

18. *On Active Nitrogen. Part IX. The Electrical Conductivity of Active Nitrogen.*

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It was observed by Burke in 1901 (*Phil. Mag.*, **1**, 342, 455) that the yellow-white after-glow which is obtained by the electrodeless discharge in air at pressures of *ca.* 0.2 mm. exhibits marked electrical conductivity which is not due to charged particles from the actual discharge, since (i) it persists long after all ionisation may be expected to have disappeared through recombination, and (ii) it may be observed in a stream of the luminous gas which has passed through an ion trap. Burke also found, *inter alia*, that cathode rays destroy the glow, but did not test the effect of this upon the conductivity. Strutt (*Proc. Roy. Soc.*, 1912, **87**, *A*, 179), working with nitrogen containing only a trace (1 : 1000) of other gases, found that the conductivity may be very high, currents of *ca.* 20 microamps. being obtained when a potential of some 200 volts was applied across two parallel plane electrodes between which glowing nitrogen was passing, but that even when a saturation current had been reached, the luminosity, and the ability of the active nitrogen to excite spectra, persisted unimpaired. He therefore concluded that charged particles are not primarily responsible for the phenomena connected with active nitrogen; rather did it appear that the conductivity was to be attributed to the production of a few

ions, probably by the effects of resonance radiation, during the reversion of the active nitrogen to the inert variety.

Constantinides (*Physical Rev.*, 1927, **30**, 95) repeated the experiments of Strutt and found that the currents obtained at saturation depend upon the geometry of the testing electrodes, the conductivity under given conditions of gas flow, pressure, etc., depending upon the area of the cathode; whence it follows that a surface effect is involved, and that the conductivity is most probably due to electrons emitted from the metal plates used as electrode either (i) under the influence of light of very short wave-length present in the after-glow, or else (ii) through impact of the active nitrogen, which was considered, from a correlation of these results with observations upon the effect of addition of other gases, to be a metastable molecule with an energy lying between 9.4 and 10.4 volts.

An interpretation of the results of Constantinides has been made possible by two recent investigations, as follows.

1. Compton and Boyce (*Physical Rev.*, 1929, **33**, 145) have shown spectroscopically that glowing nitrogen contains four separate modifications of the element, *viz.*, (i) neutral unexcited atoms, (ii) metastable nitrogen atoms with an energy of 2.37 volts, (iii) similar atoms with 3.56-volt and (iv) 8.1-volt metastable molecules.

2. Oliphant (*Proc. Roy. Soc.*, 1929, **124**, A, 228) has found that metastable atoms of helium in the 2^3S ground level of the triplet system, and having an energy of 19.7 volts, liberate electrons upon impact with gas-free molybdenum, the maximum energy of emission (E) agreeing very closely with the value calculated from the equation $E + \phi = M$, where M = the energy (in electron-volts) of the metastable atom, and ϕ = the work function of the metal (see also Webb, *Physical Rev.*, 1924, **24**, 113; Messenger, *ibid.*, 1926, **28**, 962).

We may thus expect that since this property of inducing electron emission is very probably a general characteristic of excited molecules, a phenomenon will be observed in active nitrogen similar to that obtaining in helium, and the experiments of Constantinides appear to confirm this view if we adopt the second of his suggestions as to the cause of the conductivity of the after-glow. The problem of verifying this deduction is simplified when we remember that since no metals possess work functions of much less than *ca.* 4 volts, the 2.37- and 3.56-volt metastable atoms should not be able to induce electron emission, and that the 8.0-volt metastable molecules only should be thus effective.

The present communication describes experiments upon the conductivity phenomenon which have been undertaken in the

course of a systematic physicochemical study of the properties of active nitrogen.

EXPERIMENTAL.

1. *The Possible Effect of Ions upon the Chemical Reactivity of Active Nitrogen.*

The first series of experiments was devoted to an attempt to decide whether charged bodies play any part in the chemical reactions of active nitrogen, a point which had not previously been examined.

