

## 15. ON THE PROBLEMS OF TEMPERATURE RADIATION OF GASES (PAPER C)

(Phil. Mag., Sr. VI, 41, 267, 1921)

## § 1.

The object of the present paper is to discuss and examine the present-day position of the question of temperature radiation of gases. The problem before us is, whether by simply heating a quantity of gas confined within a closed vessel (say, a silica or graphite tube), it is possible to make the gas emit its characteristic line-radiation. The experimental results on this subject are somewhat conflicting, and for different elements are widely divergent. While Pringsheim and others<sup>1</sup> found that permanent gases like H<sub>2</sub>, He, Ne, A, N<sub>2</sub>, O<sub>2</sub>, etc. remain non-luminous even at the highest temperatures which can be commanded in the laboratory, it is known that vapours of many elements easily become luminous at moderate temperatures. Such, for example, are the vapours of I, Br, As, S, Se, Sb, and other metalloids. If we take the tube-furnace spectra of King<sup>2</sup> to be cases of pure temperature-radiation, we have to admit that at temperatures varying from 2000° to 3000°K, most of the alkalis, the alkaline earths, thallium, iron, vanadium, etc. can be made to emit their line-spectra. Gibson<sup>3</sup> obtained the green line of thallium by simply heating the element contained in a quartz tube. But the conclusion drawn by him—that the intensity of the green line is the same as that of the black body-spectrum at this particular wave-length—is entirely wrong. He placed the quartz tube within a black-body chamber heated to about 1200°C., and observed that the continuous spectrum from the black body was crossed by a black absorption line corresponding to the green emission line. But this black line faded away as soon as the thallium vapour took up the temperature of the enclosure.

From this he concluded that the emission of the green line had just become as intense as that of the black body at the same part of the spectrum. But the conclusion is erroneous, for substances in temperature equilibrium within a black body enclosure would all emit like a black body, and the experiment proves nothing but this simple property of a black-body enclosure.

According to many physicists, the flame, the arc, and the spark represent gradually increasing stages of temperature, viz. 2000°K, 4000°K and 5000°K. It is well known that the spectra produced under these conditions are widely different

in their general characteristics, but the hypothesis that these variations can mainly be attributed to the varying values of a single physical variable, viz. the temperature, is not generally accepted.

I wish to point out that the value of the ionization potential, as obtained experimentally by Franck and Hertz, McLennan, and others, or theoretically from the quantum relation  $eV=h(1, s)$ , has a great bearing on the problem. As a rule, *the higher the Ionization-potential of an element, the greater is the difficulty with which it can be excited to emit its line spectrum.* This will be apparent from the following table<sup>4</sup>:

The line or lines  $\nu=(1, s)-(2, p)$  form the most important lines of an element, and experiments on the ionization potential have shown that when the vapour of an element is bombarded by electrons, this is the line which is the first to be excited, other lines appearing only when the stimulus is substantially greater. The potential  $V=\frac{h}{e}[(1s)-(2p)]$  is therefore called the resonance potential, and may be taken to be a measure of the stimulus which is required so that an element may just be excited to radiation of its fundamental line. A better name would probably be "Radiation-Potential."

We may give a number of interesting examples. It is well-known that generally it is very difficult to excite helium, the smallest trace of a foreign gas tending to quench the He-lines. According to the present theory, this is due to the fact that helium has the highest ionization and radiation potential of all elements, so that when it is subjected to a stimulus, this, by preference, passes through the more easily excitable impurities, leaving the He atoms unaffected. Franck (*Zeitschrift für Physik*, 1920, vol. i) describes an interesting experiment on the excitation, by his well-known electron bombardment method, of helium-lines contained in a tube into which a trace of mercury (less than 1 in 1000 parts) was purposely introduced. Mercury has an I.P. of 10.45 volts and R.P. of 4.9 volts, while the corresponding numbers for helium are 25.6 and 20.5. "We have then" in Franck's own words, "a strong flashing out of the lines of the element with the lower I.P., at the cost of the lines with the larger I.P."

<sup>1</sup>Pringsheim, *Verh. d. Deutsch. Phys. Gesellschaft*, 1903. Wood, *Phys. Zeits.*, viii. (1907), and other papers.

<sup>2</sup>King, *Astro. Journal*, vols. xxviii, xxxiv, xxxv, xxxvii.

