CL.—*The Effect of Gases on the Electric Charges Developed by Heated Metals.*

By Donald Hugh Bangham and Douglas Rostron Lewis.

It was shown by Hartley (*Proc. Roy. Soc.*, 1914, *A*, **90**, 61) that a metal surface, when heated in contact with different gases, tends to become charged to a definite potential characteristic of each gas. Working with a roll of gold gauze, suspended inside a glass vessel by a sealed-in gold wire which connected it to an electrometer, he found that when the apparatus was heated, not only did the gauze become charged, but the effect could be repeated an indefinite number of times between successive earthings. It follows that if the gauze were maintained—by earthing or otherwise—at a potential other than the equilibrium one, the system must have furnished a continuous current tending to produce the equilibrium conditions. It was to elucidate the nature of these currents and the chemical changes associated with their production that the present investigation was undertaken. Hartley's own suggestion is that the effects are due to " deeply occluded " gas leaving the metal in a charged condition.

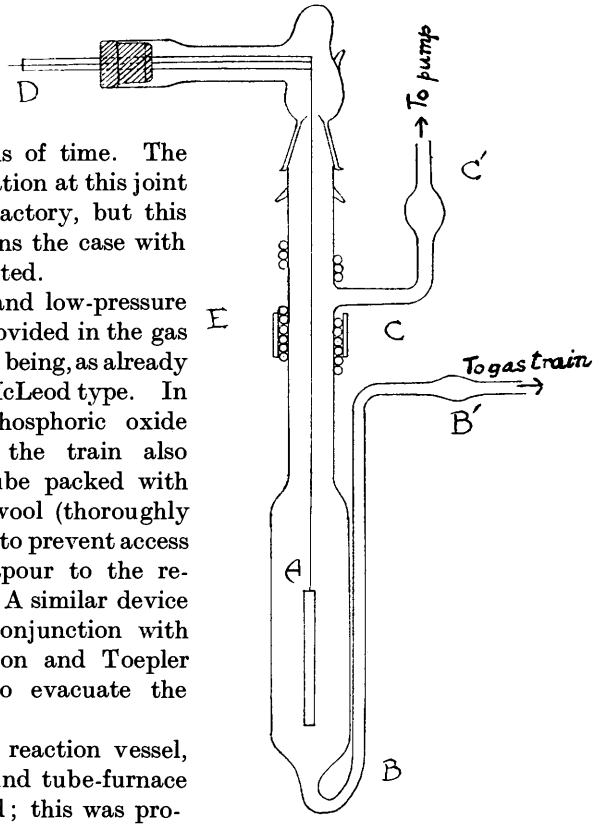
Whilst endeavouring to reproduce Hartley's experimental conditions, the authors have centred their attention, not on the equilibrium potentials themselves—it soon became evident that only qualitative agreement with Hartley's results could be hoped for—but on the rate of development of the charges, *i.e.*, the magnitude of the currents.

Experimental.

Apparatus.—A sketch of the reaction vessel is shown in Fig. 1. The wide Jena-glass tube, A, was drawn down at both ends to make a cylindrical bulb about 10 cm. long. The quill tubes, B

and C, sealed to soda-glass leads at B′ and C′, communicated respectively with the gas train and the pump. The gold gauze, rolled into a narrow cylinder 5 cm. long, was suspended centrally in the vessel by a gold wire carried through a glass capillary, D, secured in its place by an ebonite plug. The seals between wire, capillary tube, plug, and side arm of the reaction vessel were successfully made with sealing wax, a McLeod gauge sealed to the gas train showing no trace of leak when the apparatus was evacuated and left standing for long periods of time. The electrical insulation at this joint was also satisfactory, but this was by no means the case with other forms tested.

FIG. 1.



Both high- and low-pressure gauges were provided in the gas train, the latter being, as already stated, of the McLeod type. In addition to phosphoric oxide drying tubes, the train also contained a tube packed with silvered glass wool (thoroughly freed from gas) to prevent access of mercury vapour to the reaction vessel. A similar device was used in conjunction with the condensation and Toepler pumps used to evacuate the apparatus.

