

these, such as the hydration of the solute, have been determined by direct measurements made with the solution itself. Nevertheless, when the solutions are made up to equal weights of solvent instead of to equal volumes of solution, and when the volume used for calculation is the volume of the solvent used in making the solution, it has been found that the ratio of osmotic pressure to gas pressure falls to unity at 30° C. in a decinormal, and at 80° C. in a normal solution of cane-sugar. At lower temperatures, the ratio is greater than unity, probably on account of the formation of hydrates.

A similar remarkable agreement has been obtained in a final series of measurements, made under the most highly perfected experimental conditions, of the osmotic pressure of solutions of glucose at 30°, 40°, and 50° C. Twenty-four measurements are recorded, in which the average value of the ratio of osmotic pressure to gas pressure was exactly 1.000, and the average error less than  $\pm 0.001$ . In the case of mannitol at five or six concentrations, and at temperatures from 10° to 40°, the average ratio was 1.000, and the average error  $\pm 0.001$ , showing that within the limits thus far investigated, aqueous solutions of mannitol obey the laws of Gay-Lussac and Boyle.

The volume concludes with a preliminary account of some experiments on the osmotic pressure of electrolytes, which do not appear to have been published hitherto in any of the scientific journals. Potassium chloride (half-normal), barium chloride, and potassium ferrocyanide caused a rapid degeneration of the membrane, probably due to the destruction of its colloidal character. The degeneration was progressive, and could not be remedied by long soaking in water. Lithium chloride rendered the membranes very sluggish, but they retained their semi-permeability up to a concentration of 0.6 normal; a solution of this concentration was observed over a period of one hundred days, the average osmotic pressure for the whole period being 18.789 atmospheres, and for successive groups of twenty days, 18.827, 18.894, 18.799, 18.636, and 18.405. The ratios of osmotic pressure to gas pressure at 30° were as follows:—

Concentration	0.1	0.2	0.3	0.4	0.5	0.6
Ratio	1.746	1.816	1.857	1.899	1.955	1.992

This *increase* in the ratio is entirely opposed to the effects produced by variations of electrolytic dissociation, but may be explained by the diminution of the free water as a result of the formation of hydrates.

This formation of hydrates in solution is a leading feature of the work described in the second monograph, by H. C. Jones and his collaborators. The first section of the monograph receives a separate title, "The Absorption Spectra of Solutions as Studied by Means of the Radiomicrometer," but its main subject is the influence of hydrated and non-hydrated salts on the absorption of light by water. The chief result is to show that aqueous solutions of hydrated salts generally have greater transparency than pure water at the centres of the absorption-bands. The exceptions are the  $1 \mu$  band for zinc nitrate and magnesium nitrate and the 1.25 band for magnesium nitrate. Non-hydrated salts, under similar conditions, give results in many respects exactly the opposite of those obtained with hydrated salts. The remainder of the monograph deals with "The Conductivities, Dissociations, and Viscosities of Solutions of Electrolytes in Aqueous, Non-aqueous, and Mixed Solvents." The chief solvents used were water, ethyl alcohol, ethyl alcohol and water, acetone and water, and ternary mixtures of glycerol, acetone, and water. The final chapter, covering nearly sixty pages, is devoted to a "Dis-

ussion of Evidence on the Solvate Theory of Solution obtained in the Laboratories of the Johns Hopkins University." This summary extends from the time when, as the author says, "In the summer of 1893 I went to Stockholm to work with Svante Arrhenius," and extends to the present day. It deals with the work which has appeared in eighty papers, widely scattered through chemical and physical literature, and published in American, German, French, and English scientific journals, in addition to nine monographs already published by the Carnegie Institution of Washington. It is to the support of this institution that the present wide extension of these investigations is largely due.

