

larger surface temperature, say  $14,000^{\circ}\text{K}$ , B8A class, the value  $E\lambda$  for H- and K-light would be much larger, so that the radiation-pressure is still greater, and in some cases preponderates over the greater value of gravitational force on these stars. Thus  $\text{Ca}^+$ -atoms would be driven very far into the surrounding space. They will be prevented from absolutely leaving the system, because with increase of distance the solid angle subtended by the disc of the star at the atom would diminish, and a condition of equilibrium would at last be reached.

The same phenomenon occurs to a smaller extent, in the case of the sun, with  $\text{Sr}^+$  and  $\text{Ba}^+$ , which have their resonance-lines near the spectral region of maximum intensity, but owing to their greater atomic weight the compensation is not so marked. Still  $\text{Sr}^+$  is very prominent in the chromospheric spectrum, rising to a height of 6000 km.

The question may be asked: Why do we not obtain the same phenomenon in the case of the other light elements? These can be divided into two broad groups: (1) non-metals-like H, He, N, O, Ne, and A, having a high ionisation-potential, of which the resonance-lines lie in the extreme ultra-violet—*e.g.* for H, at  $\lambda=1216 \text{ \AA.U.}$ , for He, at  $\lambda=585 \text{ \AA.U.}$  (Lyman and Fricke, *Phil. Mag.*, May, 1920)—and can be detected only by subordinate lines—for helium, by  $D_3$ ,  $2p-md$ ; for hydrogen, by the Balmer lines. Naturally the effect of selective radiation-pressure is small on these elements. (2) Elements like Na, K, Mg, Al, Sc, Ti, Fe, which have an ionisation-potential varying from 5 to 8 volts. Under the conditions treated here these are mostly ionised, but the resonance-lines of these ionised elements lie mostly outside the region available for observation,

*e.g.* the resonance-lines of  $\text{Mg}^+$  are  $\lambda=2795.5$ ,  $2802.7$ . The resonance-lines of  $\text{Na}^+$  and  $\text{K}^+$  have not yet been discovered, and probably lie in the extreme ultra-violet.  $\text{Sc}^+$  and  $\text{Ti}^+$  are represented by prominent lines in the chromospheric spectrum, but it is not yet known whether these are resonance-lines of these elements.

The hypotheses thus appear to be promising, but nothing final can be said before we can calculate the absolute value of the selective radiation-pressure on an atom. According to Eddington (Monthly Notices, R.A.S., 1920, vol. lxxx., p. 723), the absolute value of the radiation-pressure is too small to account for the total neutralisation of gravitational force on the sun; but in that paper the consequences are worked on the basis of the continuous theory of light. The foregoing line of investigation at least brings out the intimate connection between the stationary character of the H- and K-lines in the space round the stars and the great prominence of these lines in the chromospheric spectrum. It shows that the higher chromospheric levels, as well as the space round B- and A-stars, may probably contain, besides  $\text{Ca}^+$ , also  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Sc}^+$ ,  $\text{Ti}^+$ , and  $\text{Mg}^+$ , but owing to the fact that our observations have to be limited between  $\lambda=3000 \text{ \AA.U.}$  and  $6000 \text{ \AA.U.}$ , and that none but the resonance-lines of  $\text{Ca}^+$  lie within this region, we can detect nothing but  $\text{Ca}^+$ . But if some day we can overcome the limitation imposed by atmospheric absorption, probably we shall be able to detect  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^+$ ,  $\text{K}^+$  in the atmospheres surrounding B-stars which show stationary H- and K-lines.

Berlin, May 8.

## 20. ON THE IONISATION OF GASES BY HEAT

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(*Jour. Dept. Sci., Cal. Univ.*, 4, 97, 1922)

### § 1. INTRODUCTION

It is well known that a column of gas, which is subjected neither to ultraviolet light, Röntgen light, or any other familiar ionising agent, possesses no electrical conductivity. Beginning from Hittorf<sup>1</sup> many investigators have performed experiments to see, if by simple heating, gases can be made to conduct electricity. As the following review will show, most of these experiments were indecisive.

In the light of modern theories of atomic structure,

the problem reduces to the knocking out of the outermost electron, or electrons, from the atomic system by the mutual collisions of atoms. The problem is thus analogous to the emission of electrons from incandescent solids and liquids. In this connection, it is well worth quoting the following passage from Richardson's "The Emission of Electricity from Hot Bodies, p. 298."

