changes into helium, it seems probable that there is a decrease of mass equal to 0.77%, but when helium changes into any other complex atomic species, the change of mass is very much smaller, so small indeed that the present atomic weights are not sufficiently accurate to indicate that there is such a change. By taking one of the masses in the form of hydrogen and the other in the form of any other element or elements, it is thus possible to compare the weights and masses of 2 bodies, one of which is composed of material which *has not* been subject to this considerable packing effect, while the other *has* been affected by it. We do not mean to indicate that the results of such an experiment are likely to show that mass is not proportional to weight, but only wish to point out that the crucial experimental test of this relationship has not, as yet been made. It is likely that some of Newton's experiments were made with materials which would meet the above conditions for such a test, except for the fact that the technique had not been developed sufficiently at that time to give the work a sufficient degree of accuracy.

Spectra as a Means of Distinguishing between Isotopes.

Since the work reported here, and also that of Merton, indicates a change in wave length with a change in the atomic weight of isotopes, it is apparent that isotopes which differ in atomic weight may be distinguished by their spectra. It might seem, also, that when a mixture of isotopes is available, as in the case of the common element chlorine, the grating spectograph might be used as an instrument to detect their existence

[1] THIS JOURNAL, **37**, 1367–1421 (1915); **39**, 856–79 (1917); *Phys. Rev.*, **15**, 73–94 (1920).

in the mixture, without either subjecting it to an extremely lengthy and tedious separation. However, this supposition does not seem to be justified, at least in the case of lead, since the line seems to be shifted and not broadened. Let us make the assumption already presented, that ordinary lead is a mixture of about 60% of lead from thorium to 40 from radium. Line λ4058 has a width which depends upon the conditions in the arc, particularly the pressure. The lead from radium which we used would be composed, on the above basis, of about 85% of lead from radium, and 15% of lead from thorium, yet when its spectrum was taken under the same conditions, line λ4058 was found to be shifted as a whole in the direction to be expected as the result of a smaller atomic weight, that is to a greater wave length, the width of the line remaining about the same. In other words, the position of the line seems to correspond to the mean atomic weight of the lead in the specimen under investigation. It is, of course, possible, though not so probable, that the atomic weight of ordinary lead is slightly lower than the determined value, and that ordinary lead is an individual. In this case it is to be expected that the spectrum of the specimen of radium-lead used by us, which contained on this basis 25 or 30% of ordinary lead, would show a broadened line, but this was not the case.

Non-Identity of Isotopes in Chemical Properties.

The differences in the vibration frequencies of the *electrons* in isotopes indicate that they are not held by identical forces, so isotopes should not be identical from the chemical standpoint, though the difference should be exceedingly slight, and not capable of detection by chemical means now available, insofar as it is due to the mass effect upon the electrons. There is another effect due to the action of the different nuclear masses upon the vibration frequencies of the *atoms*, which may or may not be of a sufficient magnitude to give differences in vapor pressure and in chemical affinity which may be detected experimentally. This effect has been discussed from the standpoint of the quantum theory by Lindemann,[1] and by Lindemann and Aston.[2] Unfortunately the quantum theory is itself so indefinite that the deductions from it are altogether uncertain. The results of Soddy seem to indicate that lead and lead from thorium have the same atomic volume, and Richards[3] has shown in very precise experiments that both the atomic volumes and the melting points of lead and lead from radium are the same within the experimental errors. The wave length of the spectrum lines is the first property, aside from mass and atomic stability, in which isotopes have been found to differ, and it is the first property

[1] *Phil. Mag.*, 38, 173–81 (1919).

[2] *Ibid.*, 37, 523–34 (1919).

[3] T. W. Richards, "Presidential Address to the American Association for the Advancement of Science" (1918), THIS JOURNAL, 38, 221 (1916).

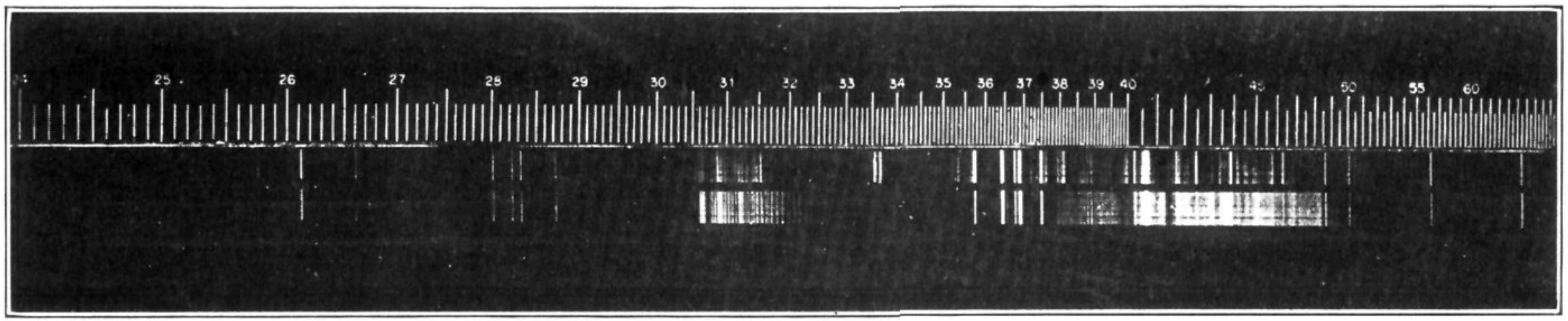

Fig. 2.—Spectrum of lead from radium (below) and ordinary lead (above). Differences in the spectra are due to small amounts of impurities. The specimens of lead used in the 16 final measurements were more highly purified than those whose spectra are given above. On the final plates comparison spectra for ordinary lead were taken both above and below. The dispersion was so high, however, that the plates give very few lines due to lead.

showing such a difference which is due to an effect on the planetary electrons.

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THE EQUILIBRIUM BETWEEN CHLORINE AND PLUMBOUS AND PLUMBIC CHLORIDES IN AQUEOUS SOLUTION.

BY ERNEST W. WESCOTT.

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1. Introduction.

Solutions of lead chloride in strong hydrochloric acid absorb chlorine in much larger quantities than can be accounted for by the solubility of the gas. The solutions exhibit a strong yellow color, and on the addition of ammonium chloride throw down a precipitate of clear yellow octahedral crystals. The composition of these crystals, which can be obtained in a state of great purity, has been found to be represented by the formula $(NH_4)_2PbCl_6$. Cesium and other chlorides produce precipitates of similar composition which in all cases are salts of the hypothetical acid, H_2PbCl_6. By treating the crystals of the ammonium salt with pure sulfuric acid at zero, there has been obtained the tetrachloride of lead, $PbCl_4$. This substance is a heavy yellowish oil, which reacts violently with water.

These facts suggest that the reaction occurring when chlorine is passed into a suspension of lead chloride in hydrochloric acid may be written as follows

$$PbCl_2(s) + Cl_2(g) + 2HCl = H_2PbCl_6; \text{ or}$$

$$PbCl_2(s) + 2Cl^- + Cl_2(g) = PbCl_6^{--}.$$

The purpose of this investigation was to determine the equilibrium conditions of this reaction, with a view also to estimating the plumbous-plumbic reduction potential. Experiments were also made with acid concentrations small enough to permit the precipitation of solid lead dioxide; and the free energy of this compound was calculated from the equilibrium conditions of the reaction

$$PbCl_2(s) + 2H_2O + Cl_2(g) = PbO_2(s) + 4HCl.$$

This research has been carried out with the coöperation of Professor A. A. Noyes and with the aid of the grant made to him by the Carnegie