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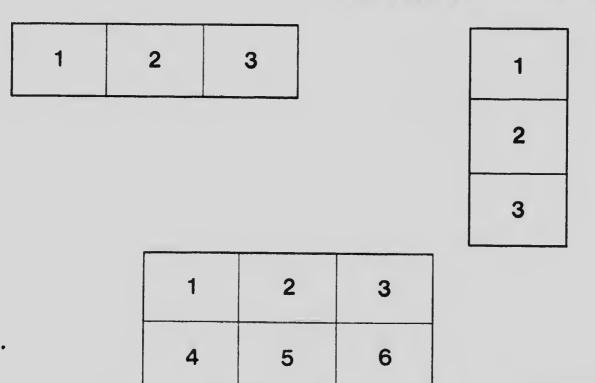
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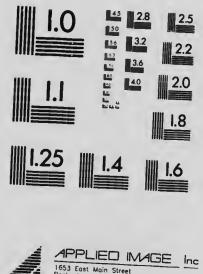
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> PAPERS FROM THE PHYSICAL LABORATORIES

No. 53: ON THE IONISATION POTENTIALS OF MAGNESIUM AND OTHER METALS, AND ON THEIR ABSORPTION SPECTRA, BY PROFESSOR J. C. MCLENNAN

(REPRINTED FROM THE PROCEEDINGS OF THE ROYAL SCC. 1, VOL. 92.)



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[Reprinted from the PROCEEDINGS OF THE ROYAL SOCIETY, A. Vol. 92]

On the Ionisation Potentials of Magnesium and other Metals, and on their Absorption Spectra.

By Prof. J. C. MCLENNAN, F.R.S., University of Toronto.

(Received July 17, 1916.)

[PLATES 7 AND 8.]

1. Introduction.

In a paper vecently published by the writer,* on the single-line spectrum of magnesium, experiments were described in which it was found that when magnesium vapour in a vacuum was bombarded by electrons it was possible if the electrons possessed the requisite amount of kinetic energy to cause the vapour to emit a radiation consisting of the single spectral line $\lambda = 2852.22$ Â.U. At the time these experiments were made and the paper was written it was not known by the author whether this line was the first member of the series whose frequencies are given by $\nu = (1.5, S) - (m, p_2),^{+}$ or of the series

* McLennan, 'Roy. Soc. Proc.,' A, vol. 92, p. 305 (1916).

+ In the symbolic equation $\nu = (n, X) - (m, Y)$, the frequencies are given by $\nu = \frac{N}{[n+X+x(n, X)]^2} - \frac{N}{[m+Y+y(m, Y_j)]^2}$, where N is Rydberg's number, n has a fixed where integral can one of the numbers 1.5, 2.5, 3.5, i.e. and w has successive

value either integral or one of the numbers 1.5, 2.5, 3.5, etc., and m has successive integral values, each one giving the frequent v of a member of the series.

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Prof. J. C. McLennan. On the Ionisation

whose frequencies are represented by $\nu = (1.5, S) - (m, P)$. Since the single line spectra of mercury, zinc and cadmium consisted of the single spectral line whose frequency is given by $\nu = (1.5, S) - (2, p_2)$, it was assumed that the line $\lambda = 2852.22$ Å.U. also had a frequency represented by this formula. On the basis of -1.5 assumption it was deduced from well-known data regarding the magnesium series spectra that the wave-length of the line whose frequency is $\nu = (1.5, S) - (2, P)$ should be approximately $\lambda = 2073:36$ Å.U.

As in some experiments made by the writer, in collaboration with Mr. Evan Edwards,[•] it had been shown that the absorption spectra of the vapours of mercury, zinc, and cadmium consisted of bands at lines whose frequencies were given by $\nu = (1.5, S) - (2, p_2)$, and $\nu = (1.5, S) - (2, P)$ it was expected that the absorption spectrum of magnesium vapour would also exhibit bands at $\lambda = .2852.22$ Å.U. and $\lambda = .2073.36$ Å.U.

Wood and Guthrie⁺ had already noted absorption by magnesium vapour at $\lambda = 2852 \cdot 27$ Å.U., but as no other absorption band had been found with this vapour an attempt was made to look for it at $\lambda = 2073 \cdot 36$ Å.U.