T. M. L.

### ELECTRONS AND HEAT.<sup>1</sup>

WHEN electrified bodies are heated they are found to lose the power of retaining an electric charge. The charge leaks away from their surfaces. This is not a novel phenomenon. It has been known for nearly two centuries that solids glowing in air are capable of discharging an electroscope. Thus you observe that the electroscope is at once discharged when I bring near it a red-hot poker withdrawn from the furnace on the lecture table. These effects are due to the emission of ions by the hot solids. For example, if the electroscope is negatively charged it draws positive ions from the hot poker and so becomes discharged.

Most bodies when heated in air at low temperatures emit only positive ions. At sufficiently high temperatures ions of both signs are emitted simultaneously. We can show this by a simple experiment in which the hot body consists of a loop of platinum wire and acts as its own electroscope. When a charged rod is brought near the loop a charge of opposite sign is induced on the latter, which is thus deflected owing to the electrostatic attraction of the rod. When the loop is cold this happens whatever the sign of the charge on the rod. If the wire is at a dull red heat it can only be deflected by a positively charged rod. When a negatively charged rod is brought near it the emission of positive ions causes the induced positive charge at once to stream away. Thus the wire is incapable of retaining a positive charge, and so no deflection is produced by a negatively charged rod. At very high temperatures you observe that the loop is undeflected whatever the sign of the charge on the rod. The wire is now liberating both positive and negative ions, and so is unable to retain either a positive or a negative charge.

If these effects are investigated in a vacuum, instead of in air at atmospheric pressure, it is found that the emission of positive ions gradually disappears with continued heating, so that a wire which has been well glowing out in a vacuum emits only negative ions in appreciable quantity. Thus if we repeat the last experiment with an incandescent lamp, using one in which the filaments are not anchored, we see that the loops are attracted by a negatively charged rod, but not by one which is charged positively. They show, in fact, a behaviour which is precisely opposite to that of a wire at a dull red heat in air.

Now let us consider the nature of the ions which carry these thermionic currents, to use a term which I have ventured to apply to the currents which leak away from the surfaces of hot bodies in this manner. As is well known, the negative electrons which play such an important part in physical phenomena are very readily deflected by moderate magnetic fields, whereas ions of atomic or greater magnitude are not.

<sup>1</sup> Discourse delivered at the Royal Institution on Friday, May 7, by Prof. O. W. Richardson, F.R.S.

I have here an arrangement which will enable us to apply this test to the ions emitted by hot bodies. An exhausted tube carrying a horizontal hot wire is placed in a vertical electric field. The electric field is arranged so as to drag the negative ions emitted by the wire to a suitable electrode, whence they flow through a galvanometer, the deflection of which is registered by the spot on the screen. Around the tube an electromagnet is arranged, so that, when it is excited, there is a horizontal magnetic field which tends to curl up the paths of the ions. If I now switch on the electromagnet you observe that the current is at once reduced to a small value, showing that the magnetic field curls up the paths of the ions; so that they are now unable to reach the electrode. The carriers of this negative discharge are, in fact, electrons.

I have here a second tube arranged to give a conveniently large positive discharge. When this is tested by the electromagnet in a similar way, the magnetic field is found to have no influence on the thermionic current. The positive ions are, in fact, much more massive than the electrons; more elaborate experiments have shown that they are charged atoms.

We see from these experiments that the negative emission is characterised by the electronic nature of the carriers and by its permanence in a vacuum. The presence of a gaseous atmosphere is not necessary in order to maintain these currents. Thus the electrons must come from the heated body itself. I believe that this emission is a process which is closely analogous to evaporation. The essence of evaporation, of a liquid, for example, lies in this: that, as the temperature is raised, the molecules acquire sufficient energy to overcome the forces which attract them to the liquid, and so become free molecules of the vapour. We know that all material substances contain electrons, and it is not unreasonable to expect these to behave, when the temperature is high enough, in a way analogous to the molecules of a liquid. Another analogy, in some ways more accurate, would liken the emission of electrons to the reversible evolution of a gas by the decomposition of a solid such as calcium carbonate. The similarity of this process to evaporation is well known to chemists.

