

24. ON AN EXPERIMENTAL TEST OF THERMAL IONISATION OF ELEMENTS

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Though the theory of thermal ionisation of gases has been given by one of the authors in a number of papers¹ about three years ago, its application has hitherto been confined mostly to the realm of astrophysics. The theory still lacks experimental confirmation in the laboratory, and the present communication is the outcome of an attempt just to remove this desideratum.

The underlying idea may be thus stated:

If we take any element in the vapour state, and go on heating it, its electrical and optical properties will undergo a gradual change. To visualize matters, let us start with Ca-vapour at 800°C. At such a low temperature, it is most probably a non-conductor of electricity and will show only the lines $\lambda=4227$, 1S-2P, $\lambda=6573$, 1S-2p₂ and other lines of the principal series in absorption. If we go on heating the gas, a stage will come when an appreciable fraction will be ionised. The vapour space will now conduct electricity, and will show the principal lines of Ca, $\lambda=396$ (H), and $\lambda=3933$ (K) in absorption. Between these two stages, the lines of subordinate series of Ca may also come out in absorption.

For sometime past, one of the authors has been trying to follow this process in the laboratory. The first attempt was made with the vapours of the alkali metals, because as these elements possess the lowest ionisation-potentials, it was expected that they would be copiously ionised even at such low temperatures as 800°C—1000°C. But it may be mentioned here that these metals are not suitable for the spectroscopic test, as their chief ionised lines lie far down in the ultraviolet.

The experiments on the electrical conductivity of heated alkali vapours were first undertaken at the laboratory of Prof. Nernst at Berlin, and the preliminary results which we obtained quite confirmed our expectations. It was found that Cs-vapour² at 1250°C possessed an enormous specific conductivity of (50 ohm)⁻¹, which diminished

gradually as the temperature was lowered, and at 850°C, was certainly smaller than (10000 ohm)⁻¹. It was also found that the specific electrical conductivities were in the order Cs > R > K > Na, just as their ionisation-potentials would lead us to expect.

The furnace in which these experiments were carried out was not suitable for combined electrical and optical investigation as described above. Moreover, according to theory, the fraction of atoms ionised is a function of not only the temperature, but also of pressure. Hence it is desirable that a furnace be designed in which both temperature and concentration can be varied at will. In Nernst's furnace, pressure could not be varied at all.

In order to remove these defects, another arrangement was devised, which is described below.

This consists of two furnaces in vacuum. The material which is experimented upon is placed within the small furnace, which is heated to a varying temperature. The vapour pressure of the substance is known from this temperature. The substance in the vapour form is led to the bigger furnace which is maintained at a higher temperature. The volume within the big furnace containing heated vapour forms the experimental space, of which the electrical and spectral properties are studied. The great advantage in this type of furnace is that they allow both the temperature and concentration to be varied at will, which is not possible in the type used by A. S. King in the Mount Wilson Solar Observatory.

THE FURNACE.

The furnace is shown diagrammatically in Fig. 1. It is simply an adaptation of Prof. Compton's furnace (described in the Journ. Opt. Soc. America, Oct., 1922), with some modification to suit our convenience.

B=A rectangular hollow brass base, made of thick sheets of brass cooled by water, by inlet and outlet pipes at P and P'.

T=Heavy box of cast iron in the form of a rectangular parallelepiped, open at the bottom, and provided with flanges on all sides at the bottom for air-tight contact with the brass base. The joint was kept air-tight by a preparation of resin and bee's wax.

¹ Proc., Roy. Soc. Lond., Vol. 99, p. 136, *et seq.*, Z. f. Physik, Vol. 6, p. 40.

² Lewis reports in his Thermodynamics (p. 460). Urey carried out at his suggestion a similar experiment on the electrical conductivity of heated Cs-vapour. The full details of the paper are not yet available. The experiment mentioned above is fully described in the Journ. Dept. of Science, 1922, Calcutta University.