<sup>3</sup>Gibson, *Phys. Zeits.*, xii. pp. 1145-1148 (1911).

<sup>4</sup>McLennan, *Proc. Lond. Phys. Soc.*—Guthrie Lecture, Dec. 1918; Franck and Hertz, *Verh. d. Deutsch. Ges.* vol. xx. (1919).

TABLE I

Element	Mg	Ca	Sr	Ba	Na	K	Rb	Cs
Ionization Potential	7.65	6.12	5.70	5.21	5.11	4.32	4.16	3.88
Element	Zn	Cd	Hg	H	He	Ne	A†	N‡
Ionization Potential	9.4	9	10.45	13.6-17.1	20.5-25.6	17.23†	16	17-18

This also explains quantitatively why, with the range of temperatures available in the laboratory, it is not possible by purely thermal means to excite the permanent gases. In the case of the alkalis and the alkaline earths, the value of the ionization potential is low and gradually decreases as we proceed to elements with higher atomic weight in the same group, and it is found that the difficulty with which the spectrum can be excited lessens in a parallel manner. Thus under all conditions, if we classify the alkaline earths according to the ease with which they can be excited, the order is Ba, Sr, Ca and Mg. The same can be said of the other elements.

In the present paper I have used the word "Stimulus" to denote, in a general manner, all physical agencies tending to make the atoms luminescent. We shall discuss how a high temperature alone can bring about this state. The question can best be approached from the theoretical side.

## §2

Modern spectroscopic works have shown that the lines of an element may be grouped under the following headings<sup>5</sup>:

(1) *Lines due to the normal atom.*—In this case the lines are produced by the quantum-changes of orbit of the outermost electron, the nucleus and the remaining electrons behaving as a single charge. The characteristic

Rydberg number in the series-formula is  $N \left( = \frac{2\pi^2 e^4 m}{h^3} \right)$ .

These lines are produced under the comparatively low stimulus.

(2) *Lines due to the atom which has lost one electron (the outermost one).*—In this case the lines are produced by the quantum changes of orbit of the now outermost electron, the nucleus and the remaining charges behaving as a net double charge. The characteristic Rydberg number is  $4N = \left\{ \frac{2\pi^2 e^2 m}{h^3} (2e)^2 \right\}$ . These lines are produced at a

higher stimulus, and generally, but not always<sup>6</sup>, lie in the ultraviolet.

(3) The atom may lose two electrons, and now a new series of vibrations may begin with the new outermost electron. The Rydberg number is  $9N$ .

The lines of any of these groups are as distinct from each other as if they belong to different elements altogether. According to Sommerfeld<sup>7</sup>, when an atom loses one electron, its spectral properties become similar to those of the element just preceding it in the Periodic Tables. Thus the system of lines of  $\text{Ca}^+$  are constituted in the same manner as those of K; similarly, the relation between Sr and Rb, Ba and Cs.

Lines of these different groups may be simultaneously present, but generally one group gains in intensity at the expense of the other. Thus in the flame Ca lines (the H, K) are very faint, the Ca-lines (*g*-line) is very strong. Now "*g*" begins to lose relatively in intensity as the (H, K) are strengthened with rise of temperature. At the spark-conditions, the most intense lines are the H, K, while the "*g*" is almost evanescent.

Let us now examine how the transition from the neutral state to the ionized states (from Ca to  $\text{Ca}^+$ ) takes place, under the influence of heat alone. In *Phil. Mag.* Oct. 1920 ("Ionization in the Solar Chromosphere", called henceforth paper A), it has been shown that the problem can be attacked with the aid of the "New Thermodynamics" of Planck and Nernst<sup>8</sup>, and the statistical equilibrium between atoms (neutral) and ionized atoms can be calculated in terms of temperature and pressure, when the energy of ionization is known. The calculations for alkaline earths will be found in paper A, and those for the alkalis are given in paper B<sup>9</sup>.

According to the mechanical theory, the outermost electron of the neutral atom revolves in a stable orbit when the atom is not subject to any stimulus. Ionization means the transference of this electron to infinity. But the process is not an abrupt one, for, according to the quantum theory of spectral emission, the electron may

†Rentschler, *Phys. Rev.* vol. xiv p. 503 (1919); Horton and Davies, *Proc. Roy. Soc. Lond.* vol. xcvi. p. 124.

‡Davis and Goucher, *loc cit.*, Jan 1919; also Smyth, *loc cit.*, 1919.