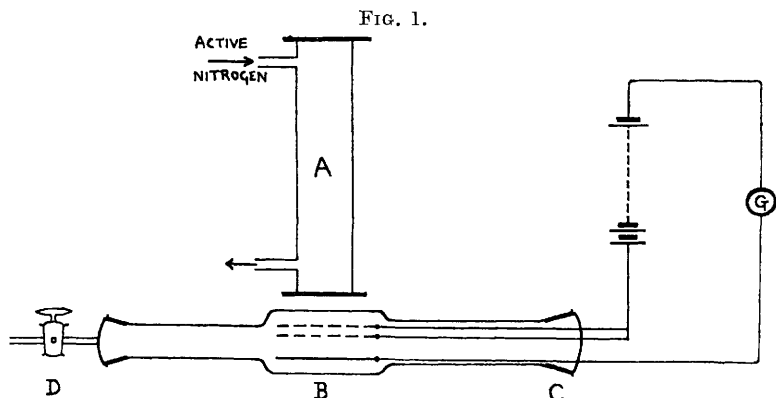
Nitrogen, freed from oxygen by hot copper and from carbon dioxide and water vapour by soda-lime and phosphorus pentoxide, was activated by a condensed A.C. discharge, and passed first between two aluminium plates 10 cm. long and 1 cm. apart, and then into a bulb to which nitric oxide could be admitted. Determinations of the concentration of chemically active nitrogen were made alternately (a) with both plates connected to earth, and (b) with up to 400 volts across the plates; 48 such experiments, conducted under widely varying conditions of pressure and gas-flow speeds, showed that the results obtained with a saturation field on and off differed by less than the errors of the determination, from which we conclude that the removal of all charged bodies from active nitrogen is without effect upon its chemical activity. In view of the entirely negative result of these investigations, it did not seem worth while to apply the test to other reactions of active nitrogen such as that with atomic hydrogen and with mercury (compare Tiede and Chomse, *Ber.*, 1930, **63**, 1839). This does not, of course, eliminate the possibility that the charged bodies may act in proportion to their concentration relative to the active nitrogen (*ca.* 1 : 1500, see below), but it is clear that they cannot initiate any chain reactions, etc.

2. (A) *The Conductivity of the Glow as a Surface Effect and (B) the Alternative Mechanisms of Ion Production.*

(A) Active nitrogen was drawn down a tube into which were sealed two plane electrodes of polished zinc, one 33.7×2.5 cm., the other 33.7×0.9 cm., and 2 cm. apart; with the larger electrode as cathode, the current obtained at saturation was 2.6 times that obtained with the smaller as cathode; since the areas are as 2.8 : 1, our result agrees with that found by Constantinides.

Addition of another ion-trap up-stream from the main one merely reduced the over-all conductivity due to the increased natural decay of the active nitrogen before it reached the testing electrodes, the current ratio being the same as before.

(B) 1. The apparatus used here is shown in Fig. 1. Glowing nitrogen was drawn through the tube *A*, which was 35 cm. long, 3.7 cm. in diameter, and fitted with plane quartz windows at each end. A second tube *B*, also made of thin quartz, was supported just below *A* and contained three aluminium electrodes, one a plate 10×1 cm., and the others gauze of 1.2-cm. mesh and made of wire of 0.5-mm. thickness, which were sealed to platinum leads brought in through the ground joint at *C*; a mercury-diffusion pump with liquid-air trap attached at *D* enabled the tube to be highly evacuated, and attached to the exhaust tube were connections to the McLeod gauge and a small gas burette from which the pressure in *B* could be adjusted to any desired value. It was hoped that the grid-plate arrangement might permit of the approximate evaluation of the energy of emission of any photo-



electrons ejected from the plate, whereupon, the work function of the aluminium being known, the wave-length of the light concerned could be estimated.

A preliminary experiment, in which both grids were connected to the anode, showed, however, that when the glow in *A* fell upon the plate in *B* no current at all could be detected in the electrode circuit even by a galvanometer of sensitivity 3×10^{-10} amp./mm.; it was thought that the failure to detect emission from the plate might be due to unfavourable surface conditions, so attempts were made to activate the plate (i) by degassing it by heating in a vacuum, and (ii) by degassing followed by admission of oxygen, carbon dioxide, and other gases over a wide range of pressures according to the technique employed in the construction of gas-filled photocells; negative results were obtained in all cases, however.

A final test of the photo-emission properties of the plate was made by irradiating it with the unscreened light from a mercury

arc in a quartz tube placed above the upper end of the tube *A*, the intense illumination thus passing through inert nitrogen in *A* and thence to the aluminium surface in *B*; a decided emission was obtained, but at most only *ca.* one-hundredth of that when the metal was actually *in* active nitrogen.

