

22. ON THE PHYSICAL PROPERTIES OF ELEMENTS AT HIGH TEMPERATURES*

(Phil. Mag., Sr. VI, 46, 534, 1923)

The investigation of the physical properties of elements at high temperature is at present exciting a considerable amount of interest, on the theoretical as well as on the practical side. The present paper is the outcome of certain investigations undertaken by the author, which were withheld from publication because no positive result was obtained. But in view of the recent works, it appeared advisable to give publicity at least to certain points which appear to have been rather lightly passed over by recent workers.

Let us picture to ourselves a quantity of gas, elementary or compound, which is being raised to higher and higher temperatures. The physical changes occurring in the mass under such an increasing stimulus have been discussed in previous papers¹. It has been shown that the gas will become luminous, will emit its characteristic lines—principal lines, sharp and diffuse lines, Bergmann lines—and ultimately will be ionized. The problem before us is: (1) to determine the statistical distribution of the atoms in the various quantum orbits, and from this to deduce the intensity of the different lines of the characteristic spectrum; (2) to determine the electrical and optical properties of such a mass of ionized gas.

The method which the present writer followed was purely thermodynamical. It consisted in the application of a form of the law of reaction-isochores, which was originally developed by Nernst for the study of the dissociation-equilibria of gaseous compounds from their physical properties, to the problem of ionization. The same method was followed in the extension of the method to mixtures of different elements by H. N. Russell². But in this, as in other cases, thermodynamics lead us rather blindfolded to the goal, and do not enable us to see the details of the intervening stages.

A very powerful method has recently been developed by Messrs. Darwin and Fowler³ in a number of important papers published in the *Phil. Mag.* and *Proc. of the Camb. Phil. Soc.* Probably with the aid of this method the problem is brought much nearer to solution, but it seems that there

are a number of important points on which the authors have not laid sufficient stress. The first point to which I wish to call attention is that “no theory of dissociation-equilibrium can be said to be complete unless it takes account of the mutual interaction between matter (atoms) and radiant energy, because at high temperatures, exchange of energy takes place mainly by radiation, and only to a slight extent by collision.”

Binding of an Electron with a Proton (H⁺).

To make the above point clear, we shall consider the simplest case conceivable—namely, the binding of an electron with a proton to form an H-atom. This case can rightly be called the simplest, because, thanks to the Bohr theory, all the possible states of combination are known, and the dynamics can be handled with easy mathematics—advantages which are not present in such cases as the reactions



Let us first treat the dynamical part. An electron starts from infinity with velocity v and passes past a stationary proton. What are the conditions that this will be captured by the proton? A little consideration will show that as long as the energy of the system remains conserved, the electron will describe an hyperbola with the proton as the inner focus, and thus, after wheeling round the proton, will pass off to infinity. In other words, it can never be captured by the proton and lodged in one of the stationary Bohr orbits (having the energy $-\frac{N^2 h^2}{2m^2}$) unless the system loses the energy $\frac{1}{2}mv^2 + \frac{N^2 h^2}{2m^2}$ presumably by radiation.

From physical ground, it seems to be fairly well established that such a process actually takes place in nature in all cases of ionization, giving rise to a continuous spectrum beginning from the limit of the series lines. In the case of hydrogen, the continuous spectrum was first detected by Huggins during the observation of the eclipse spectra, and was confirmed by Evershed. The explanation cited above is due to Bohr. (See ‘*Atombau und Spektralanalyse*,’ p. 547, 3rd edition).

But the dynamical interpretation of this process from the standpoint of quantum mechanics is far from satisfactory, as

* Communicated by the Author.

¹ M. N. Saha, *Proc. Roy. Soc. Lond.* May 1921; *Phil. Mag.* vol. xli. p. 267 *et seq.*, see particularly p. 274.

² Russell, *The Astrophysical Journal*, vol. lv. p. 143; Milne, *The Observatory*, vol. xlv, Sept. 1921.