In making the examination a small quartz spectrograph with low dispersion was used, and it was found that a sharp clearly defined band came out at what appeared to be $\lambda = 2073 \cdot 36^{-9}$ This result was therefore taken as indicating that the assumption that the frequency of the line $\lambda = 2852 \cdot 22$ Å.U. was given by $\nu = (1.5, S) - (2, p_2)$, was correct.

A few weeks ago, however, the attention of the writer was very kindly drawn by Prof. F. A. Saunders, of Vassar College, to an inaugural dissertation by Lorenser of Tübingen, of which there appears to be as yet but one copy in America, in which it was established that $\lambda = 2852 \cdot 22$ Å.U. was the first member of the series $\nu = (1.5, S) - (m, P)$, and $\lambda = 2026 \cdot 46$ Å.U. the second member of the same series.

With this information it was easy to deduce that the line whose frequency was given by $\nu = (1.5, S) - (2, p_2)$, must have the wave-length $\lambda = 4571.38$ Å.U. With this knowledge it followed that if magnesium vapour acted as regards absorption in a manner analogous to the vapours of mercury, zine and cadmium, bands should appear in its absorption spectrum, at $\lambda = 4571.38$ Å.U., $\lambda = 2852.22$ Å.U., and possibly at $\lambda = 2026.46$ Å.U. and at still higher members of the $\nu = (1.5 S) - (m, P)$ scries. The absorption of magnesium vapour was, therefore. Examined by the writer, and the following paper contains an account of these experiments and of others which followed on from them.

* McLennan and Edwards, 'Phil. Mag.,' vol. 30, p. 695 (November, 1915).

+ Wood and Guthrie, 'Astrophys. Journ.,' vol. 39, No. 1, p. 211 (1909).

Potentials of Magnesium and C'er Metals.

2. Absorption Spectrum of Magnesium Vapour.

In making these experiments a large Hilger quartz spectrograph, type (, possessing high dispersion was used. Some metallie magnesium was placed in the centre of a steel tube about 3 cm, in diameter and 20 cm, long. The ends of this tube were provided with erystal quartz plates sealed in with wax. The tube was highly exhausted by a Gaede pump and when a low vacuum was reached the metal was vaporised by heating the centre of the tube with a blowpipe, the ends of the tube being kept cool by wrappings of cloth kept soaked with water.

Some difficulty seems to have been experienced in photographing lines in the magnesium emission spectrum in the neighbourhood of $\lambda = 2000$ Å.U. on account of their feeble intensity, for, a. 'ough the elliptic tender of the line $\lambda = 202646$ Å.U. was predicted by Lorenser, Saund appears to have been the only one who as yet has observed it. Some difficulty was also experienced by the writer in obtaining a photograph of it with ordinary or panchromatic plates. When, however the Sebu again plates, recently put on the market by the Adam Hilger Company, were used, it was found that the line came out clearly and with considerable intensity.

The upper spectrum in fig. 1 was obtained with the light and from a spark in air between magnesium terminals and the lower one with the light from a magnesium arc of the type already described in a previous communication by MeLennan and Henderson.* The second spectrum in the figure is that of the light from a spark between zinc terminals in air, while the third is that of the light from an are between magnesium terminals in air. The line $\lambda = 2026.46$ A.U., it will be seen, comes ont clearly in both the spark and are spectra of magnesium and practically coincides with the last line in the zinc spectrum, an exceedingly strong line, whose wave-length is given by Saunders† as $\lambda = 2026.19$ Å.U.

It is of interest to note that the arc spectrum of magnesium in an shows a strong reversal at $\lambda = 3838$ Å.U. and a fainter though well marked one at $\lambda = 2852 \cdot 22$ Å.U. The fourth spectrogram in fig. 1, which was obtained with the light of the magnesium are *in vacuo*, was taken on a plate sensitive to the green, which was specially made for me by Dr. Mees of the American Kodak Company.

On account of the strong intensity of the line $\lambda = 2026.19$ Å.U. in the zinc spectrum, and its close proximity to the magnesium line $\lambda = 2026.46$ Å.U., the spark spectrum of zinc in air was used in looking for the absorption of

^{*} McLennan and Henderson, 'Roy. Soc. Proc.,' A, vol. 91, p. 485 (1915).