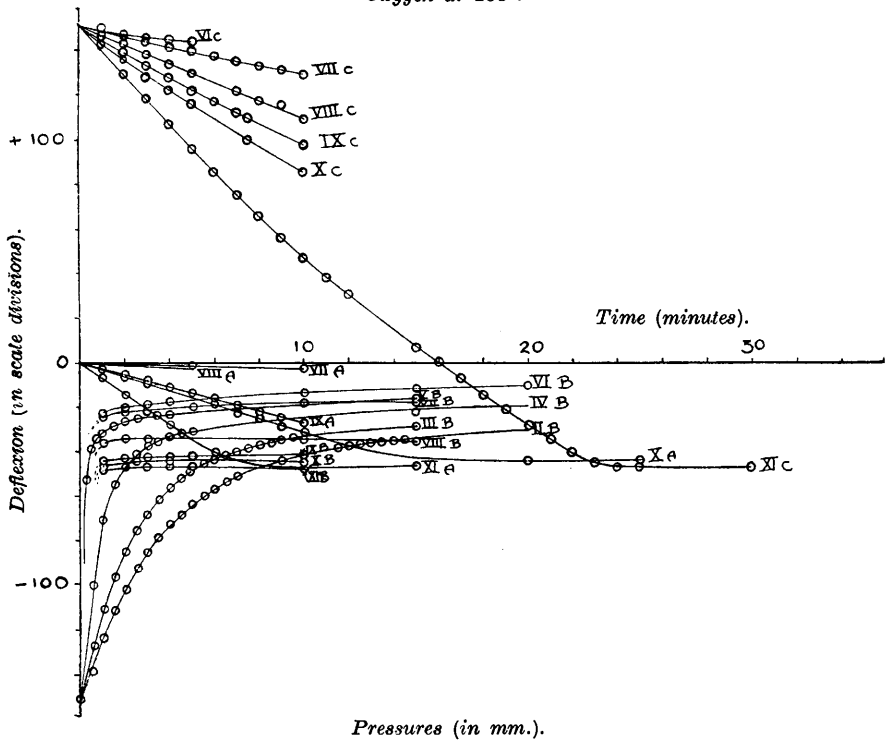
To heat the reaction vessel, a specially wound tube-furnace was constructed; this was provided with an earth-connected lining to screen out the disturbing effects of the heating current. With proper precautions, it was found that the heating current could be switched off for some seconds without in any way influencing the results obtained.

The electrometer, which was of the Dolezalek pattern, was shielded by enclosing it in a tin box supported on shock-absorbers. One pair of quadrants was permanently connected to earth, and the second to earthing and " mutating " keys placed inside the box.

The mutating key permitted connexion to be made, as desired, to the gold electrode, the potentiometer, or both. Careful experiments were made to test the trustworthiness and sensibility of the electrometer system, to determine its optimum working conditions, and to eliminate stray fields by the provision of suitably placed screens and guard rings. Throughout the series of experiments with gases, the electrometer needle was charged to 132 volts; the

FIG. 2.

Oxygen at 468°.



Pressures (in mm.).

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
152	59	25	8·0	1·83	0·307	0·038	0·0175	0·0081	0·0023	<0·0002

phosphor-bronze suspension used gave, under these conditions, a deflexion of 52 scale divisions per volt.

Experiments with Oxygen.—Dry oxygen was admitted to the reaction vessel to a pressure of *ca.* 400 mm., and the temperature gradually raised. No appreciable charging-up was observed at Hartley's working temperature (*ca.* 370°), and it was not until about 100° higher that the charging rate became conveniently large.

Systematic measurements were made at two temperatures, *viz.*, 468° and 497°, the procedure being as follows: (i) The insulated quadrants were placed in communication with the gold electrode, the earthing key being down; the latter was then lifted and the deflexion of the needle noted after definite intervals of time (see curves A, Fig. 2). (ii) The gauze was charged to − 3 volts and the deflexion noted; connexion to the potentiometer was then broken, and the rate of discharge observed (see curves B). (iii) The gauze was charged to + 3 volts and the same procedure followed (curves C).

Part of the gas was then removed by means of the pump, and a new series of measurements taken at a lower pressure. The process was continued until the pressure of gas remaining could no longer be measured with accuracy.

It was found important to adopt a uniform plan of procedure throughout the experiments, since the results obtained depended (as indicated below) on the past history of the gold gauze. For this reason experiments (i), (ii), and (iii) were carried out at each pressure in the order stated.