³ Darwin & Fowler, *Phil. Mag.* vols. xlv. & xlvi. *Proc. Camb. Phil. Soc.* vol. xxi. parts 3 & 4.

has been pointed out by Nicholson⁴ in a recent paper. Eddington⁵ has thrown out the suggestion that during its orbital motion the electron loses energy by radiation just as an accelerated electron would do according to the classical theory. But here we are treading on rather dangerous ground, as the satisfactory working out of the suggestion means nothing less than the discovery of the linkage between the classical theory and the quantum theory.

In the case of hydrogen, the continuous spectrum has been observed at the limiting frequency of the Balmer series (quantum orbit 2, or 2_2), but this is owing to the fact that observations do not probably extend up to the limit of the Lyman series. In the case of the alkali elements, the continuous spectrum has been observed extending towards the short wave-length side from the limiting frequency of the principal series. These facts are very decisive in favour of the view that combination of an ionized atom with an electron is always accompanied by liberation of energy in the form of continuous waves of light.

The Statistical part; deduction of the Law of Reaction-isochore for the Ionization of the H-atom.

This part has been worked out by Fowler, but before taking up his method of deduction, I shall give another deduction based on the older methods, because this may serve to bring out the details of the case in a more intelligible manner.

The problem which we are discussing is only a special case of the general problem of association of particles and dissociation of compound particles which was first treated from the standpoint of the kinetic theory by Boltzmann, Natanson, and J. J. Thomson about thirty years ago. A masterly discussion is given in Jeans' 'Dynamical Theory of Gases', p. 213 *et seq.*, 3rd edition. This treatment is applicable, of course with some alteration, to the combination of protons and electrons.

Suppose we have a system consisting of $2v_1$ particles of type A, and v_2 particles of type A_2 formed by the combination of two particles A. Let $v=2(v_1+v_2)$: *i.e.*, v is the total number of particles if there be no aggregation at all.

Then Jeans shows that an encounter between two particles of type A can never result in an association unless the quantity $\frac{1}{2}mv^2+2\psi$ (where 2ψ =mutual potential energy of the particles, v relative velocity of the two particles) assumes a negative value. According to Jeans, "this might be effected by collision with a third molecule [*it is not at all clear how*], or possibly, if $\frac{1}{2}mv^2+2\psi$ were small at the beginning of the encounter, sufficient energy might be dissipated by radiation for $\frac{1}{2}mv^2+2\psi$ to become negative before the termination of the encounter."

Jeans continues: "we may leave the consideration of this second possibility on one side for the present, with the remark that if this were the primary cause of aggregation, we should no longer be able to use the equations with which we have been working, since they rest upon the assumption of conservation of energy."

The simplest illustration of association is the binding of a proton (H^+) with an electron. As has been already shown, here it is not possible to leave on one side the action of radiation, for that will be tantamount to staging the play of Hamlet without Hamlet's part: for physical evidences decisively prove that radiation is emitted in all cases of the binding of an ionized atom with the electron. Similarly, absorption of radiation is essential for the splitting up of an atom M into M^+ and e .

In spite of rather uncertain knowledge regarding the role of radiant energy in these processes, Boltzmann deduced a formula on the assumption that potential energy exists between two molecules (here we should say between H^+ and e), when the centre of the second (e) lies within a sensitive region surrounding the first (H^+). With this assumption, Boltzmann obtains a formula (formula 503 of page 199, 3rd edition, Jeans' 'Dynamical Theory of Gases') which, with a slight change in notation, can be put in the form

$$\frac{x^2}{1-x^2} P = \frac{kT}{4w} e^{-\frac{U}{RT}} \quad \dots \quad (A)$$

where w =volume of the sensitive region.