<sup>5</sup>For example, compare Fowler's work on the "Emission Spectrum of Magnetism", *Phil. Trans.* vol. 214.

<sup>6</sup>For example, in case of alkaline earths. All alkaline earths are distinguished by having large (*2, p.*) terms, which causes the principal lines to occur in the visible region.

<sup>7</sup>Sommerfeld, *Atombau und Spektralanalyse*, Chap. 4, § 6 and Appendix.

<sup>8</sup>Planck, *Wärmestrahlung*; Nernst, *Das Neue Wärmesetz* etc.

<sup>9</sup>"Elements in the sun", *Phil. Mag.* Dec. 1920.

have an infinite number of orbits distinguished by different quanta-numbers.

The theory of stable orbits has been formulated by Sommerfeld<sup>10</sup> in the following manner. Let  $n_1, n_2$  denote the rotational quantum numbers for an orbit, and  $n'$  the radial quantum number, i.e.  $r, \theta, \phi$  being the coordinates of the electron: then,

$$\int \left( \frac{\partial T}{\partial r} \right) dr = n'h, \int \left( \frac{\partial T}{\partial \theta} \right) d\theta = n_1 h, \int \left( \frac{\partial T}{\partial \phi} \right) d\phi = n_2 h,$$

the integration extending over the whole orbit. The energy of the system is now given by the expression

$$A - h \left[ \frac{N}{\{n+n'+f(n_1, n_2, n')\}^2} \right], \quad n_1 + n_2 = n,$$

where  $A =$  a constant,  $f(n, n')$  is a function, the value of which decreases with increasing values of  $n$  and  $n'$ .

The possible orbits can now be thus classified by assigning different sets of values to  $n$  and  $n'$ .

TABLE II

Rotational quantum No.	Radial quantum No.	Energy of the system $\frac{N}{h}$	Remarks
$n$	$n'$	i.e. $\frac{N}{\{n+n'+f(n_1, n_2, n')\}^2}$	
1	0	$-(1, s)$	This is the orbit the electron possesses when it is subject to no stimulus. $m > 1$ , the $s$ -orbits.
1	$m-1$	$-(m, s)$	
2	0	$-(2, p)$	The $p$ orbits $m > 2$
2	$m-2$	$-(m, p)$	
3	0	$-(3, d)$	The $d$ orbits $m > 3$
3	$m-3$	$-(m, d)$	
4	0	$-(4, f)$	The $f$ orbits $m > 4$
4	$m-4$	$-(m, f)$	
5	0	$-(5, k)$	The $k$ orbits $m > 5$
5	$m-5$	$-(m, k)$	

$(1, s), (2, p), (3, d), \dots (m, s), \dots$  are the familiar expressions which in Paschen's notation, denote the terms of which a series-formula is composed. Thus, for the principal series, the series-formula is

$$\nu = (1, s) - (m, p), \quad m \geq 2.$$

When the atom is in a free gaseous condition, and is not subject to any stimulus, it has the energy  $A - h(1, s)$ . The higher orbits are produced only when a stimulus is applied. The lines are emitted as the electron changes its habitat from one stable orbit to another with less energy. Thus the line  $(1, s) - (2, p)$  is emitted when the electron changes its habitat from the  $p$ -orbit  $(2, p)$  to the  $s$ -orbit  $(1, s)$ , etc. The law according to which these changes take place has been thus formulated by Rubinowicz<sup>11</sup> and Bohr.

Let  $n_0$  and  $n$  denote the rotational quantum numbers of the initial and final orbits. Then

$$n - n_0 = 1, 0, \text{ or } -1.$$

We can thus distinguish among the following different types of combination:

Group I... Positive combination,  $n - n_0 = 1$ .

$$\begin{array}{l} \text{Combination.} \\ \text{Accepted Appellation} \end{array} \left. \begin{array}{l} (1, s) - (m, p) \\ m \leq 2 \\ \text{Principal Series} \end{array} \right\} \left. \begin{array}{l} (2, p) - (m, d) \\ m \leq 3 \\ \text{Diffuse Series} \end{array} \right\} \left. \begin{array}{l} (3, d) - (m, f) \\ m \leq 4 \\ \text{Bergmann Series} \end{array} \right\} \begin{array}{l} (2, s) - (m, p) \\ m \leq 3 \\ (3, p) - (m, d) \\ m \leq 4 \end{array}, \text{ etc}$$