The previous history of the quartz apparatus enabled the assumption to be made that it was fairly transparent down to 1800 Å., from which we conclude that if the photo-emission hypothesis is correct, the light which is responsible for it must be of wave-length less than this. In view of the very thorough investigations made by numerous workers upon the active nitrogen spectrum (see Kneser, "Ergeb. exakt. Naturwiss.," 1929, pp. 229 *et seq.*), it is difficult to assume the existence of any radiation of such wave-lengths and in sufficient intensity to give rise to such marked effects, and we therefore conclude that the conductivity cannot justifiably be ascribed to a photo-emission process and that another explanation must be sought.

2. Assuming that the conductivity is attributable to a deactivation of metastable molecules at the electrode surfaces, we may proceed (*a*) to calculate the probable magnitude of the conductivity; (*b*) to examine the effect of processes which are supposed to destroy the 8-volt metastable molecules, *e.g.*, heating and the passage of a weak high-frequency spark in the glowing gas (Strutt, *Proc. Roy. Soc.*, 1916, **92**, *A*, 438; Bay and Steiner, *Z. physikal. Chem.*, 1930, *B*, **9**, 93; Cario and Kaplan, *Z. Physik*, 1929, **58**, 369); (*c*) to investigate how far it is affected by the wall poisoning which is known to be of such importance in active-nitrogen phenomena; and (*d*) to determine the energy of the metastable bodies by a technique similar to that employed by Oliphant.

(*a*) According to the Cario-Kaplan theory of the nature of active nitrogen, the 8-volt metastable molecules to which we attribute the conductivity are formed in a triple collision: $2N + N_2 \longrightarrow N_2^8 + N_2$. We may calculate, by means of the equation for triple collisions given in Part VII (J., 1930, 336), what will be the rate of production of these metastable molecules, assuming them to be formed in the reaction just given. In nitrogen at 3 mm. pressure and containing 1% of such atoms, the average value obtained in ordinary discharges (see Wrede, *Z. Physik*, 1929, **54**, 53; Crew and Hulbert, *Physical Rev.*, 1927, **30**, 124), we have $\lambda_1 = 7 \times 10^{-1}$ cm., $v_B = 10^{17}$, with other values as before, whence the mean rate of formation of the N_2^8 is 2.86×10^{12} /c.c./sec. We may show that each of these metastable molecules will collide with the testing electrodes *ca.* 10^3 times in passing through an ion trap consisting of two parallel plane electrodes 2×30 cm.

and 1 cm. apart, and hence, assuming that all are deactivated by impact upon the metal surfaces and that each metastable molecule yields one electron, we have :—

$$i_{\text{calc.}} = 2 \times 30 \times 2.86 \times 10^{12} \times 1.6 \times 10^{-19} = 2.75 \times 10^{-5} \text{ amp.}$$

In a typical experiment, nitrogen flowing at 2700 c.c./hour (measured at N.T.P.), the pressure in the apparatus being 3 mm., gave a saturation current of 1.6 microamps.; hence the ratio

$$i_{\text{calc.}}/i_{\text{obs.}} = 2.75 \times 10^{-5}/1.6 \times 10^{-6} = 17.$$

We may thus say that the concentration of 8-volt particles as calculated is of the order demanded by hypothesis, but if any undergo deactivation in the gas phase as a luminiferous process, the conductivity observed will clearly be less than that expected; this point will be discussed later.

(b) The thermal and/or electrical destruction of the active nitrogen glow first observed by Strutt has been attributed to a deactivation of the 8-volt metastable molecules (Kaplan; Bay and Steiner, *loc. cit.*), and we should thus expect that when the luminosity is removed the conductivity should also vanish if the phenomenon be, as we suppose it is, due to these molecules. Experiments showed that this is the case, although, as found before (J., 1927, 2831), it is possible to maintain the chemical activity almost unimpaired by an appropriate choice of working conditions.