Discussion of Results with Oxygen.—The results of experiments carried out with oxygen at 468° are shown graphically in Fig. 2. A study of these diagrams leads to the following conclusions:

(i) The rate of attainment of the final equilibrium potential is considerably retarded by the presence of oxygen, even at low pressures.

(ii) The non-appearance of the effect observed by Hartley (*i.e.*, the charging-up from zero potential) at high oxygen pressures is probably due to this retardation, and does not indicate that the equilibrium potential is zero in such cases.

(iii) Increased pressure of oxygen causes a marked shift of the equilibrium potential towards the positive side, as indicated by the intersection of the high- with the low-pressure curves B in Fig. 2. It remains an open question whether, at still higher pressures, this displacement would be sufficient to give rise to the positive equilibrium potential observed by Hartley in the case of oxygen.

(iv) The mode of approach to the equilibrium potential is widely different according as the equilibrium value is approached from the positive or from the negative side. In the latter case, the rate of change is a highly sensitive function of the momentary potential; in the former, it is markedly insensitive, the rate being nearly uniform.

Explanation of Curves in Terms of Thermionic Emission Theory.—The dissimilarity in form between the B and C curves is readily

explicable if it be supposed that the leakage currents are carriee mainly or entirely by ions of one sign between the hot metal and the glass wall of the containing vessel, which acts as a second electrode. Since, at the low temperatures used, it is the positive emission which is predominant, it may be safely presumed that the carriers are positive ions.

Supposing a positive potential to be given to the gauze (curves C), a very weak field suffices to drive all the ions emitted by it across to the glass wall, simply on account of the size of target which the latter offers. For the same reason, ions emitted by the wall are also made to return. The current is therefore saturated, or nearly so,* and does not decay until the potential of the metal has fallen nearly to its final or equilibrium value.

If, on the other hand, a negative potential of 3 volts is given to the metal, the carriers are the positive ions emitted by the glass wall. There is little difficulty in crediting glass with the power of emitting such ions: it was shown by Richardson that the positive emission from a well glowed-out wire could be enormously increased if the walls of the glass containing vessel were only slightly heated.† Since, however, the metal electrode offers only a small target as compared with the emitting surface, the proportion of ions reaching the former is a highly sensitive function of the field strength. The feebler the field, the greater will be the proportion of ions reabsorbed by the wall.

The Nature of the Ions.—As regards the identity of the positive carriers, there are two possibilities to be considered: they may be either (i) charged atoms or molecules of oxygen, or (ii) ions of the type shown by Richardson to result from heating new metal wires in a vacuum. Type (i) was found by Richardson (*op. cit.*, pp. 30 *et seq.*) to result when platinum is heated in oxygen to temperatures of 700° and above.

In striking contrast to the results of the experiments here described, Richardson found that this emission *increased* with the pressure of oxygen, the saturation currents being nearly proportional to the pressure when the latter was small. There is little reason, therefore, to identify as type (i) the emission from a gold surface at a temperature some hundreds of degrees lower.

On the other hand, if the above explanation of the function of

* As will be shown later, the ionic currents were far too small to give rise to "space charge" effects.

† Richardson, "The Emission of Electricity from Hot Bodies," Longmans, 2nd edtn., p. 203. Since the usual procedure in thermionic experiments is to work with electrically-heated wire sealed by heavy leads inside a cold vessel, it is clear that the emissive power ascribed to glass would not be a disturbing factor.

the glass wall is correct, we must ascribe to the metal gauze all the properties of " new " wires described by Richardson, and identify the ions as those of potassium and sodium (*idem*, *ibid.*, p. 210), for even at the high temperatures used by him, Richardson found that unless the metal filament were well glowed-out, these ions, though present only as impurities, entirely masked the positive emission due directly to the oxygen. So far from this being practicable in our experiments, the conditions were actually those which favoured the revival of type (ii) emission in " glowed-out " wires : there can be little doubt, therefore, that the observed effects were due to alkali-metal carriers.