Group II.—Negative combination,  $n - n_0 = -1$

$$\begin{array}{l} \text{Combination} \\ \text{Accepted Appellation} \end{array} \left. \begin{array}{l} (2, p) - (m, s) \\ m \leq 1 \\ \text{Sharp Series} \end{array} \right\} \left. \begin{array}{l} (3, d) - (m, p) \\ m \leq 2 \end{array} \right\}, \text{ etc.}$$

Group III.—Neutral combination.

$$\text{Combination} \dots (1, p) - (m, p) \quad (2, p) - (m, p) \quad (3, d) - (m, d)$$

Each of the terms  $(m, s), (m, p), (m, d)$  may have double or multiple values owing to the different possible orientations of the vibrating electron with regard to the remaining atom<sup>12</sup>.

Thus far we have dealt with the electrodynamics of the atomic system, i.e. the possible stable orbits of the vibrating electron calculated according to quantum-mechanics. We have now to deal with the statistics of the case, for the higher stable orbits are produced in sufficient proportion only with increasing stimulus, which we obtain only at higher temperatures. The intensity of a line will depend upon the product of the numbers which show the relative proportions of orbits in the initial and final stages at any instant, and also upon the chance of changing from one orbit to another.

Thus the intensity of  $(1, s) - (2, p)$  will be proportional to  $\lambda \lambda' \epsilon$ , where  $\lambda$  is the number of orbits in state  $(1, s)$ ,  $\lambda'$  is the number in state  $(2, p)$  and  $\epsilon$  is the chance that the orbit will change from the state  $(2, p)$  to  $(1, s)$ .

When the stimulus is sufficiently great, some of the electrons will pass off to infinity, and we shall have partial ionization. This problem can be treated thermodynamically, for here we have to consider a sort of chemical equilibrium between three distinct phases—the neutral atom, the ionized atom, and the electron. But radiation cannot be so treated, for this is a case of internal change of orbits only, not involving any phase-changes.

The problem before us can therefore be thus stated: "How to find out the statistical distribution of atoms into different possible stable orbits when the mass of the gas is subjected to a given thermal stimulus?" According to the theory of ionization sketched in paper A, if Ca-vapour is enclosed in a vessel, such that the pressure is always

<sup>10</sup>Sommerfeld, *Verh. d. Deutsch. Phys. Ges.*, Vol. xxi (1919).

<sup>11</sup>Rubinowicz, *Phys. Zeits.*, vol. xix. pp. 441-465 (1918). Sommerfeld, *Atombau und Spektralanalyse*, pp. 390-403.

<sup>12</sup>For a theoretical treatment of the case, see S. N. Basu, "On the Deduction of Rydberg's Law from the Quantum Theory of Spectral Emission," *Phil. Mag.* Nov. 1919.

maintained at  $10^{-3}$  atm., we have seen that with increasing temperature the proportion ionized varies as follows:

Temperature	2000°	3000°	4000°	5000°	6000°	7000°
Percentage of ionisation	$3 \times 10^{-4}$	$2 \times 10^{-1}$	6	47	91	100

The non-ionized atoms cannot all be with the primitive orbit (1,  $s$ ), but a good proportion will be found with the other possible stable orbits, for the electron while detaching itself from the neutral atom, has a chance of taking its habitat in some of these stable orbits, and hence some must be found in these states. The phenomena of line-radiation therefore comes before the ionization becomes complete.

### §3.

At the present time, the electro-dynamical part,—i.e., the manner in which the lines of an element originate from the quantum-vibrations of the constituent electrons of the atomic system—has been worked up in the case of the H-atom alone. For the other atoms, it is only in the process of making<sup>13</sup>.

But the thermodynamical part of the problem—that is, how the proportion of different possible stable orbits varies according to temperature, and how the orbits change from one into the other giving rise to line-radiations—has not even been clearly formulated. In his interesting development of the quantum theory applied to systems with more than one degree of freedom, Planck<sup>14</sup> has laid the foundations of a new method for dealing with the statistical aspect of the question. The second aspect—namely, radiation following as a result of mutual interchange of stable orbits—has been dealt with by Einstein<sup>15</sup>. But there are still many difficulties to overcome. When this is done, a new and fruitful chapter—that of line radiation of gases—will be added to thermodynamics.