(c) When another gas is added to a stream of luminous nitrogen, four things may happen, *viz.*, (i) chemical reaction (*e.g.*, as with nitric oxide), (ii) catalytic destruction of any or all of the metastable atoms and molecules present (*e.g.*, as with oxygen), (iii) enhancement of the glow through diminution of the wall reaction (compare Parts VII and VIII, J., 1930, 336, 1146), and (iv) a mere dilution effect. Of these possibilities, (i) and (ii) can be eliminated by an appropriate choice of the gases added, while (iii) may be considered in the light of previous findings upon the decay of the glow in the presence of other gases. This leads to the supposition that addition of a gas which is not effective under considerations (i) and (ii), but is strongly adsorbed by the walls, will probably lead to an increase in the glow intensity and a diminution in the conductivity through reducing the surface available for deactivation of the metastable molecules.

A tube was therefore constructed (Fig. 2) and provided with two parallel plane electrodes of aluminium 35×2 cm. and 1.5 cm. apart; the ends of the tube were blown to be as thin and as flat as possible, and side tubes were provided just beyond the ends of the electrodes so that active nitrogen could be drawn through. Two caesium photocells used in earlier investigations (Parts VII

and VIII, *loc. cit.*) were mounted in parallel at the end of the tube so that measurements could simultaneously be made of current and glow integrals; a side tube on the active-nitrogen inlet enabled other gases to be added as desired, regulation of the gas concerned being effected by a capillary valve. Previous experiments having shown that both carbon dioxide and nitrous oxide are probably strongly adsorbed under these conditions (Parts VII and VIII), these gases were admitted in gradually increasing quantities while simultaneous measurements of glow and current were made. It was found that in both cases the glow intensity gradually increased to a maximum beyond which further addition of diluent had little or no effect, while the current first rose to a maximum and then fell away, the decrease being very rapid in the case of nitrous oxide.

We explain these observations as follows. The addition of a small amount of the diluent gas gives rise to a photogen, *i.e.*, a wall-poisoning, effect, which stabilises the active nitrogen in the tubes leading to the conductivity-measuring part of the apparatus, with the result that much more active nitrogen reaches this zone than when no photogen is provided; but when the amounts of diluent are small, the surfaces are not well covered by a film of adsorbed gas (which will be in equilibrium with that in the gas phase proper), and hence there is a high electron emission due to the exposure of the metal to the impacts of the metastable particles. As the quantity of gas added is increased, the adsorbed film becomes thicker and more extensive, so that finally a point is reached where the active nitrogen entities can reach the metal only upon rare occasions and are compelled instead to suffer deactivation as a luminiferous process in the gas phase. It is a consequence of this hypothesis that, for a given concentration of active nitrogen, the current minimum will coincide with the point of maximum glow, and *vice versa*, which was very nearly the case in our experiments, but the nitrous oxide is apparently a much more effective inhibitor of the deactivation process in which the electron is emitted, although the photogenic actions of this and of carbon dioxide are, as found earlier (Part VII); practically identical.

Oxygen, when added in minute traces, enhanced both conductivity and luminosity (*i.e.*, acted photogenically), but above *ca.* 0.03% feed, both glow and current fell away, the curves running approximately parallel. This would suggest that the 8-volt metastable molecules are catalytically destroyed, as well as the 2.3- and 3.5-volt metastable atoms (compare Parts I and II).

When hydrogen was added under similar conditions, the current rose to a very high maximum when small amounts were present,

and then decreased rapidly to a point beyond which further addition diminished the conductivity only slightly. The glow similarly increased a little, but to nothing like such a great extent, the peak in the plot of glow intensity against quantity of diluent added being not at all marked, and occurring, moreover, at a point where the current had fallen to well beyond half of its highest value.

The effects of traces of the diluent were even more marked when the gas was caused to exhaust itself slowly from the apparatus by turning off the inlet tap; in such a case a point was eventually reached when the conductivity momentarily rose to *ca.* 20×10^{-6} amp. and then fell to less than 10^{-7} amp. A somewhat similar "kick" was also observed with nitrous oxide when the diluent was similarly shut off, but no rise to a maximum could be detected in the curves in this case; it may perhaps occur with very small additions of diluent which our apparatus could not handle, and hence may have been overlooked.