Comparing this with the formula for reaction-isobar derived by me, *viz.*

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} \quad (B)$$

we find that

$$w = \frac{1}{4} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} \quad \dots \quad (C)$$

or r , the radius of the sensitive layer,

$$r = \left(\frac{3}{16\pi} \right)^{1/3} \left(\frac{h^2}{2\pi m k T} \right)^{1/2};$$

i.e., the radius of the sensitive layer varies as

$$\frac{2.95 \times 10^{-8}}{T^{1/2}} \text{ cm.}$$

Fowler's work on the Reaction-isobar of the Ionization of the H-atom.

We now turn to the very interesting and novel method of deriving the law of reaction-isochore by Messrs. Darwin and Fowler. Fowler deduced the law

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} + B(T), \quad (D)$$

which differs from my formula in the term $B(T)$.

⁴ Nicholson, Phil. Mag. vol. xlv. p. 193 (1922).

⁵ Eddington, Monthly Notices R. A. S. vol. lxxxiii. p. 43.

In the thermodynamical way of derivation of the reaction-isochore the roll of radiation is left obscure. The same remark may be applied to Fowler's method of deduction, as has been admitted by Fowler in the following passage (page 13, Phil. Mag., Jan. 1923):—

“In conclusion, a possible objection may be raised to all the reasoning on which these results are based—namely, that it ignores radiation, whereas in fact a change of quantum state in the molecule probably seldom or never occurs without the emission or absorption of the appropriate radiation.”

I would like to add to this passage: Likewise ionization of the H-atom, or association of the proton (H⁺) and the electron, seldom or never occurs without the absorption or emission of the appropriate radiation.

Fowler continues: “It is, however, perfectly possible to include the temperature radiation in the statistical discussion, as has been shown elsewhere.”

In the passage referred to above (Proc. Camb. Phil. Soc. vol. xxi. p. 263), Messrs. Darwin and Fowler, starting from the partition-function of a Planck line-vibrator, have given an interesting method of deduction of the laws of black-body radiation; but I find it difficult to agree with the view that this includes the temperature radiation in the statistical discussion. They have treated radiant energy as the energy of a single system, the æther, and neglected matter altogether, except through that somewhat shadowy medium, the Planck line-vibrator. But the problem before us is to find out the exact nature of exchanges between Bohr vibrators and radiant energy which has not been covered in the above treatment.

We now come to the consideration of the term B(T) in Fowler's formula.

The term B(T) represents the energy distribution amongst the Bohr vibrators, and is simply another form of the partition function for the internal energy of the Bohr atom. According to Fowler this partition function $b(\theta)$ is given by

$$b(\theta) = \sum_{n=1}^{n=\infty} n(n+1)\theta^{\chi} \left(1 - \frac{1}{n^2}\right)$$

[equation 7·22, p. 20, Phil. Mag., Jan. 1923], where

$$\theta = e^{-\frac{1}{kT}}, \quad \chi = Nh, \quad N = \text{Rydberg number.}$$

As Fowler himself points out, this is a divergent series, and cannot therefore be regarded as solution of the problem. But his suggestion, that the series ought to be cut down to a finite number of terms because the higher terms correspond to orbits with large radii, does not seem to lead out of the difficulty, as imagined by him. For whatever may be the origin of the higher Balmer lines, they are not unknown, nor do they require very special physical conditions for their development. For example, Mitchell could

detect 35 lines of the Balmer series within the lower 2000 kms. of the solar chromosphere, and Wood has recorded 21 of them in his vacuum tubes. The difficulties of dealing with the higher orbits on the quantum conditions

$$\oint p \delta q = nh$$

also been emphasized by Nicholson.

To me, the divergence of Fowler's formula (7·22) appears to be a clear indication that Bohr's hypothesis regarding the weight factor of the higher quantum orbits, viz. $p_n = n(n+1)$, is wrong. In fact, any consideration⁶ which tends to assign to the larger quantum orbits larger probability seems to be opposed to physical facts.⁷

Electrical and Optical Properties of Ionized Gases.