We may provisionally proceed along the following lines: Let us suppose that the orbits having the rotational quanta 1, 2, ...  $m$  ... vary as a geometric progression

$$(1-f) [1, f, f^2, f^3, \dots],$$

where  $f$  is a fraction and a function of temperature and concentration. Similarly, let us suppose that the orbits having the radial quanta 0, 1, 2, 3 etc., vary according to the terms of the geometric progression

$$(1-g) [1, g, g^2, g^3, \dots],$$

where  $g$  is a similar fraction.

Then at any instant the proportion of orbits with the

rotational quantum number  $n+1$  and the radial quantum number  $n'$  is

$$f^n g^{n'} (1-f) (1-g),$$

since at low temperatures and high concentrations almost the whole number of atoms is in the state (1,  $s$ ) corresponding to  $n=1, n'=0$ .

We see that  $f$  and  $g$  are very small quantities under these conditions and gradually increase as the temperature is raised or the concentration is lowered. As an example, we may take that the distribution of the Ca atoms in the orbits at 2000°K follow according to the scheme (we are considering only  $f$  here)

$$\left(1 - \frac{1}{10}\right) [1, 10^{-1}, 10^{-2}, 10^{-3}, \dots],$$

while at 4000°K, the distribution is

$$(1 - \frac{1}{2}) [1, \frac{1}{2}, (\frac{1}{2})^2, (\frac{1}{2})^3, \dots],$$

so that the relative intensity of the lines

$$(1, s) - (2, p), (2, p) - (3, d), (3, d) - (4, b)$$

will be  $1 : 10^{-1} : 10^{-2}$ , etc.;

but fully 80 percent. of the atoms will remain inactive, while at 4000°K, the ratio will be

$$1 : \frac{1}{2} : (\frac{1}{2})^2,$$

but now only 25 percent. of the non-ionized atoms remain inactive.

The above considerations are not based upon any theoretical argument, but are given here as a sort of *construibar vorstellung* of the statistics of line-radiation of gases. We can say that, under all physical conditions, a very small concentration of radiant atoms suffices for the production of the series  $\nu = (1, s) - (m, p)$ , especially the fundamental line  $\nu = (1, s) - (2, p)$ . The  $(2, p) - (m, d_i)$ ,  $(2, s) - (m, p)$ ,  $(3, d) - (m, f)$  lines require gradually increasing concentrations of radiant matter in addition to the condition that the stimulus should be sufficiently great. For example, if we take sodium gas at a temperature of 1500°K (an ordinary Bunsen flame tinged with sodium vapour), and gradually decrease the amount of vapour in the flame, the order in which the lines disappear are  $(3, d) - (m, b)$ ,  $(2, s) - (m, p)$ ,  $(2, p) - (m, d)$ ; the  $(1, s) - (m, p)$  lines, of which the leading members are the  $D_1$  and  $D_2$ , are the last to disappear, a fact which was recognised by Du Gramont, when he conferred the appellation "*raies ultimes*" upon this class of lines<sup>16</sup>. This state of affairs persists when the temperature is raised and gradually increasing percentages of atoms are ionized.

If a line is represented by the series formula  $\nu = (n, f) - (n', f')$ , the difficulty of detection of the line will be greater the larger are the values of  $n$  and  $n'$ .

In the following table we give the temperature of

<sup>13</sup>According to Bunsen and Kirchhoff,  $7 \times 10^{-12}$  of sodium in the Bunsen flame is quite sufficient to show the  $D_1$  and  $D_2$  line (Pringsheim, *Physik der Sonne*, p. 121).

<sup>13</sup>Sommerfeld, *Atombau und Spektralanalyse*.

<sup>14</sup>Planck, *Verh. d. D. Phys. Ges.* vol. xxii. p. 407 (1915); *Ann. d. phys.* Vol. 50. p. 385 (1916).