We find it very difficult to explain this phenomenon, but suggest that it may be connected with the observations of Rupp (*Z. Elektrochem.*, 1929, **35**, 586) and Suhrmann (*Physikal. Z.*, 1929, **30**, 939). The former has shown that hydrogen may penetrate into metals to a considerable distance even at ordinary temperatures and comparatively low partial pressures of the gas, and the latter has observed that when a metal containing such adsorbed hydrogen is heated in a vacuum, the photoelectric threshold is momentarily displaced towards longer wave-lengths, resulting in a temporary increase in both photoelectric sensitivity and emission. It has furthermore been shown by Kingdon (*Physical Rev.*, 1924, **24**, 510) that the thermionic emission from a metal is very sensitive to minute changes in the fraction of metal surface covered by an adsorbed film of gas, and both his investigations and those of Fowler (*Proc. Roy. Soc.*, 1930, **128**, *A*, 123) go to show that the maximum electron emission may be expected from a surface which is neither very clean nor very dirty, in the chemical sense, but at some intermediate condition (see also Langmuir, *Physical Rev.*, 1913, **2**, 450).

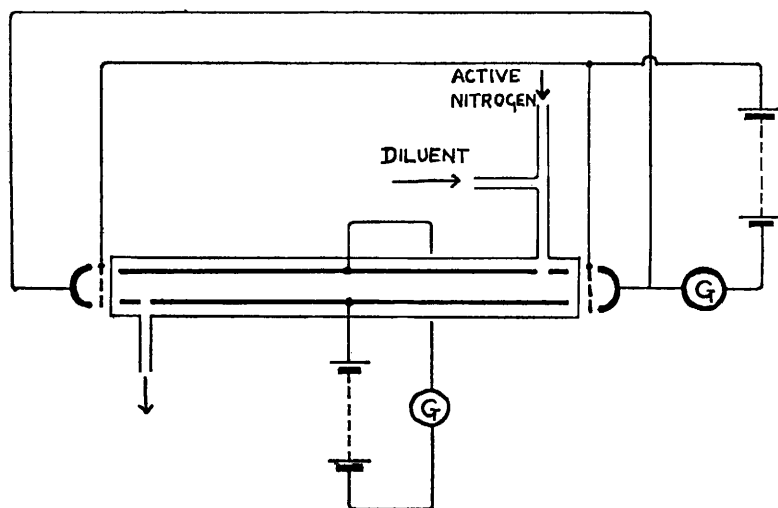
We are, therefore, of the opinion that the hydrogen or other gas which is present upon the surface when but a minute concentration exists in the gas phase may so alter the work function that the probability of electron emission following an impact of a metastable molecule will be greatly increased for the short time during which the state of affairs exists, and hence the observed conductivity will approach more nearly to that calculated.

These observations suggest that the conductivity would be greatly enhanced were the testing electrodes to be kept free from

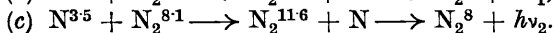
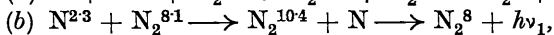
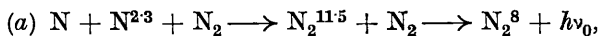
an adsorbed gas film through being heated, and in experiments now in hand upon the evaluation of the energy of the metastable molecules by a method similar to that used by Oliphant, indications have been obtained that this explanation may be realised. Details will be published later, but it may briefly be stated that so far the results obtained agree with those which are anticipated.

In conclusion, we suggest that these experiments offer a valuable physicochemical clue to the nature of the mechanism of emission

FIG. 2.



of the after-glow. According to spectroscopic data, quoted by Kneser (*loc. cit.*), the choice lies between the processes

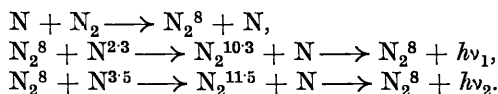


The mechanism (a) was suggested by one of us (E. J. B. W.) in an earlier communication (Part VII), the author having overlooked the fact that it was also favoured by Birge (see Kneser, *loc. cit.*, p. 244, etc.); and its advantages in connection with purely physicochemical work upon active nitrogen were there fully discussed: mechanisms (b) and (c) are, as stated by Kneser, necessary to explain intensity distributions in the after-glow spectrum, but it does not yet appear possible to decide whether (a) is the principal reaction with (b) and (c) as simultaneous but subsidiary processes, or whether these last-named are really the most important.

In these experiments we have, however, presented evidence that

the high electrical conductivity, which we attributed to electron emission consequent upon the deactivation of N_2^8 at the electrode surfaces, is to be associated with weak after-glow; moreover, when we should expect the electrodes to be well covered with a protective film of adsorbed gas the glow is strong. This clearly suggests that the 8-volt metastable molecules play an important part in the glow-emission, and that mechanisms (b) and (c) are probably to be preferred to mechanism (a).