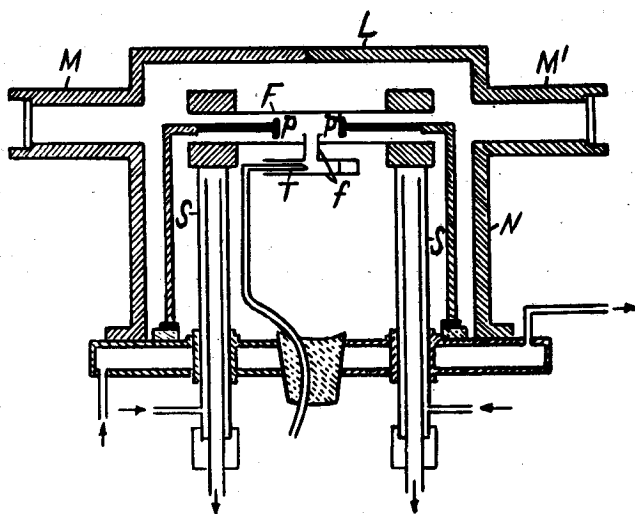


Fig. 1

M, M' = Projecting tubular pieces, of one piece with the box, and closed by glass or quartz plates, which are cemented to it by means of shellac.

L = Removable circular lid with a ground conical periphery and fitting into a ground, and sloping circular opening on the top of T. By taking out L, easy readjustments could be quickly made in the interior. This was just to avoid taking off the whole box T after every experiment for the necessary readjustments. The two surfaces of contact were ground with great care till they fitted exactly into each other.

F = Furnace which in the preliminary experiments consisted of a sheet of iron rolled into the form of a circular tube. It was clamped by means of a head piece and screws on the water-cooled stands, — S and S' which consist of thick iron tubes with a rectangular top of solid iron. The stands were water-cooled as shown in the diagram. The surface of the sheets was cleaned by the pickling process used in enamelling and then smoothed by emery paper.

D = A thick wire of iron, clamped on the stand *s* at one end and sliding in a groove at the head of the stand *s'* at the other end.

About half the space inside the furnace F was clear.

A current of 500-1000 amperes was applied to F under 6-10 volts directly from a battery of accumulators with a sliding resistance of mercury. Owing to the large size of the furnace, and the limited energy supply at our disposal, temperature could not be raised higher than 1250°C, as eye observations would indicate. A low tension transformer as used by King would have been much better, but as we had not the means to buy one, we had to make the best use of a set of discarded storage cells. One great disadvantage was that after about 5 minutes the connecting wires became very hot, and less current flowed through F, and temperature rapidly fell. This defect would probably

be cured if the furnace could be heated by current from a low-tension transformer, with very short and water-cooled leads. The furnace was evacuated by a Gaede oil pump, which was kept continuously running during the experiment. The leak was so small, that even at a temperature of 1250°, iron did not appreciably oxidise though the experiment lasted from 5-10 minutes.

f = Another furnace of much smaller dimensions, heated directly by current from accumulators, the substance which was to be vaporised was kept inside the furnace here. The ends were blocked by iron-plugs, through one of which passed a thermocouple of iron and constantan shielded by Pyrex glass tubing.

t = Small porcelain tubing, leading the vapour through an orifice at the top of *f* to the heated space inside F.

The connections to *f* for leading the heating current consisted of thick copper rods (not shown in the diagram) passing through an India rubber cork, which closed an orifice at B. The leads for thermocouple were also taken through this cork.

The temperature to which *f* was heated could be obtained from the readings on the millivoltmeter to which the couple was connected. Then from the data on the variation of vapour pressure with temperature, the pressure in *f* could be obtained. The pressure in *f* is equal to that in F, if the free flow could be prevented by stopping the ends of F by quartz plates. This has not yet been attempted.

By this arrangement, it was hoped that the vapour of any element could be maintained at a definite pressure for any length of time. Experimental difficulties have, however, not been completely overcome, but the progress hitherto made has been sufficient to justify the expectations placed in this arrangement.

DESCRIPTION OF THE ARRANGEMENT FOR MEASURING THE ELECTRICAL CONDUCTIVITY.

The arrangement for measuring the electrical conductivity is shown in diagram No. 2.

B—Battery.

V—Voltmeter for measuring the potential difference between the central wire and the furnace.

F—Furnace.

R—Resistance for varying the voltage.

K₁ K₂—Two three-way keys.

M. A—is a milliamperemeter placed between one set of knobs of K₁ and K₂.

Mic. A—is a microammeter placed between another set of knobs.