This position is strengthened when we examine the way in which the electron emission depends on the temperature of the hot body. This may readily be done by surrounding the hot wire with a cylindrical electrode to catch the electrons, which then flow through a galvanometer, the deflection of which measures their number. The hot wire is arranged to lie in one arm of a Wheatstone's bridge, so that its temperature may be deduced from its resistance. Innumerable experiments with different substances have shown that this emission increases with great rapidity as the temperature rises, just as does the corresponding phenomenon in the case of evaporation. The correspondence is, in fact, exceedingly close. We may take the rate of emission of molecules from the surface of an evaporating liquid to be proportional to the vapour pressure. The proportionality is not exact, but it is sufficiently so for our purpose. The crosses on the next slide represent values of the vapour pressure of water, on the vertical scale, plotted against the corresponding temperatures from  $0^{\circ}$  C. to  $96^{\circ}$  C., on the horizontal scale; whilst the circles represent the emission currents from platinum plotted similarly against temperature over the range  $1000^{\circ}$  C. to  $1250^{\circ}$  C. All the points lie on the same continuous curve within the limits of experimental error. To bring about this coincidence it is, of course, necessary to plot the temperatures on quite different scales in the two cases, but the agreement demonstrates in a

simple way the similarity of the laws which govern the temperature variation in both cases.

Numerous cases of electron emission have now been examined, and it has invariably been found, provided there is no reason to suspect changes in the chemical nature of the emitting surface, that the relation between the current  $i$  and the absolute temperature  $T$  is expressed by a very simple equation. This is  $i = AT^{\frac{1}{2}}e^{-b/T}$ , or  $\log i - \frac{1}{2} \log T = \log A - b/T$ , where  $A$  and  $b$  are constant quantities for any particular substance. The theory underlying this equation shows that the quantity  $b$  is very nearly equal to twice the energy change, expressed in calories, when one gram-molecular weight of the electrons is emitted. Pursuing the analogy with evaporation, this quantity may be called the molecular latent heat of evaporation of the electrons. It is not, however, with the theory underlying this equation that I particularly wish to concern you now; but I do wish to impress the fact that this formula is not an empirical affair covering a small range of temperature and current. The most recent measurements, made with tungsten, have shown that the formula expresses the results within the limits of experimental error, over the range of temperature from  $1050^{\circ}$  K. to  $2300^{\circ}$  K. At the lowest temperatures the currents were less than one-millionth of a microampere per square centimetre, and had to be measured with a sensitive electrometer, whilst at the highest temperatures they were comparable with one ampere per square centimetre, and could be measured on a commercial ammeter. Thus the equation holds true, whilst one of the variables changes by the enormous factor of  $10^{12}$ . There are not many physical laws which will stand so severe a test as this.

Let us now turn to some other consequences of the hypothesis that the emission of electrons is analogous to evaporation. One of the familiar effects of evaporation is to cool the liquid which gives off the vapour, owing to the latent heat of vaporisation. In an exactly analogous manner a wire which is giving off electrons will be cooled thereby. I think I can succeed in demonstrating this effect to you, although the lowering of temperature to be looked for is not very large, and delicate means have to be employed to detect it. This tube contains a hot tungsten wire which is made to act as its own thermometer by placing it in one arm of a sensitive Wheatstone's bridge. Minute changes in its resistance can thus be measured. The bridge is balanced with the electrode surrounding the hot wire negatively charged, so that the thermionic current does not flow. If I reverse the potential and thus start the thermionic current, keeping the heating current constant, you observe a sudden deflection of the spot of the bridge galvanometer. The direction of this deflection corresponds to a reduction of the resistance of the hot wire and thus to a lowering of its temperature. By experiments of this kind Prof. Cooke and I succeeded in measuring the latent heat of evaporation of the electrons directly.