⁺ Saunders, 'Astrophys. Journ.,' vol. 43, No. 3, p. 239 (1916).

this line by magnesium vapour. The light from this spark was sent through the steel tube described above which contained the magnesium vapour, and photographs were taken of the spectrum when the tube was both strongly and gently heated. Two of the spectrograms taken in this way are shown in fig. 2.

The upper reproduction is that of the ordinary zinc spark in air with the light sent directly into the spectrograph, the second was obtained with vapour of low density, and the third when the tube was strongly heated. In the second spectrogram it will be seen that while the intensities of all the lines are much lessened, absorption at $\lambda = 2852 \cdot 22$ Å.U. is clearly marked. The intensity of the line $\lambda = 2026 \cdot 19$ Å.U. is also very greatly diminished. In the third spectrogram the line $\lambda = 2026 \cdot 19$ Å.U. has completely disappeared and absorption is widespread in the neighbourhood of $\lambda = 2852 \cdot 22$ Å.U.

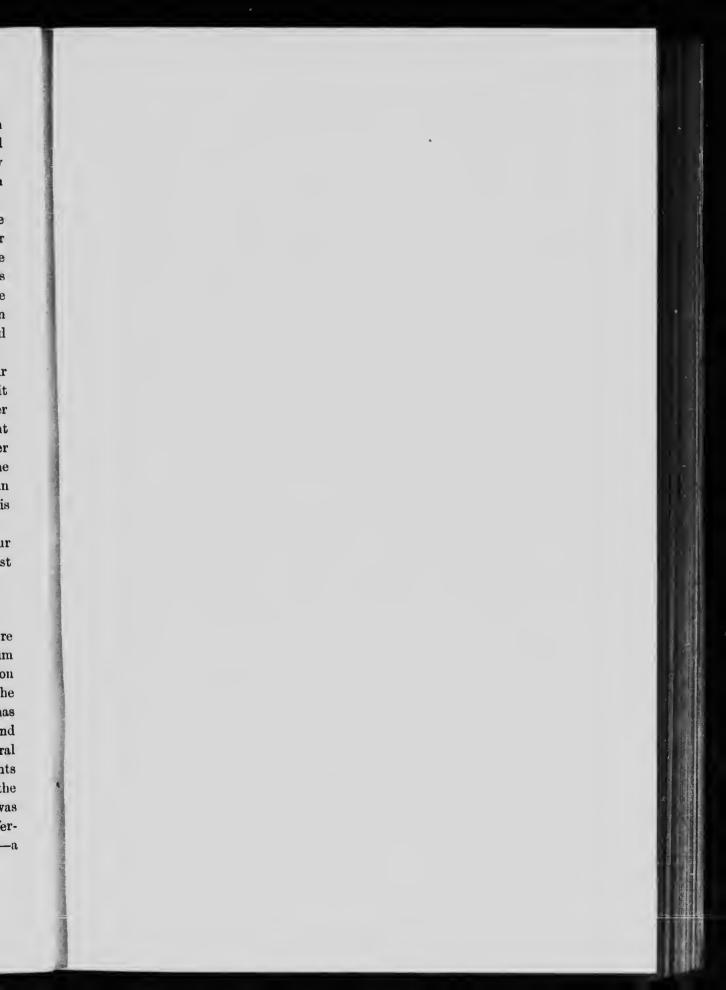
Repeated attempts were made to see if absorption by magnesium vapour could be obtained at $\lambda = 4571.38$ Å.U., but in no case was any trace of it observed. Fig. 3 shows the results of one of these attempts. The upper photograph was obtained with the light from an incandescent Nernst filament after it had passed through magnesium vapour of high density, and the lower one with the light from the zinc spark after passing through the same vapour. Absorption at $\lambda = 2852.22$ Å.U., it will be seen, is well marked in the second spectrum, but there is no trace of it at $\lambda = 4571.38$ Å.U. in this photograph or in the spectrum of the light from the Nernst filament.

As far as all these experiments go, then, absorption by magnesium vapour was obtained only at $\lambda = 2852.22$ Å.U. and at $\lambda = 2026.46$ Å.U., the first and second lines in the singlet series $\nu = (1.5, S) - (m, P)$.