G—is a sensitive galvanometer placed between another set of knobs, with a variable megohm in series. By manipulating the keys K₁ K₂ the furnace may be connected either through the milliammeter, the microammeter or

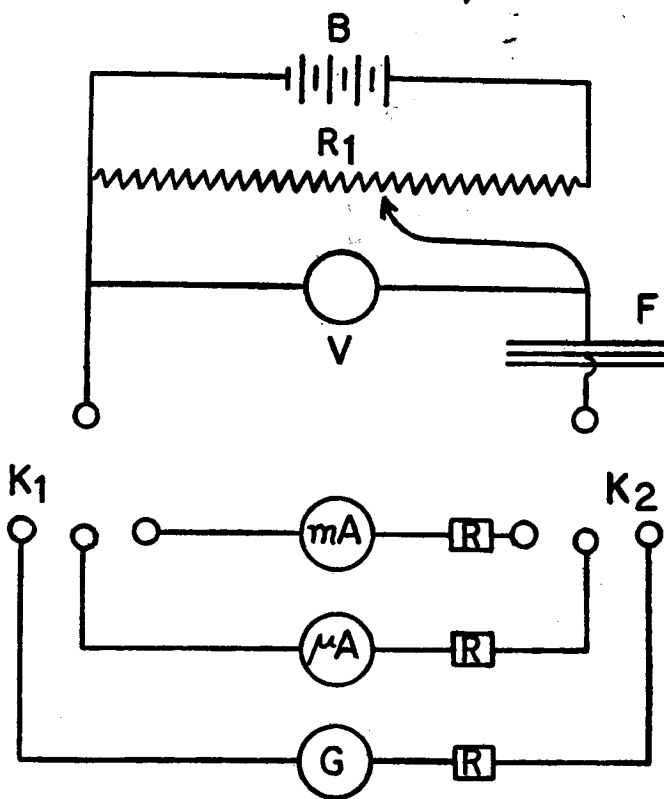


Fig. 2

the galvanometer. Voltage divided by the current gives the resistance of the vapour-space in the furnace.

ACTUAL EXPERIMENT.

The results which are communicated here are only of a preliminary nature.

The actual procedure was as follows:

Firstly, the central furnace was heated, and the thermionic current between the furnace and the central wire was measured. In most cases, this could be done by means of the galvanometer.³ The thermionic current is a very good indication of the temperature of the furnace *F*. Then current was applied to the small furnace *f*. The substance vaporised, and the vapour passed into *F*. Then the observer at the galvanometer noted whether the spot of light in the galvanometer scale shifted its position. Simultaneously, another observer noted the readings on the millivoltmeter connected with the thermocouple.

³ It will be interesting in this connection to recall the experiment of Pring and Parker who investigated the thermionic emission from large carbon rods by heating them with the aid of very large currents. They found that with larger currents thermionic emission died down. Richardson pointed out that this was due to the large magnetic field of the heating current, which prevented the electrons to escape from the heated surface. In our experiment though we are using currents of the order of 10^3 Amp. the experiment is being performed *inside* the heated space, where the magnetic field is zero, so there is free thermionic emission. Incidentally, it may be mentioned that in this method the temperature of the emitting surface can be more precisely measured, if we direct the optical pyrometer to the interior, for radiation coming from inside the furnace approximates to the black body condition. The point is receiving attention.

If the spot of light went off the scale, the galvanometer circuit was shunted off, and the microammeter circuit was put in, and the current observed. If this did not suffice, the milliammeter circuit was inserted.

The pump was kept running during the whole course of the experiment, which generally took from 5 to 10 minutes.

When experiment with one substance was finished and the furnace cooled down, the lid was taken off. Then the small furnace *f* was replaced by a fresh one, because the old furnace is generally contaminated by deposits of the metal with which the previous work has been done. The big furnace *F* was replaced, only if it was broken, as frequently happened, probably owing to stress developed during expansion.

Series 1. Experiments with Hg, Cd and Zn.

These three metals are interesting because the electrical conductivity of their vapours in a flame were investigated by McLennan⁴ a few years ago. The electrical conductivity of heated mercury vapour has formed the subject of investigation by many workers including Maxwell, Hittorff, J. J. Thomson and Strutt, but the results were mutually contradictory. McLennan's results also were quite indecisive.

We have proved decisively that when vapours of these elements are introduced into the furnace, between the temperature 850°C to 1300°C , the thermionic current remains completely unaltered. The voltage applied was 1.34, and at the highest temperature employed by us (1300° as judged by visual observation), the thermionic emission was 10 microamperes, with $R=9000$ ohm in series. The temperature of the small furnace was 650°C , corresponding to a vapour pressure of 27.23 mm, of Zn. It was found that when Zn-vapour was evolved, there was not only no increment in the thermionic current but there was actually a slight falling off, owing probably to the cooling of the furnace by the passing Zn vapour. The same phenomena was observed with Hg and Cd, the last being operated at a temperature of 740°C , vapour pressure = 557.2 mm. of mercury.⁵

These experiments prove conclusively that vapours of Zn, Cd, and Hg are not ionised at all by heat up to temperatures of 1250°C . This is quite expected as the ionisation-potential of these elements are rather high, viz., 9.45, 9.40, 10.45 volts.