"There is no satisfactory *a priori* reason for expecting emission of ions at a high temperature to be confined to the matters in solid or liquid states. It is however to be

anticipated that the thermal ionisation of gases will only be appreciable at the very highest temperatures, on account of the large value of the ionisation energy of gases. This quantity which has been measured by experiments on impact ionisation and photoelectrical action, has in all cases been found to be much greater than the energy changes governing the liberation of an ion in the phenomena which have been considered in this book. Up to the present there is no evidence that purely thermal ionisation has been observed in any of the common gases. It seems likely that the ions present in flames, are to be attributed to the chemical actions occurring rather than to the direct effect on the gases of the high temperature which prevails. In the case of gases which have been heated in the presence of metal electrodes, there is no evidence of the formation of ions except by interaction between the gases, and the electrodes or by the emission from the electrodes themselves.

A possible exception to these statement is furnished by some experiments made by J. J. Thomson<sup>2</sup> on sodium vapour. He found that when a current was made to pass between two electrodes immersed in this vapour at about 300°C, metallic sodium collected on the negative, but not on the positive electrode, indicating that the sodium atoms in the vapour has dissociated into an electron and a positive sodium ion. The phenomenon could also be accounted for if the bombardment of the positive electrode by electrons present made it hotter than the negative electrode. The optical properties of sodium vapour make it probable that it will dissociate, in the manner indicated, below 1000°C. It is necessary to add that Thomson's experiments have been repeated by Fredenhagen (Phys. Zs. Bd. XII, p. 398, 1911), without success; so that it does not seem absolutely certain that the phenomenon has yet been discovered."

Another series of experiments have been made on mercury vapour to discover this effect. We take the following history of these experiments from a paper by McLennan (Proc. Roy. Soc. Lond., Vol. 92, p. 592).

"Though numerous investigators have experimented on the electrical conductivity of salts of different metals in flames, but few appear to have made a study of the conductivity of the vapours of the simple metals themselves. Hittorf, who investigated the conductivity of the mercury vapours by heating the metal in a tube and passing the discharge from an induction coil through it came to the conclusion that it was nonconducting. Herweg however found that mercury vapour, when heated to 1000°C. did exhibit electrical conductivity.

Sir J. J. Thomson also found that mercury vapour, even at a very high temperature was a good insulator, a better one in fact than air, under the same conditions. Strutt, who investigated the electrical conductivity of mercury vapour in an evacuated quartz tube heated to redness, also found it to be an insulator."

In the paper just mentioned, McLennan and Keys

investigated the conductivity of vapours of mercury, cadmium, zinc and thallium, in a Bunsen flame, but the results were very much discordant. Mercury seemed to be ionised, but zinc and cadmium showed absolutely no trace of ionisation. The ionisation potential of these elements are respectively 9.4, 9.00 and 10.45 volts, so that if the observed conductivity of mercury vapour arose from the heat ionisation, there is no reason why zinc and cadmium vapours would not be ionised under the same conditions. McLennan himself concludes that the experimental results were quite indecisive.

## § 2

The effect may therefore be regarded as yet experimentally undiscovered.

It follows *a priori* that the chance of success depends to a large extent on the choice of the right substance for experimental work. The force with which the outermost electrons are bound to the parent atomic system is different in different elements. In the case when the elements are in the solid state of aggregation, the measure of this force is the quantity ' $\phi$ ' in Richardson's equation for thermoelectric emission  $i = AT^{\frac{1}{2}} e^{-\frac{\phi}{kT}}$ . In the case of gases the force can now be measured with great accuracy either from spectroscopic data or from the experimental works<sup>3</sup> on ionisation-potential. It is known from these works that of all elements, Caesium is the one having the least ionisation potential, *viz.*,—3.88 volts and then follows the other alkali metals in the reverse order of their atomic weights, *e.g.*, Rb—4.16, K—4.32, Na—5.1 volts. These figures may be compared with the following values of  $\phi$  for some solids. (W—4.25, Ta—4.04, Mo—4.04, Na—2.65 volts, Richardson, *loc. cit.*, p. 69).

The chance of success is therefore greatest when one starts with Caesium vapour. Mercury, which has usually been used in these experiments (probably owing to the ease with which it can be handled) is a rather unfortunate choice, for its ionisation potential is very high, *viz.*, 10.40 volts. The permanent gases like H<sub>2</sub> (13.6—17.1 volts), He (25.4 volts), Ne (23.8 volts), O<sub>2</sub> and N<sub>2</sub> would even be still worse.

New light has been thrown on the subject by a series of papers<sup>4</sup> published elsewhere by one of the authors. In these papers in addition to a formula which enables us to calculate the ionisation of a gas, under different conditions of temperature and pressure, it has been shown that besides the electrical tests, the ionisation can also be detected from a scrutiny of the spectra of the gas.