3. Single-line Spectrum of Magnesium.

In a previous communication some experiments by the writer were described in which it was found that if magnesium vapour in a vacuum were bombarded by electrons the vapour could be made to emit a radiation consisting of the single spectral line $\lambda = 2852 \cdot 22$ Å.U., provided the electrons possessed the requisite amount of kinetic energy. Since it has been shown that the frequency of this line is given by $\mathbf{v} = (1.5, S) - (2, P)$, and since with mercury, zinc, and cadmium vapours the frequency of the spectral line in their single-line spectra is given by $\mathbf{v} = (1.5, S) - (2, P)$, the experiments were repeated to see if the magnesium vapour could not be made to emit the line $\lambda = 4571.38$ Å.U.—frequency (1.5, S)-(2, p₂). The apparatus used was the same as that described by McLennan and Henderson.* Potential differences, gradually increasing, were applied between the Wehnelt cathode—a

* McLennan and Henderson, 'Roy. Soc. Proc.,' A, vol. 91, p. 485 (1915).









Potentials of Magnesium and other Metals.

tungsten filament—and the vapour, but no radiation characteristic of the magnesium spectrum was obtained until a voltage of approximately 5 volts, was reached. With this applied potential difference the spectral line $\lambda = 2852 \cdot 22$ Å.U. came out strongly. Repeated experiments failed to bring out either the line $\lambda = 4571 \cdot 38$ A.U. or the line $\lambda = 2852 \cdot 22$ Å.U. until the electrons were given kinetic energy, corresponding to something like 5 volts. With potential differences higher than 5 volts, the line $\lambda = 2852 \cdot 22$ A.U. was the only one which came out on the plates until the are struck, which it did when the applied potential was about 7.5 volts. When the arc struck, the many-lined spectrum of magnesium was obtained.

The reproductions in fig. 4 show, firstly, the many-lined arc spectrum of magnesium, and, secondly, the single-line spectrum with the spectral line $\lambda = 2852 \cdot 22$ Å.U. alone. This was obtained with an applied potential of 5.9 volts. The third spectrum was obtained with an applied potential of 2.2 volts, and, as it shows, the only radiation recorded was that which came from the incandescent thugsten which constituted the Wehnelt eathode.

The spectrum shown in fig. 5 was obtained with an applied potential of 5.9 volts, using a Hilger quartz spectrograph, Type C, and it shows only the line $\lambda = 2852.22$ A.U.

It is interesting to note that the potential fall which was necessary to bring ont the line $\lambda = 2852 \cdot 22$ Å.U. was close to that given by the quantum relation $Ve = h\nu$, for if in this relation we insert the frequency of the hat $\lambda = 2852 \cdot 22$ Å.U. we find that the value of V comes out 4.28 volts. Moreover, the arc striking voltage, 7.5 volts, by the quantum relation connotes the frequency of the line $\lambda = 1626 \cdot 66$ Å.U., which is very close to $\lambda = 1621 \cdot 7$ A.U., the last line in the singlet series given by $\lambda = (i \cdot 5, S) - (m, P)$. This last result is also of special interest, for it coincides with what was obtaited with mercury, zine, and cadmium vapours. With these the arcing voltage was also practically that which corresponded to the frequency of the last line in the $\nu = (1 \cdot 5, S) - (m, P)$ series, *i.e.*, the frequency $\nu = 1 \cdot 5$, S.

4. Ionising Potentials of Magnesium.

In the experiments with merency, zine, and cadmium vapour, bombarded by electrons, it was found that the line whose frequency is given by $v = (1.5, S) - (2, p_2)$, was the one which came out most easily. Moreover, with mercury vapour Frank and Hertz* showed that the least applied potential difference which would bring out this line was 4.9 volts, and they+ also

* Frank and Hertz, 'Verh. d. Deutsch. Phys. Ges.,' vol. 11, p. 512 (1914).

† Frank and Hertz, 'Verh. d. Deutsch. Phys. Ges.,' vol. 10, p. 457 (1914).

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showed, by direct experiments, that for electrons to ionise mercury vaponr they must have kinetic energy at least equal to that acquired in a fall of potential of 4.9 volts. This voltage it will be remembered also is that given by the quantum relation for the frequency of the line $\lambda = 2536.72$ Å.U., the well known line in the single-line speetrum of mercury. In so far then as mereury, zinc, and cadmium are concerned, the ionising potential would appear to be deducible from the quantum relation by the use of the frequency $\nu = (1.5, S) - (2, p_2)$. With magnesium vapour, however, the matter appears to be different, for the spectral line which came out most easily was the one whose frequency is given by $\nu = (1.5, S) - (2, P)$, and not the one whose frequency is given by $\nu = (1.5, S) - (2, p_2)$ ($\lambda = 4571.38$ A.U.).