A mass of gas at ordinary temperatures, and not subjected to ultra-violet light, Röntgen light, or any other familiar ionizing agent, possesses no electrical conductivity, because there are no free carriers of electricity present. But if the gas be raised to a high temperature and partially ionized, it will acquire considerable conductivity.

This was pointed out by me in previous papers⁸, and the non-success of previous experiments, as those of J. J. Thomson and McLennan, on the electrical conductivity of mercury vapour were discussed in detail. It was shown that these investigators chose a substance which has too high an ionization-potential (10·45 volts), and hence at the temperature employed by them the mass of gas (mercury-vapour) remained practically unionized.

Caesium is the element having the lowest ionization-potential, and hence I pointed out that this is the element with which success can be expected at temperatures available in the laboratory. Some preliminary experiments undertaken by me at Prof. Nernst's laboratory at Berlin confirmed these expectations. At 1250°C., Cs-vapour was found to have a specific resistance of only 50 ohms, which increased to about 100 ohms when the temperature was lowered to 1050°C. The current could be measured with a milliammeter with a voltage difference of 1 to 2 volts across the ionization-cell containing Cs-vapour, and obeyed Ohm's law throughout the range 1 to 6 volts. These figures are very rough, but they, taken along with the figures for Rb and K (which were found to have increasingly higher resistance), completely confirm the view that the ionization potential is the deciding factor in determining the electrical conductivity of heated vapours.

But great difficulty was encountered when I tried to calculate the conductivity from the Drude-Thomson theory. It was felt that if this theory were applicable to

⁶ For example, Planck, *Berl. Sitzungsberichte*, p. 407, 1915.

⁷ M. N. Saha, *Phil. Mag.* vol. xli. p. 274.

⁸ “On the Ionization of Gases by Heat,” by M. N. Saha and P. Gunther, *Journ. Dept. Sci., Calcutta University*, vol. iv. See also A. A. Noyes and H. A. Wilson, *Ast. Journ.* vol. lvi. p. 21.

any case, it was the present one. But calculations have not answered to this expectation.

Suppose we have a mass of vapour, say of Cs, which is ionized by heat. Let n_1 denote the number of free electrons or Cs⁺-ions per unit volume, λ_1 and λ_2 the mean free paths, u_1 and u_2 the average velocities of the electrons and the positively-charged particles respectively. Then, according to the Drude-Thomson theory, the conductivity

$$\sigma = \frac{n_1 e^2}{6kT} (\lambda_1 u_1 + \lambda_2 u_2) \dots \dots \dots \quad (E)$$

According to the kinetic theory of gases, if we have a mixture of gases of different kinds (1, 2, . . . r, s, . . .), then the mean free path λ_r of any particular type r is given by the expression

$$\frac{1}{\pi \lambda_r} = \sum_{s=1} n_s A_{rs}^2 \sqrt{1 + \frac{m_r}{m_s}} \dots \dots \dots \quad (F)$$

[see Jeans, 'On the Dynamical Theory of Gases,' p. 268], where $A_{rs} = A_r + A_s$; the sum of the radii of the "r" and "s" particles, n_s is the concentration of the "s" particle.

In the present case we have to deal with Cs, Cs⁺, and e-, Cs-particles of course including different types distinguished by the quantum orbits (n_k). Let us neglect all the higher orbits and retain only the fundamental orbit (1_1), a step which will not be acceptable to many, but which is difficult to avoid or improve under the present state of our knowledge.