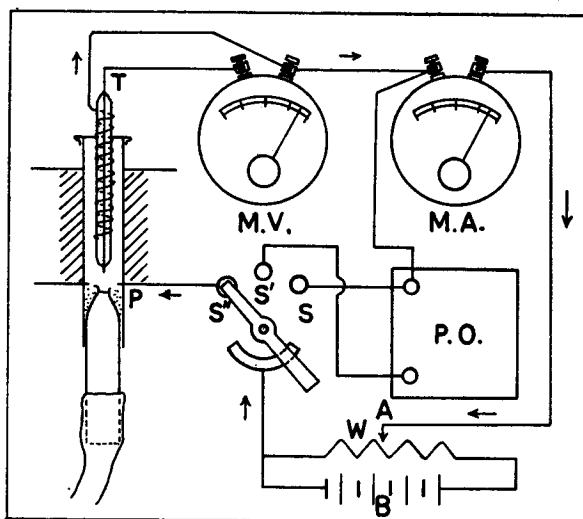
According to these papers, permanent gases first begin to show traces of ionisation only in stars having the highest temperatures (B—stars, having surface temperature of 13000° to 20,000°K) which, it is needless to add, are not reproducible in the Laboratory.

On the other hand, when we apply the same spectroscopic test to the case of the easily ionisable gases Rb, and Cs, we find that they are completely ionised even in the G<sub>0</sub> class of stars ( $T=7000^{\circ}\text{K}$ )<sup>5</sup>. In these stars even Potassium is for the most part ionised. According to calculations given in these papers, the heat ionisation of Rb, Cs and K would be appreciable even at temperatures available in the laboratory, and some amount of success may be expected when one tries the experiment with these gases.

These considerations led the authors to choose Cs, Rb and K for the experimental investigation of the effect. But the great chemical activity of these substances was a great hindrance, and after much effort and failure, the experiment reported in the following section was successfully carried out, establishing, probably for the first time, the ionisation of gases by heat.

### § 3. Description of the Apparatus \*

After some unsuccessful attempts to measure the conductivity of Cs-vapour contained within an evacuated quartz tube heated by the electric furnace, we adopted the following arrangement. The arrangement may be grasped from the accompanying diagram.



The essential parts consist of the platinum tube furnace P and the thermo-couple T. The platinum tube furnace was vertical and had its lower end closed with a conical-shaped quartz tube having a narrow opening, which was overlaid with a layer of fused pieces of pure magnesia. The quartz tube was connected by a rubber tubing to a hydrogen-generating apparatus. The thermocouple consisted of a capillary porcelain tube of Marquardt mass, carrying a platinum, platinum-rhodium junction.

Hydrogen was allowed to stream through the furnace displacing the air, and the furnace was heated up to  $1200^{\circ}\text{C}$ . Then a piece of Cs, Rb or K, was dropped from a

pincette into the furnace. The metal completely vaporised, and the vapour, on account of its heaviness, displaced hydrogen. Thus we had an atmosphere of Cs-vapour, which was partly ionised owing to the high temperature.

The space within the furnace, containing a fair proportion of free electrons and Cs, may now be compared to an electrolytic cell. The conductivity of the cell was measured by using the walls of the furnace P as one electrode, the pyrometer as the other electrode, according to the ammeter-voltmeter method. The rest of the apparatus easily explains itself.

M. V. is a millivoltmeter (from Siemens & Halske) graduated in temperatures up to  $1800^{\circ}\text{C}$ , for use with the thermo-couple. The graduation was tested anew by a fresh determination of the melting point of sodium chloride.

B is a battery of accumulators, W is an adjustable resistance. By slipping the end A, any voltage could be employed between P and T. M. A. was a millivoltmeter converted into a milliammeter with the aid of a shunt. S, S', S'', are the knobs of a three-way key, P. O. was a post-office box inserted between the two knobs, S, S'. By turning the handle the battery can be put in electrical contact either with S' or S''.

The course of the current while passing through the ionisation space is shown by the arrows. The current was measured by the milliammeter M. A. In this position the post office box is out of the circuit. By simply turning the handle of the key from S'' to S', the cell P, T, is disconnected and the post office box inserted in the circuit. Then proper resistance could be taken out from P, O, till the same deflection, as with the cell, was obtained at M. A. The resistance at P. O. now directly gives the resistance of the ionisation space. The measurement of temperature and the conductivity could not be done at the same moment, because when the space T, P becomes conducting, the voltage from W interferes with the readings of M. V. Hence during the reading of temperature the battery was disconnected. Then the battery was again connected to B, T was disconnected and the deflections in the M. A. observed in the ordinary way.

Hydrogen gas was made anhydrous by passing it through sulphuric acid. The furnace consisted of the platinum tube P, embedded in a concentric porcelain case stuffed with pure magnesia, and was heated by means of a low-tension transformer giving a current of 300 to 1000 amperes under about 2 Volts. The maximum temperature used was about  $1200^{\circ}\text{C}$ . The furnace was the same as that used by Nernst and his students for determining the vapour density of silver.