Moreover, McLennan and Thomson* have shown recently that the magnesium radiation emitted by a Bunsen flame supplied with the vapour of this metal consists of the single line $\lambda = 2852.22$ AU. In none of their experiments was any trace of the line $\lambda = 4571.38$ Å.U.⁺ observed. It would seem, therefore, that the line which is most easily stimulated in the magnesium spectrum is $\lambda = 2852.22$ Å.U.

McLennan and Keys‡ have also shown that when a Bunsen flame, fed with magnesium vapour, emits the line $\lambda = 2852.22$ Å.U., it is strongly ionised as well. From all these experiments then it would appear that the ionising potential, with magnesium vapour as with mercury, zinc, and cadmium vapours, can be obtained by a direct application of the quantum relation, and using the frequency $\nu = (1.5, S) - (2, P)$, of the line $\lambda = 2852.22$ Å.U., it comes out as 4.28 volts.

5. Ionising Potentials of Calcium, Strontium, and Barium.

De Watteville,§ in a paper on "Flame Spectra," has shown that if the spray of aqueous solutions of salts of calcium, strontium, and barium, be fed into a Bunsen flame, the latter emits a spectrum consisting of but a single line. For calcium the wave-length of this line is $\lambda = 4226.91$ A.U., for

* McLennan and Thomson, infra, p. 584.

+ It should be stated here that Eder and Valenta, in their 'Atlas Typischer Spektren,' refer to experiments in which it was found that the radiation from a Bunsen flame fed with what appears to have been metallic magnesium consisted of light of the wavelengths $\lambda = 5183.79, 5172.87, 5164.49, 4571.38, 3336.82, 3332.33, 3330.04, 3097.00, 3093.09,$ 2852-22 A.U. Liveing and Dewar, 'Roy. Soc. Proc.,' p. 189 (1881), also found the line $\lambda = 4571.38$ Å.U. among others, including $\lambda = 2152.22$ Å.U., in the spectrum of the light from burning magnesium in air.

‡ McLennan and Keys, infect, p. 591.

§ De Watteville, 'Phil. Trans.,' vol. 204, p. 139 (1904), and 'Comptes Rendus.' vol. 142 (1906).

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strontium it is $\lambda = 4607.52$ Å.U., and for harium $\lambda = 5535.69$ Å.U. Moreover, Ramage* has found that Bunsen flames fed with the pure vapours of these respective metals, or with the spray of aqueous solutions of their salts, also emit monochromatic radiations of the wave-lengths mentioned. Further, Lorenser, in the dissertation referred to, established the fact that these three lines are the first members of the series spectra of these three elements given by $\nu = (1.5, S) - (m, P)$. It would seem, therefore, that the frequency given by $\nu = (1.5, S) - (2, P)$, is the one most easily stimulated in atoms of calcium, strontium, and barium, as well as in the atoms of magnesium. Following the same argument as that just presented in the case of the element magnesium, it would seem likely, therefore, that the ionising potentials for the three metals mentioned will also turn out to be deducible from the quantum relation $Ve = h\nu$, by using the frequency $\nu = (1.5, S) - (2, P)$. If this surmisc should prove to be correct it would follow that the ionising potential for calcium is 2.89 volts, for strontium 2.65 volts, and for barium 2.20 volts.

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Element.	Ionising potential.	Remarks.				
Helium*	volts. 20 · ö	Direct experiment.				
Neon*	16.0	97				
Argon*	12.0	32				
Hydrogen*	11 .0	3 2	,,			
Oxygen*	9.0	37	31			
Nitrogen*	7.5	33	,,			
Mercury						
Zinc		Deduced	l from	single-lin	e spectrum	
Cadmium			,,	,,,	,,,	
Magnesium†			97	,,,	33	
Calcium			,,	,,,	,,	
C	9.65					

2.65

2.20

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* Frank and Hertz, ' Ber. d. Deut. Phys. Ges.,' Heft 2, p. 44 (1913).