The overall glow-emission process will then be

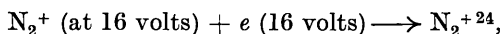


The bimolecular excitations of the N_2^8 molecules will naturally be much more frequent than the termolecular processes of formation, and hence the latter will be the rate-determining step in the total reaction; this accounts for the apparent third-order decay process of the glowing nitrogen found by Kneser and also by Willey.

It is worthy of note, in this connexion, that no very definite suggestions have hitherto been made as to the origin of the $N^{2\cdot3}$, which we still believe, on the balance of evidence, to be the chemically active modification of nitrogen, and we now suggest two possible methods for its formation.

(a) The 24-volt excited ion N_2^{+24} is well known to dissociate upon collision into one neutral and one ionic atom; $N_2^{+24} \longrightarrow N + N^+$ (see Smyth, *Proc. Roy. Soc.*, 1924, **108**, A, 116; Turner and Samson, *Physical Rev.*, 1929, **34**, 373; Hogness and Lunn, *ibid.*, 1926, **26**, 786).

Since the heat of dissociation of $N_2 \longrightarrow 2N$ is 9.5 volts, the energy left for the system $N + N^+$ is $24 - 9.5 = 14.5$ volts, of which the process $N \longrightarrow N^+ + e$ will account for 12.2, leaving 2.3 volts for the atom N. This conclusion is supported by experiments of Kenty and Turner (*Physical Rev.*, 1928, **32**, 799), who found that, when active nitrogen is passed over a chemically clean hot tungsten filament, a surface layer of adsorbed nitrogen is formed which appears to be about one atom thick; the layer does not form when the nitrogen is activated by controlled electron bombardment unless the accelerating voltage exceeds the ionisation potential of nitrogen ($N_2 \longrightarrow N_2^+ + e$ at ca. 16 volts), and its rate of formation is greatly accelerated at ca. 24 volts. Our hypothesis is well in accord with these observations; since we may expect a certain amount of electronic excitation of ions already produced at the lower potential, *i.e.*,



the appearance of the layer at the ionisation voltage is explained (compare also Lukirsky and Ptizyn, *Z. Physik*, 1931, **71**, 339).

(b) A further hypothesis, admittedly somewhat speculative, is based upon the recent observations of Oliphant and Moon (*Proc. Roy. Soc.*, 1930, **127**, A, 373). They have shown that a positive ion of helium may capture an electron from a metal to form a highly excited atom which immediately passes to its nearest stable state, in their case the 19.77-volt metastable level. This follows since the ionisation potential of helium is 24.6 volts, and the work function of their nickel target 4.77 volts, whence the energy of the excited atom is $24.6 - 4.77 = 19.83$ volts: to account for the difference of 0.06 volt is not germane to our argument.

The excited body formed from a nitrogen ion N_2^+ would have an energy of *ca.* 16 volts, whence, taking 4 volts as an approximate value for the work function of the electrode in a discharge tube, we see that a molecule with $16 - 4 = ca.$ 12 volts might be formed in a similar manner. This, being very unstable, would dissociate to give one neutral and one excited atom: $N_2^{12} \longrightarrow N + N^*$, and since the reaction $N_2 \longrightarrow 2N$ requires 9.5 volts, the energy of the N^* would be *ca.* 2.5 volts.

It is hoped that experiments now in progress upon the production of active nitrogen in various zones of the discharge will provide decisive information upon this very interesting question.

Summary.

1. The removal of charged particles from active nitrogen does not affect its reaction with nitric oxide and presumably its general chemical reactivity.

2. Experiments by Constantinides have been confirmed, showing that the conductivity of active nitrogen is most probably due to emission of electrons from the testing electrodes.

3. The emission is not photoelectric in character, but due to actual impact of the active nitrogen upon the electrodes.

4. The conductivity appears to be due to ejection of electrons from the metal testing electrodes by deactivation of 8-volt metastable molecules incident thereupon.

It is a pleasure to express our acknowledgments to Professor F. G. Donnan, F.R.S., and Major F. A. Freeth, F.R.S., for their provision of means to conduct these experiments; we are also indebted to Mr. W. A. Bayliss for assistance in the experimental work.

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