Just as a liquid is cooled by evaporation so it is heated to a corresponding extent when the vapour condenses. In fact an elementary experiment with which every student of physics is familiar consists in measuring the latent heat of evaporation by blowing steam into water. A precisely analogous experiment can be made with electrons. A large electron current from a hot wire is driven on to a fine strip of the metal of which the latent heat of condensation for electrons is to be tested. The cold strip is made to act as its own thermometer by placing it in one arm of a sensitive Wheatstone bridge. When the hot wire is charged positively there is no electron current to

the strip, and the bridge is balanced under these conditions. The wire is then charged negatively so as to make the electrons flow on to the strip. There is then an increase in resistance, due to the heat liberated by the condensation of the electrons, which is measured. In these experiments only part of the observed change of resistance arises from the effect under consideration. The remainder is caused by the kinetic energy given to the electrons by the auxiliary field used to drive them from the hot wire to the strip. This, however, is easily determined and allowed for.

I have now indicated to you three independent methods of deducing the values of the latent heat of emission of the electrons. Let us see how the latest and most accurate values obtained by these methods agree with one another. The numbers found, and the names of the experimenters responsible for them, are shown in the following table:—

*Values of Latent Heat of Emission Reduced to Equivalent Temperatures.*

(1) From the temperature variation of the rate of emission:—

Tungsten (Langmuir) ...	$10.5 \times 10^4$ — $11.1 \times 10^4$	calor i c s j o m
(K. K. Smith)	$10.94 \times 10^4$	"    "
Platinum (various) ...	$12 \times 10^4$ — $16 \times 10^4$	"    "

(2) From cooling due to emission:—

Tungsten (Cooke and Richardson) ...	$11.24 \times 10^4$	"    "
Tungsten (Lester) ...	$11.04 \times 10^4$	"    "
Platinum (Wehnelt and Liebreich) ...	$13.9 \times 10^4$ — $14.5 \times 10^4$	"    "

(3) From heating due to condensation:—

Platinum (Richardson and Cooke) ...	$13.5 \times 10^4$	"    "
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Unfortunately, the vacuum value for platinum given by the first method is still uncertain owing to complications caused by gaseous contaminants. Except for this the agreement between the different methods is very satisfactory.

We come now to the very interesting question of the velocity and kinetic energy which these electrons possess when they are emitted. The fact that they are electrically charged enables us to find out a great deal more about their emission velocities than we can do in the corresponding case of the emission of ordinary molecules. By applying an external electric field we can influence the motion of the emitted electrons, and the precise nature of the effect exerted by the field depends on the velocity with which the electrons are shot off from the hot body. It is clear that we have no such method of controlling the motion of ordinary molecules.

I shall now consider one of the arrangements which has been used in applying these principles to the analysis of the emission velocities. The hot emitting surface is a small strip of platinum, electrically heated, which lies at the centre of a much larger metal plate. The upper surfaces of the strip and the plate are flush with each other, and are maintained at the same potential. Vertically above this lower plate and a short distance away from it is a parallel metal plate connected to the insulated quadrants of an electrometer. An arrangement is provided by which a suitable difference of potential can be maintained between the two plates so as to oppose the motion of the electrons from the strip towards the upper plate. It is clear that if the electrons have no velocity when they are emitted, any retarding field, however small, will be sufficient to stop them from reaching the upper plate and charg-

ing up the electrometer. If, on the other hand, they are shot off with a definite component of velocity normal to the strip they will reach the upper plate, provided the corresponding kinetic energy exceeds the work they have to do to overcome the opposing difference of potential. Thus if the electrons are not at rest when they are emitted, they will give rise to currents capable of flowing against an applied electromotive force if this is not too large. I have here an arrangement, similar in principle to that just described, which will enable me to show to you the existence of these currents flowing against an applied electromotive force. The platinum strip is replaced by a very short tungsten filament, the upper plate by a surrounding cylinder, and the electrometer by a galvanometer. The apparatus is thus different in detail from that already referred to, but the principle is the same. You observe that the current is largest when the opposing difference of potential is zero, and falls off uniformly and rapidly as the potential difference is increased. By increasing the temperature I can cause a considerable current to flow against an opposing difference of potential of one volt.