Strontium

Barium

+ If it should turn out by later experiment that for magnesium, calcium, strontium, and barium the fundamental frequency is given by $\nu = 1.5$, S-2, p_2 instead of by $\nu_2 = 1.5$, S-2, P, then the ionising potentials of magnesium, calcium, and strontium would be respectively 2.67 volts, 1.86 volts, and 1.77 volts, the line possessing this frequency for the spectrum of barium not being known.

In the present communication, as well as in two previous ones, the writer has endeavoured to extend the field opened up by Frank and Hertz by their experiments with mercury vapour. With metals possessing high vaporisation temperature it is difficult, if not impossible, to apply direct methods to

* Ramage, 'Roy. Soc. Proc.,' No. 459, vol. 30, p. 1 (1901).

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the determination of such a magnitude as the ionisation potential. The evidence which has been accumulated so far, however, seems to show that in the frequency of the spectral line constituting the single-line spectrum of an element, we have a magnitude which, through the agency of the quantum relation Ve = hv, gives us the ionisation potential with ease and great accuracy.

Up to the present the ionisation potential has been determined by direct experiment for but seven of the elements, and by the method of single-line spectra it has been deduced for six others. With mercury it has been determined both by direct experiment and by the application of the quantum relation to the frequency given by the single-line spectrum of this element. In Table I, the results obtained up to the present by both methods are collected.

6. Experiments with Thallium Vapour.

From the evidence collected so far, it would appear that either the frequency given by $\nu = (1.5, S)-(2, p_2)$, or that given by $\nu = (1.5, S)-(2, P)$, is the one to look for in the spectrum of an element in endeavouring to ascertain its ionising potential. The radiation from a Bunsen flame fed with the vapour of an element, the absorption by the vapour, and the bombardment of the vapour by electrons, are three agencies which have proven useful in revealing one or other or both of these frequencies in the spectra of seven of the elements.

For thallium neither of these frequencies is known. Experiments by McLennan and Thomson* showed that the radiation from a Bunsen flame fed with thallium vapour consisted of light of the wave-lengths $\lambda = 5350.65 \text{ Å.U.}$, and $\lambda = 3775.87$ Å.U. But these are the first members of the well known second subordinate doublet series given by $\nu = (2, p_1) - (m, s)$, and $\nu = (2, p_2) - (m, s)$. Wood and Guthriet found that the absorption spectrum of pure thallium vapour consisted of well defined bands at $\lambda = 3230$ Å.U., $\lambda = 3092$ Å.U., $\lambda = 2530$ Å.U., and $\lambda = 2380$ Å.U., and that when mercury vapour was added to that of thallium the only band which appeared was at $\lambda = 2380$ Å.U., and that with a moderate amount of thallium in the absorption tube all these bands, except $\lambda = 2380$ Å.U., disappeared when mercury was added. Increasing the quantity of thallium, they found, caused this band to reappear, and then, finally, to become much stronger than with pure thallium. On again adding mercury other bands also appeared which were not found with pure thallium. Among these were bands corresponding to emission lines at $\lambda = 2580$ Å.U., $\lambda = 2768$ Å.U., and $\lambda = 3776$ Å.U.

* McLennan and Thomson, infra, p. 584.

+ Wood and Guthrie, 'Astrophys. Journ.,' No. 1, vol. 29, p. 211 (1909).

Potentials of Magnesium and other Metals.

In some experiments which were made by the writer, by the method adopted in photographing the absorption spectrum of magnesium, the only absorption which was observed in the region between $\lambda = 6000$ Å.U. and $\lambda = 1900$ Å.U., with low vapour density, was at $\lambda = 3775.87$ Å.U. At this wave-length the absorption consisted of a narrow sharply defined band. When high vapour densities were used, marrow diffuse absorption bands appeared at approximately $\lambda = 3230$ Å.U. and $\lambda = 3000$ Å.U. as well. No absorption was observed at $\lambda = 2768$ Å.U., $\lambda = 2580$ A.U., $\lambda = 2530$ Å.U., or at $\lambda = 2380$ Å.U.