The Rôle of the Gas.—Since, after the partial removal of gas from the system, the leakage currents did not attain the values characteristic of the new pressure until after the lapse of some time, it follows that the electrical effects were conditioned, largely at any rate, by absorbed or occluded oxygen, and not directly by the pressure of dead-space gas. On this basis only does it become explicable that, although the general effect of a pressure reduction was invariably to increase the leakage currents, the gradual accumulation of occluded gas in the dead space (following such a reduction) was associated with an increase in the current strengths under corresponding conditions.

The following table, based on a series of experiments carried out at 497°, illustrates this point; it is important to note that since the currents approximate to saturation, the results are not affected in any way by what is happening at the glass wall.

The values of the " limiting deflexion " given in the table indicate that a similar argument applies also to the " equilibrium " potential, which displays a noticeable drift with time. In this case, however, the drift may be partly associated with processes taking place at the second electrode, *i.e.*, the glass wall.

Expt.	Time after pressure reduction (mins.).	Deflexion in first minute after earthing (mm.).	Limiting deflexion (mm.).	Pressure (mm.).
XII A′	16	—20	—	—
	25	—	—40·5	0·0102
XII A″	28·5	—23	—	—
	38·5	—	—41·5	0·0105
XII A‴	68	—35	—	—
	70	—	—42·9	0·0116

It has been established by Richardson and Robertson (*Phil. Mag.*, 1922, **43**, 162) that the influence of occluded gas on the *electronic* emission of metals is due primarily to their effect on the contact *E.M.F.*, which is a measure of the work ϕ necessary to remove the electron from the interior of the metal to a point at

infinity. The effect of gases generally, and of oxygen invariably, being to depress the electronic emission, it follows that ϕ is increased thereby. Since an exactly corresponding effect must also be operative in the case of the positive emission, it seems at first sight that the effect of oxygen should be to increase this emission from the metal. There is, however, a material as well as the electrical factor here to be considered (Richardson, *op. cit.*, p. 243), and it does not therefore follow that an influence which depresses the negative emission must stimulate the positive : on the contrary, the work done in removing both a positive ion and an electron to infinity must depend on the magnitude of the cohesive force in the interior of the metal, which may be considerably influenced by the presence of occluded gas (Bangham, *Phil. Mag.*, 1928, **5**, 737).

Measurement of True Ionic Currents.—If a probable value is assigned to the capacity of the electrical system of which the insulated quadrants and the gold electrode form the extreme elements, approximate values of the currents may be calculated by taking tangents to the potential–time curves illustrated in Fig. 2. On the basis of a capacity of 10^{-10} farad, the family of curves VI to XI C is found to represent initial currents ranging from 5×10^{-14} to 3×10^{-13} amp. These figures do not necessarily, however, represent the true ionic currents, for the reason that glass, even when hot, is but a poor conductor, and, by allowing the charges partly to accumulate on its surface, may give rise to induction effects. This accumulation continues until the leakage current through the glass (passing perhaps to the outer surface of the vessel, and thence to the earth-connected coil of piping) becomes equal to the ionic current passing between the electrodes.

To eliminate these secondary effects from the measurement of the currents and from the determination of the characteristic potential–current curves, a static method of measurement was adopted. The apparatus was so modified that the gold electrode could be connected to the potentiometer either (i) as before, by a lead of negligible resistance, or (ii) through a known liquid resistance (about 10^{12} ohms).

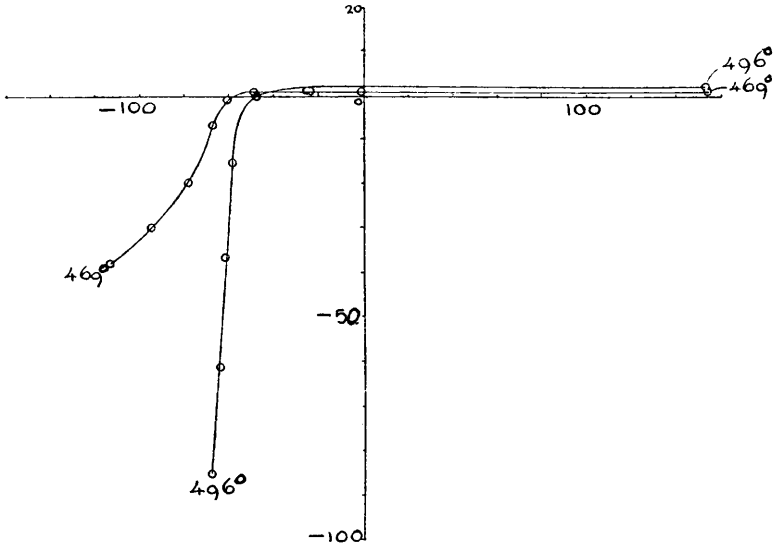
The procedure was then as follows : A known potential was given to the gauze, and the deflexion noted. By means of the mutating key the high-resistance lead was then substituted for the direct one. Under these conditions the ionic current manifested itself by setting up an appreciable *P.D.* between the potentiometer terminal and the gold electrode. To measure the current, now flowing equally through all parts of the system, it was necessary only to note the difference between the new and the old deflexion, and