The experiments just referred to are a kind of electrical analogue of the high jump, in which the measuring tape is replaced by a voltmeter. Corresponding to each emission velocity there is a definite equivalent voltage. The fact that the current falls off continuously as the opposing voltage increases shows that the electrons are not emitted with a single velocity but with different velocities extending over wide limits. Careful experiments of this kind have enabled us to discover what proportion of them are shot off with velocities within any stated limits, to determine, in fact, what is the law of distribution of velocity among the emitted electrons.

More than fifty years ago Maxwell concluded from rather abstruse theoretical considerations that the velocities of the molecules of a gas or vapour should not all be equal, but should be distributed in a certain way about the average value. This law, known as Maxwell's law of distribution of velocity, is somewhat similar to that which governs the density of bullet marks on a target at different distances from the bull's eye. The theoretical considerations which led Maxwell to establish this law for gases apply equally to the atmospheres of electrons outside hot bodies. Let us see whether the results of our experiments agree with Maxwell's predictions or not. If the law of distribution of the normal velocity component for the emitted electrons is that given by Maxwell, it is necessary (and sufficient) that the currents  $i_1$  and  $i_2$  which flow against potentials  $v_1$  and  $v_2$ , respectively, should satisfy the equation—

$$\log i_1/i_2 = \frac{Q}{RT} (v_1 - v_2),$$

where R is the constant in the equation  $p v = RT$  of a perfect gas, and Q is the quantity of electricity which liberates half a cubic centimetre of hydrogen at 0° C. and 760 mm. in a water-voltmeter. The requirements of this formula are found to be fully satisfied by the results of the experiments. Thus the logarithms of the ratios of the currents are found to be accurately proportional to the differences in the corresponding opposing potentials at a given temperature. Again, since Q is a well-known physical constant, and the value of T was estimated during the experiments, we can use the experimental data to obtain a value of the gas constant R. Eight experiments, made under conditions as varied as possible, when treated in this way, gave values of R which varied between the extreme limits  $3.08 \times 10^8$  and  $4.46 \times 10^8$  ergs per c.c. per degree C. These values

exhibit a rather wide variation, which, however, is believed to be fortuitous; so that the mean value should be much more accurate. The mean of the eight values gives  $R=3.72 \times 10^3$ , whereas the number given by the gas equation is  $R=3.711 \times 10^3$  in the same units.

The fact that the value of the gas constant can be deduced in this way from purely electrical measurements must be regarded as a remarkable confirmation of the general position. The results of these experiments, and of others of a similar nature which I have not time to describe, show not only that the velocities of the electrons are distributed about the average value in accordance with Maxwell's law, but also that the emitted electrons are kinetically identical with the molecules of a hypothetical gas of equal molecular weight at the temperature of the hot metal. The experiments referred to formed the first direct experimental demonstration of the truth of Maxwell's law of distribution of velocities, and, although many of the consequences of this law have been made visible by the beautiful experiments of Perrin on the Brownian movement, I believe that they still furnish the most direct experimental verification of its truth.

Quite recently a number of experimenters have called in question the general position which I have taken as to the nature of the process of electron emission from hot bodies, and have asserted that this effect is caused by chemical action between the hot solid and traces of contaminants, usually supposed to be gaseous, which have access to it. Whilst I feel that the value of the evidence in favour of the latter hypothesis has, generally speaking, been greatly over-estimated, it would take too long to discuss this question with the completeness which it demands. I shall therefore content myself with directing your attention to some experiments with tungsten filaments which prove that only an insignificant fraction, if any, of the emission from this substance can be attributed to chemical action.