As mercury vapour is known to absorb at $\lambda = 2536.72$ Å.U. and at $\lambda = 2338$ Å.U., it is just possible that the absorption observed by Wood and Guthrie with thallium vapour in the neighbourhood of these two wavelengths was due to the presence of mercury in their absorption tube. As the second member of the series spectrum of thallium given by $\nu_1 = (2, \rho_1) - (m, s)$, has the wave-length $\lambda = 3229.88$ Å.U., the absorption observed by Wood and Guthrie at $\lambda = 3230$ Å.U. is accounted for. Just what the absorption observed by them at $\lambda = 3092$ Å.U. means is, however, not very evident. This wave-length has not as yet been associated with auy series in the spectrum of thallium. It may possibly be related to one or other of the series $\nu = (1.5, S) - (2, p_2)$, and $\nu = (1.5, S) - (m, P)$, but this does not seem likely, for any evidence which we have points to the probable occurrence of all the members of these two series in the extreme ultra-violet.

The method of electronic bombardment has not as yet been applied to the vapour of thallium, but experiments in this direction are now in hand, and it is expected that some information will soon be obtained, which may not only indicate the significance of the occurrence of absorption at $\lambda = 3092$ Å.U., but which may also enable one to definitely locate the wave-lengths in the spectrum of thallium, whose frequencies are given by $\nu = (1.5, S) - (2, p_2)$, and $\nu = (1.5, S) - (2, P)$.

7. Summary of Results.

1. The absorption spectrum of non-luminous magnesium vapour in a vacuum consists of narrow sharp bands at $\lambda = 2852 \cdot 22$ Å.U. and $\lambda = 2026 \cdot 46$ Å.U. These lines are the first two members of the singlet series whose frequencies are given by $\nu = (1.5, S) - (m, P)$.

2. When magnesium vapour in a vacuum is bombarded by electrons, no radiation characteristic of the spectrum of this metal is emitted until the electrons possess kinetic energy equal to that which would be acquired in a fall of potential of approximately 4.5 volts. With a field corresponding to 5.9 volts the spectrum obtained consisted of a single line $\lambda = 2852.22$ Å.U.

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With this voltage the line came out with strong intensity. When a field of 2.2 volts was used no radiation characteristic of magnesium was obtained.

3. No indication of the line $\lambda = 4571.38$ Å.U. was obtained under electronic bombardment until the electrons possessed sufficient kinetic energy to cause the are to strike. The arcing voltage was approximately 7.5 volts. This, by the quantum theory, corresponds to the frequency of the line $\lambda = 1626.66$ Å.U., which is very close to $\lambda = 1621.7$ Å.U., the last line in the series given by $\nu = (1.5, S) - (m, P)$. With the vapour of mercury, zine, cadminm, and magnesinm, the arcing voltages appear to be connected by the quantum relation with the frequency $\nu = 1.5$, S.

4. As the simplest Bunsen flame spectrum of magnesium vapour consists of the single line $\lambda = 2852 \cdot 22$ A.U., and as the vapour in the flame when emitting this radiation has been shown to be ionised, it would appear that the ionisation potential of magnesium vapour also follows the quantum theory law, and is given approximately by 4.28 volts.

5. Arguments have been presented in the paper which support the view that while the ionising potential for mercury, zinc, and cadmium may be deduced by the quantum theory by the use of the frequency represented by $\nu = (1.5, S) - (2, p_2)$, in the case of magnesium, calcium, strontium, and barium the frequency which must be used is given by $\nu = (1.5, S) - (2, P_2)$.

6. The absorption spectrum of non-luminous thallium vapour, with low densities, consists of a narrow sharp band at $\lambda = 3775.87$ Å.U., and with high vapour densities of this band and somewhat diffuse ones at $\lambda = 3230$ Å.U. and $\lambda = 3000$ Å.U. Of these the line $\lambda = 3775.87$ Å.U. is the first member of the second subordinate doublet series given by $\nu = (2, p_2) - (m, s)$, and $\lambda = 3230$ Å.U. is the second member of the second subordinate doublet series given by $\nu = (2, p_2) - (m, s)$, and $\lambda = 3230$ Å.U. is the second member of the second subordinate doublet series given by $\nu = (2, p_1) - (m, s)$. No sign of absorption was observed at $\lambda = 5350.65$ Å.U., the first member of the second subordinate series $\nu = (2, p_1) - (m, s)$. The frequencies given by $\nu = (1.5, S) - (2, p_2)$, and $\nu = (1.5, S) - (2, P)$, have not as yet been located in the spectrum of thallium.

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