Then

$$\frac{1}{\pi \lambda_1} = n \frac{A^2}{4}, \quad \frac{1}{\pi \lambda_2} = n A^2 \sqrt{2}, \quad \frac{1}{\pi \lambda} = n A^2 \sqrt{2}.$$

Assuming that the degree of ionization is small (i.e., n_1 is small compared with n , the concentration of Cs-atoms), A denotes the radius of Cs-atom, then $\lambda_1 = 4\sqrt{2}A$ (a well-known result) and

$$\lambda_2 = \lambda, \quad u_1 = \sqrt{\frac{3kT}{m}}, \quad u_2 = \sqrt{\frac{3kT}{M}}.$$

Since Cs⁺ is $1836 \times A$ (atomic weight) times heavier than m , we see that u_2 is negligible compared with u_1 . This only means that the conductivity is mainly due to electrons.

We have now

$$\sigma = \frac{2\pi e^2}{\sqrt{3mkT}} \frac{1}{A^2} x, \dots \dots \dots \quad (E')$$

where x =fraction ionized.

Now "x" can be calculated from the formula of reaction-isochore.

$$\text{We have } \frac{x^2 P}{1-x^2} = \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} T^{5/2} e^{-\frac{U}{RT}} \dots \dots \dots \quad (B')$$

and $P = n(1+x)kT$,

$$\text{or } \frac{x^2}{1-x} = \left(\frac{2\pi mkT}{h^2}\right)^{2/3} \frac{1}{n} e^{-\frac{U}{RT}} = \frac{B}{n}; \dots \dots \dots \quad (B'')$$

therefore

$$x = \sqrt{\frac{B}{n}}, \quad \text{or } \frac{B+n}{B+2n},$$

according as "n" is large, or "small" compared with "B."

The second case will never arise, unless we have to deal with a case of very high temperature and very low pressure (e.g., in the giant stars).

Hence the conductivity

$$\sigma = \frac{(2\pi)^{7/4}}{\sqrt{3}} \frac{(mkT)^{1/4}}{h^{3/2}} e^2 \exp\left(-\frac{U}{2RT}\right) \frac{1}{\sqrt{n}} \dots \dots \dots \quad (E'')$$

The only thing to notice about this complicated expression is that σ varies inversely as $\sqrt{\text{concentration}}$.

This is an unexpected result, and is not corroborated by my experiments, for I found that the conductivity diminishes gradually as the vapour-content diminishes. *A priori*, it seems rather paradoxical that the conductivity will vary as $1/\sqrt{n}$.

Therefore, either we cannot calculate the percentage of ionization from the law of reaction-isobar at very low concentrations, or the Drude-Thomson theory of conduction which makes the conductivity proportional to the percentage of ionization, and not to the total number of ionized particles present, fails to give us a true picture of the phenomena.

The Mean Free Path of an Electron in a mass of Ionized Gas.

The cause of this failure is not far to seek. We have to calculate the "free life" of an electron in a mass containing normal atoms of Cs, atoms with higher quantum orbits, and Cs⁺-particles. The mean free path, as deduced in formula (F), is based upon the idea of elastic collisions, which is rather the opposite of what actually takes place. As has been explained in the previous sections, in representing the complicated reactions which occur when a free electron encounters a Cs⁺-atom, or a Cs-atom in normal or higher orbits, the idea of elastic collision is of no avail, the exchanges of energy through radiation must be taken into account.

The same considerations apply to the optical properties of ionized gases discussed by Prof. J. Q. Stewart in a letter to 'Nature,' Feb. 10, 1921, but the discussion is deferred to a future date.

[Note: Since the above paper was written, I have been made acquainted, through the courtesy of Messrs. Fowler and Darwin, with a paper by them "On the Intensities of Absorption Lines in Stellar Spectra, etc.," published in the M. N. R. A. S. vol. lxxxiii. p. 403. In this paper Fowler and Milne have given an interesting method of deducing the pressure in the reversing layer by applying a theory of maximum intensities of subordinate lines which they have worked out. It must be admitted that the idea is pregnant with great possibilities, and would lead to important results if the correct partition function $b(\theta)$ can be discovered. But Fowler and Milne have used the function $b(\theta)$ mentioned above, which, being a divergent series, is rather unconvincing.—M. N. S.]