divide the corresponding voltage by the resistance of the liquid column.

The graphs in Fig. 3 are typical of the results so obtained. The flat portions on the right represent the saturation positive-ion currents passing from the gauze to the wall when the former is positively charged; these currents were of the order of 10^{-13}—10^{-14} amp. according to the temperature of the system and the pressure of the gas. With the gauze negatively charged, much greater currents (up to about 10^{-12}) were found, and here, as the graphs indicate, there was no approach to saturation.

FIG. 3.

Current-potential curves for oxygen vacuum.



Abscissæ = Potential of gold.
Ordinates = Resultant current from gold.

A comparison of the saturation currents at the two experimental temperatures (and otherwise corresponding conditions) permits a rough calculation to be made of the characteristic constant b in the thermionic equation $i = A\sqrt{T}e^{-b/T}$, where i is the (saturation) current and A a constant. Such calculations, though subject to considerable uncertainty on account of the smallness of the temperature range, indicate that b probably does not exceed $1{\cdot}5 \times 10^4$. Since this constant never appears to fall below 3×10^4 in the case of the electronic emission from different metals, whilst in the case of the positive emission it certainly takes much smaller values ($1{\cdot}34 \times 10^4$ in the case of silver; Richardson, *op. cit.*, pp. 205, 206;

Brit. Assoc. Reports, 1904, 473), there can be little doubt as to the sign of the charges carrying the current.

Experiments with Nitrogen and with Hydrogen.—Following the series described, similar experiments were carried out with nitrogen and hydrogen at 468°. The former gas gave results strikingly similar to those with oxygen. The equilibrium potentials were invariably lower (*i.e.*, more negative) and the saturation currents greater than at corresponding pressures of oxygen.

With hydrogen the results were somewhat different. Even at the lowest working pressure (0·0238 mm.) the equilibrium potential was about 0·30 volt lower than the standard *in vacuo* measurement of 0·90 volt, whilst a 100-fold increase of pressure was without appreciable influence on its value.

With regard to the magnitude of the currents, hydrogen at 80 mm. had very little effect on the initial current from the gold to the glass when the former was charged to + 3 volts and then insulated, although it had some effect on the initial " post-earthing " current. At lower pressures the effect of this gas was markedly to stimulate the positive-ion emission from the metal. At a pressure of 0·0238 mm. the saturation current was nearly four times its normal *in vacuo* value.

Summary and Conclusions.

(1) The attempt here described to reproduce quantitatively the phenomena observed by Hartley has proved unsuccessful. This is by no means surprising in view of the known dependence of the effects in question on the past history of the metal.

(2) Nevertheless, at the temperature used, oxygen was found to give rise to a positive displacement of the " equilibrium potential," and hydrogen to a negative. Whilst the displacement caused by the former gas was found to be a function of its pressure, that of the latter was independent of the pressure over a wide range.

(3) The charging-up of the metal is in the nature of a Volta effect, depending on an intrinsic difference of potential between the metal and the glass wall of the containing vessel. As such, it is dependent for its manifestation (but not for its existence) on the dynamical exchange of ions between the two surfaces.

(4) Under the conditions of the experiments, the ions in question were neither electrons nor charged oxygen corpuscles, but were probably of the same nature as those found by Richardson to be emitted from " new " wires of various metals; they are therefore identified as ions of potassium and sodium.

(5) The power of the metal to emit these ions is diminished by the presence of occluded oxygen or nitrogen. Hydrogen at low

pressures stimulates the emission—a fact undoubtedly connected with the direction of its influence on the equilibrium potential.

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