Tungsten is peculiarly suited to these experiments on account of its great refractoriness. It can be heated in a vacuum for considerable periods at temperatures so high that all known impurities are volatilised out of it. The preliminary treatment of the experimental lamps furnishes some novel features which may prove of interest. The ductile tungsten filaments are electrically welded to the supporting leading wires in an atmosphere of hydrogen. After mounting, the lamps are exhausted in a vacuum furnace (with an external air pressure of about 1 cm.) at 550–600° C. for about twenty-four hours, until the evolution of gas becomes very small. A Gaede pump is used for the internal exhaust at first, and, later on, liquid air and charcoal in addition. In the final stages the tungsten is glowed at about 3000° absolute, and, for the best results, the anode is heated by subjecting it to an intense electron bombardment from the hot wire. The conditions as to freedom from gaseous contamination which have been attained in this way are far superior to those which result from any other method of treatment.

With lamps thus prepared I have carried out simultaneous measurements of the rate of emission of electrons on one hand, and either of the variation of the pressure of the gas present or of the rate of loss of matter by the filament on the other. Particular experiments have led to the following numbers:—

- (1) For each molecule of gas given off the number of electrons emitted by the filament may be as high as 260,000,000.
- (2) At each impact of a gas molecule with the filament 15,000 electrons would have to be emitted, and
- (3) Each atom of tungsten which disappears from

the filament would have to cause the emission of 984,000 electrons.

The magnitude of these numbers entirely precludes the possibility that chemical action plays any significant part in this emission. Again, the mass of the electrons lost by a filament may exceed the mass of tungsten lost in the same interval, proving that the emitted electrons are not furnished at the expense of the tungsten. They must therefore flow in from outside points of the circuit. Thus these experiments furnish a direct proof that the electric current in metals is carried by moving electrons. The mechanism of metallic conduction becomes more mysterious every day, but this, at any rate, is a fact which has to be reckoned with.

Perhaps I can drive these matters home to you more effectually by means of a simple experiment which shows that these electron currents from tungsten in high vacua are not minute affairs requiring elaborate apparatus for their detection, but, at high temperatures, are of such magnitude as to be worthy of the consideration of the practical electrician. I have here a tungsten lamp, containing a filament 14 mm. long and about 3 mils. in diameter, in series with an ammeter, a resistance, a battery, and a second ammeter. They are arranged in the order named, so that there is an ammeter at each end of the lamp. In addition there is a side line from the cylindrical electrode of the lamp which can be switched through either a millammeter or an electric bell to the positive end of the battery. There is no auxiliary voltage in this side line. When I turn the current on you observe that the ammeters read differently, showing that more current is flowing into the filament at one end than out of it at the other. The difference is, in fact, equal to the electron current which flows into the wire sideways, and is registered by the millammeter. Those of you who cannot see the instruments will, at any rate, hear the electric bell when I switch the electron current through it. With a lamp which was somewhat better designed for the purpose than the present one, I have recorded a current of 0.7 ampere at one end, 0.45 at the other, and 0.25 in the branch circuit. So far as my experience goes, the only limit to the size of these electron currents is that which is set by the magnitude of the current which fuses the filament, provided the requisite driving voltage is available.

#### UNIVERSITY AND EDUCATIONAL INTELLIGENCE.

CAMBRIDGE.—Mr. C. T. R. Wilson, F.R.S., University lecturer in experimental physics, has been elected to a fellowship in Sidney Sussex College for a period of five years.

Messrs. C. C. Bissett, of Emmanuel College; H. B. Cronshaw, of Gonville and Caius College; H. Ogden, of Emmanuel College; and E. P. Farrow, of Trinity College, research students of the University, have qualified for the degree by the presentation of theses, which have been approved, in chemistry, mineralogy, physics, and botany respectively.

The Harkness Scholarship in geology and palaeontology has been awarded to Mr. W. H. Wilcockson, of Gonville and Caius College, and the Wiltshire prize in geology and mineralogy to Mr. D. B. Briggs, of Jesus College. The Frank Smart prize in botany has been awarded to Mr. E. J. Maskell, Emmanuel College, and that in zoology to Mr. L. T. Hogben, of Trinity College.

The following lecturers have been reappointed for five years from October 1, 1915:—Dr. Searle and Mr. C. T. R. Wilson, in experimental physics; Dr. Marr,