<sup>15</sup>Einstein, *Verh. d. D. Phys. Ges.* vol. xviii. p. 318 (1916); *Phys. Zeit.* 1918, p. 124.

complete ionization of a few elements, with the temperatures at which luminescence just begins and attains its maximum intensity. But it will be clear from what has been said that the ordinary way of speaking "the gas is heated to incandescence or luminescence just begins"—has no meaning in itself unless we say which particular line is emitted, or which orbit is produced. The orbits which are produced are specified in column 3. Under the heading "Remarks", the manner in which these temperatures have been estimated are briefly described. In this connexion, the following section on absorption should be consulted. The pressure has been taken equal to one atmosphere unless otherwise stated.

method to the other alkali metals, i.e. Potassium, Rubidium, and Caesium, and arrived at identical results. Recently Dobbie and Fox (Proc. Roy. Soc. Vol. xcvi, p. 147) studied the absorption-spectra of Hg, Zn, and Cd vapour, and found no absorption up to  $\lambda=3200$ . But this is due to the fact that the  $(1, s)-(m, p)$  lines of these elements lie below 3000 A.U. In fact, Wood found in 1913 (Phys. Zeit. pp. 191-195) that ordinary Hg vapour absorbs the fundamental line  $\lambda=2536$   $(1, s)-(2, p_2)$ .

The explanation easily follows from our theory. The condition for absorption is that in the atoms present, there should be a fairly large number with orbits corresponding to the first term of the pulse of radiation to be absorbed.

TABLE III

Element	Temperature of Ionisation	Orbit generated	Luminescence begins at	Remarks	Luminescence is maximum at	Remarks
H	24,000	$(2, p)$	5,000°K	Temp. of Ma Stars	12,000°K	Temp. of Ao Stars
He	32,000	$(2, p)$	11,000°K	Temp. of A2 class	17,000°K	Temp. of B2A class
Mg <sup>+</sup>	24,000	$(3, d)$	7,500°K	Temp. of Go class	11,000°K	Temp. of A2F class
Ca } Sr } Ba }	10,000-8,000°K (Pressure $10^{-1}$ atm.)	$(2, p)$	1,500°K	Bunsen flame	4,000°K	The open arc.

The elements N<sub>2</sub>, O<sub>2</sub>, A, Ne etc., resemble H<sub>2</sub> and He in having large values for the ionization-potential, and therefore they fail to respond to the temperatures which can be commanded in the laboratory. The alkali metals (particularly K, Rb, Cs) are more prominent in the flame-spectra and less in the arc than the alkaline earths. Mg-lines are rather faint in the flame, but come out very prominently in the open arc. Zn, Cd, Hg, Fe, Ti lie between the alkaline earths and the permanent gases in their spectral properties. All this is in very good qualitative agreement with the hypothesis sketched in the present paper.

#### §4. Absorption.

In this connection, we may consider the puzzling question of reversal of lines. According to Kirchhoff's law, we expect that the emission-lines of an element should be reversed when a strong beam of white light is sent through cooler layers of the vapour. But this expectation is not always fulfilled. Wood<sup>18</sup> has found that if a white light be sent through a column of sodium vapour, only the lines of the principal pair series  $(1, s)-(m, p_1)$ ,  $(1, s)-(m, p_2)$ , can be obtained as absorption-lines. None of the lines of the diffuse or the sharp series are reversed. Bevan<sup>19</sup> has extended the

Thus, in order that a line  $(2, p)-(m, d)$  may be absorbed, we must have a sufficient number of atoms with  $(2, p)$  orbits. At low temperatures only atoms with  $(1, s)$  orbits are present. Hence only the lines corresponding to the combination  $(1, s)-(m, p)$  are absorbed. The lines represented by the positive combinations  $(2, p)-(m, d)$ ,  $(3, d)-(m, f)$ , or the negative combinations  $(2, p)-(m, s)$  can only occur when atoms with  $(2, p)$  or  $(3, d)$  orbits are present. This can happen only at high temperature or under electrical stimulus.

The temperature required for this purpose is very high—much higher than the temperatures used by Wood and Bevan for all elements. In fact, the atoms begin to absorb the lines  $(2, p)-(m, d)$  only when they are not enough to emit the leading terms of the principal series. A line of the Bergmann series will begin to be absorbed at even a higher temperature, viz., at the temperature of emission of the diffuse series  $(3, d)-(4, b)$ .

If the views presented here be correct, we may probably obtain the reversal of the lines of the diffuse or the Bergmann series of the alkali metals by heating the absorbing column of vapour to about 2000° to 3000°K. The most favourable element to start with is caesium, which has the lowest ionization-potential of all elements.