### RESULTS OF THE EXPERIMENT

The conductivities obtained with Es are shown in the Table. Thus the conductivity of the vapour-space becomes almost double when the temperature is raised from  $1050^{\circ}\text{C}$  to  $1250^{\circ}\text{C}$ . It was found that at about  $750^{\circ}\text{C}$ , the conductivity

\* The errors in the legends of the diagram have been corrected and duly incorporated.—Ed.

Cs.

Applied Voltage	1	2	3	4	5	
Resistance., T 1050°C	800	700		600	680	mean 736 ohms
at T 1250°C	340	370	360	370	330	mean 354 ohms

could not be measured by the milliammeter, the resistance was  $> 10000$  ohms. Owing to the nature of the experiment, the figures are of course rather uncertain, and nothing but qualitative conclusions could be drawn from them. It was also found that the conductivity depended upon the Cs-vapour-content of the cell. When it was driven away by the stream of hydrogen vapour, no trace of conductivity could be found. It is noteworthy that no trace of a saturation voltage could be found. The current increased proportionately as the voltage was raised from 1 to 6 volts. The same experiments were tried with Rubidium and Potassium. The resistance of the cell was found to be for Rb, 1100 ohms at 1200°C, 2500 ohms at 1050°C, for K, 2000 ohms at 1200°C, about 5000 ohms at 1050°C. The influence of the ionisation-potential is quite evident.

Measurements of conductivity at higher temperatures were not tried, because previous experience had shown that above 1200°C platinum becomes plastic and liable to sudden breakage. Theoretical calculations show that at 1800°C, specific resistance of Caesium vapour may be as low as 1 to 2 volts, and by varying the temperature all grades of conductivity between the metallic state [ $10^{-6}$  (ohm) $^{-1}$ ] and the most perfect insulators [ $10^{15}$  (ohm) $^{-1}$ ] can be obtained in the vapours of alkali metals. The experimental difficulties are however formidable. The Drude-Thompson theory of metallic conduction by free electrons, however, fails to lead to any satisfactory agreement. This question will be treated on a later occasion.

#### § 4.

We have now to meet the objections which may probably be raised against our contention that the observed conductivity was due to the ionisation of Cs, Rb, and K vapour by heat.

Firstly, it may be argued that the conductivity arises from the surface of the platinum tube emitting thermo-electrons. This explanation is not possible because at the temperature applied by us, the conductivity with a pure hydrogen atmosphere was so small that it could not be detected by the arrangement. This is in accord with the experiments of H. A. Wilson.<sup>6</sup> The space P. T. became conducting only when Cs, Rb or K was dropped into it, and vanished as soon as the vapours of these metals were driven away by the stream of the hydrogen gas.

Secondly, it may be supposed that the conducting electrons were produced in a secondary way. The thermo-

electrons from the surface of platinum, though by themselves not numerous enough to produce any sensible conductivity, produced new ions on collision with the metal atoms. This sort of ionisation has now become familiar from the works on ionisation potential by Franck and others. But for this effect the potential imposed must be higher than the ionisation potential of the elements. We worked with voltages from 1 to 6 and the conductivity of the ionisation space was always found to obey Ohm's Law.

Hence it is clear that the electrons emitted from the platinum surface or from the magnesia or the marquardt mass play no part, primary or secondary, in the phenomena observed.

Thirdly, it may be argued that the conducting electrons might have arisen from some sort of chemical action, *e.g.*, the action of Cs on MgO producing caesium oxide and free magnesium and the conducting electrons were those emitted by the caesium oxide.

If these were the cases, the conductivity should remain constant and ought not to vanish with the disappearance of Caesium vapour as mentioned before. In fact after the experiment the magnesia pieces were taken out and found to be quite unchanged. No chemical action is known to take place between Cs and H<sub>2</sub>. We have satisfied ourselves that even at the highest temperature employed by us, magnesia continues to be a good insulator.

These considerations coupled with the fact that the conductivities observed with Cs, Rb and K are in the reverse order of their ionisation potential just as we would expect from the theory, lead us to conclude that the conducting free electrons owe their genesis to the ionisation of the atoms of these metals by heat alone.

The work was carried out at the Physical Chemistry laboratory of the Berlin University, and it is our pleasant duty to record here our heart-felt thanks to Prof. W. Nernst for the hospitality of his laboratory and for the extremely valuable suggestions with which he was always ready to make our task lighter. The costs were borne by a grant from the Calcutta University, for which the authors wish to record their thanks to the Hon'ble the Vice-Chancellor and the Syndicate.

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5. This was predicted by the author (see Phil. Mag., Vol. 40, 1920, Elements in the Sun) to account for the absence of Rb, and Cs from the solar spectrum. The lines of Rb have subsequently been detected by Russell in the spot-spectrum where, owing to the low temperature, much of ionised Rb is re-converted to the neutral state. (The Astrophysical Journal, March, 1922, p. 128.)
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