Experiments with Mg and Ca.

Magnesium.—The small furnace was heated to 750° (measured), and the large furnace to about 1300°C (not

⁴ Proc. Roy. Soc., Lond., Vol. 92, p. 592.

⁵ These figures are taken from Landolt and Bornstein's Tables, 6th edition, pp. 1332-1338.

measured). The thermionic current was 10×10^{-6} amperes. On putting Mg-vapour, the current rose to $\frac{2}{10}$ of a milliamperere, or 200×10^{-6} Amp. or by about 20 times, so that magnesium vapour seems to have been ionised at 1300°C .

Calcium.—The small furnace was maintained at 920°C (measured), but the storage cells having run down, the temperature in the big furnace F could not be increased. It was probably 1150°C . The thermionic emission was less than a microampere, but on putting Ca-vapour, it rose to 30 microamperes. This proves that Ca-vapour is appreciably ionised at 1100°C .

Sodium

Sodium.—The small furnace was maintained at 470°C , corresponding to a vapour pressure of about 2 mm. of mercury. The temperature in the big furnace was about 900°C . The thermionic emission amounted to 40 divisions on the galvanometer scale corresponding to a total resistance 5×10^6 ohms. As one megohm was put in the galvanometer circuit, the resistance of the furnace-cell was approximately 4×10^6 ohms. On putting Na-vapour the spot went off the scale at once, so that the microampere circuit was put in. Even this went off the scale. Then the milliamperemeter circuit was put in with no resistance in series. The current was $\frac{1}{10}$ of a milliamperere, so that the

equivalent resistance with Na-vapour was only 13400 ohms. Thus at 900°C the conductivity of the space increases about three hundred times, when Na-vapour is put in.

The only objection which can be raised against the view that Na or Ca-vapour is ionised by heat is that the electrons emitted from the surface of the furnace F in falling to the central wire, produce fresh ions by collision. This possibility is excluded by the fact that the potential difference between the furnace and the central wire is only 1.34 volts, much lower than the ionisation potential of the elements investigated. But it may be contended that since the total potential fall between two ends of the furnace is from 6 to 10 volts, electrons emitted from the negative end may just slip along the surface and come out at the end with an energy corresponding to a voltage drop of 6 to 10.

Though we can think of such an eventuality, the probability of its affecting the main results seems to be rather remote. At least, in future experiments, efforts will be made to free the arrangement from the possibility of such an objection.

In conclusion, we wish to record our thanks to our colleague Mr. S. Bhargava, Reader in this University, for useful help in designing the apparatus and to Mr. K. Majumdar, Research Scholar, for help in taking observations.

25. ON AN ACTIVE MODIFICATION OF NITROGEN*

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A few years ago Prof. Strutt (now Lord Rayleigh) performed a series of experiments on an active modification of nitrogen¹, which excited a good deal of interest at the time. Nitrogen is well known to be an extremely inert gas, but Lord Rayleigh showed that if a condensed spark discharge be sent through N_2 -gas, the glow persists in the gas flowing out of the region of the discharge, which shows considerable chemical and spectral activities. The spectrum of the afterglow was investigated by Fowler and Strutt² and shown to consist of the usual α , β , and γ groups of

positive bands, with a fourth group which was observed for the first time.

The object of the present paper is to show that almost the whole series of observations recorded by Lord Rayleigh can be explained on the basis of Klein and Rosseland's theory³ of inelastic collision of the second type, which has been further developed by Franck⁴ and his students. For convenience of discussion we begin with a short account of this theory.

The experiments on ionization potential and origin of

* Communicated by the Authors.

¹ Strutt, Proc. Roy. Soc. Lond. lxxxv. p. 219; lxxxvi. pp. 56, 105, 529; lxxxvii. pp. 179, 302, 381; lxxxviii. pp. 110, 539.

² Fowler and Strutt, Proc. Roy. Soc. Lond. lxxxvi pp. 105-117.

³ Klein and Rosseland, *Zs. f. Physik*, iv. p. 46.

⁴ Franck, *Zs. f. Physik*, ix. p. 259; xi. p. 155. Cario, *Zs. f. Physik*, x. p. 105 and p. 166. Compton, Journal of the Optical Society of America, 1923.