In many cases confusion may arise about the proper identification of the  $(1, s)-(m, p)$  terms. Thus, what are

<sup>18</sup>Wood, The Astrophys. Journal, vol. xxix. pp. 97-100.  
<sup>19</sup>Bevan, Proc. Roy. Soc. vol. lxxxiii. pp. 423-428; vol. lxxxv. pp. 58-76.

usually called the Principal series of helium and parhelium (viz., the series beginning with the line 20,587 for parhelium and 10,834 for helium) do not really correspond to the combination  $(1, s) - (m, p)$  but to the combination  $(2, s) - (m, p)$ . The  $(1, s)$  term for helium is still unknown, and the series  $(1, s) - (m, p)$  lie far down in the ultraviolet.<sup>20</sup> Hence, according to our theory, none of the lines belonging to the combinations  $(2, s) - (m, p)$ ,  $(2, p) - (m, d)$  can be absorbed by a layer of helium gas.

But if by heating or some other means we can convert a good proportion to the states  $(2, s)$  or  $(2, p)$ , then and then only can these lines appear as absorption-lines. But at a pressure of  $10^{-1}$  atm. helium becomes incandescent, i.e., emits the lines  $(1, s) - (m, p)$ , and absorbs the lines  $(2, p) - (m, d)$  at probably not less than  $10,000^\circ$  or  $12,000^\circ\text{K}$ , i.e. only in stars of the B-Class.

But instead of a high temperature we may think of other

<sup>20</sup>It is quite possible that some of the  $(1, s) - (m, p)$  lines for helium and parhelium may be identical with the lines discovered by Lyman in the ultra-violet, and some with the lines discovered by Richardson and Bazzoni in the region of 300 to 400 A.U. by the photo-electric method (vide Richardson and Bazzoni, *Phil. Mag.*, 1918).

means. The spark produces mechanically the very same conditions which can be realized at very high temperatures. This is exactly what Paschen<sup>21</sup> has done. He found that the lines of the combination  $(2, s) - (m, p)$  for helium and parhelium cannot be absorbed by an ordinary layer of the helium gas. But when a spark is sent through the absorbing layer the lines are strongly absorbed, the absorbed energy being again re-emitted in all directions.

The paper thus suggests more problems than it attempts to solve. A critical examination and further development of the hypothesis advanced here requires an overhauling of the whole data on the line-radiation of gases—such as are contained in Kayser's *Handbuch der Spektroskopie* and further works. But this programme requires much more time and more extensive study, both practical and theoretical.

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May 25, 1920.

<sup>21</sup>Paschen, *Ann. d. Physik*, Vol. xlv. p. 625 (1914).

## 16. THE ATOMIC RADIUS AND THE IONISATION POTENTIAL

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Prof. Eves' interesting contribution to *Nature* of June 30, p. 552, on the relation between the ionisation potential and the atomic radius induces me to publish certain similar ideas of mine on the same subject to which I referred some time ago before the Royal Society in some remarks on Prof. Rankine's paper "On the Proximity of Atoms in Gaseous Molecules" (Proc. Roy. Soc., February, 1921). I did not publish the results, because I desired to wait for further data. These ideas may be stated as follows:—

According to the Rutherford-Bohr model of the atom, by the radius of the atom is meant the distance from the nucleus of the outermost electron, i.e. the electron the quantum vibrations of which cause the radiation of the arc lines of the atom. Sommerfeld has shown that in the normal (unexcited) state the orbit is characterised by the azimuthal quantum-number unity and the radial quantum-number zero. This orbit is circular, but to calculate its radius we must know what is the field of force exerted by the central nucleus and the remaining  $(n-1)$  electrons upon the

vibrating electron. This is at present an insoluble problem, but Mr. S. N. Basu (*Phil. Mag.*, November, 1920) has shown that we can at least arrive at a qualitative explanation of Rydberg's laws of spectral regularity by assuming the attracting system to be equivalent to a net central charge unity, with a doublet of strength  $L$ . On the bases of this theory, if  $a_w$  is the radius of the monoquantic orbit, it is easy to show that

$$\frac{e^2}{2a_w} = -\text{energy of the vibrating electron.}$$

$$= h(1s) \text{ where } (1s) = \text{convergence frequency of the principal series of the element in absolute measure.}$$

$$= eV_w, V_w = \text{ionisation potential in } e.s. \text{ units.}$$

For the H-atom we have, according to Bohr's theory,

$$a_H = \frac{h^3}{4\pi^2 e^2 m} \quad (a_H = \text{radius of the electron in the normal state})$$

$$= 0.532 \times 10^{-8} \text{ cm,}$$

and