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With aluminium cylinders on the other hand, the measurements show that approximately two-thirds of the ionization was due to the gamma rays, and one-third to the secondary rays excited by this radiation in the metal.

5. Calculations based on observations on the conductivity of air confined in different receivers lead to the conclusion that approximately 9 ions per c.c. per second are generated in free air by the penetrating radiation from the earth.

Before concluding I wish to acknowledge my very great indebtedness to Mr. V. E. Pound, for his kindness in repeating and verifying many of the observations described in the first part of this paper.

The Physical Laboratory,
University of Toronto,
July 1, 1907.

LXXXVI. *A Gas generated from Aluminium Electrodes.*

By R. v. HIRSCH, *Ph.D.*, and F. SODDY, *M.A.**

IN a recent paper (R. v. Hirsch, *Phys. Zeit.* vol. viii. p. 461, 1907) one of us showed that when cathode rays were generated by means of an influence machine in pure gases, the relation between the gas pressure p and the discharge potential V could be represented by

$$p^2V = \text{constant}.$$

This relation holds for the pure gases examined independently of the amount of current flowing through the tube, but does not hold at all for gaseous mixtures. During the passage of the discharge, a gas is continuously evolved from the electrodes if these are of aluminium, which renders the gas initially filling the tube impure, so that the above relation ceases to hold. But if the discharge is passed for some hours, the gas being pumped out as evolved so as to maintain the pressure within the range required for the production of cathode rays without unduly increasing the resistance of the tube, the value of p^2V again becomes a constant independent of the nature of the gas initially filling the tube and about one-quarter of the value for hydrogen.

The value of p^2V appears to depend in some way on the molecular weight of the gas, for it is almost exactly fourteen

* Communicated by the Authors.

times less in nitrogen than in hydrogen. In the case of carbon monoxide and oxygen, the values of p^2V are about two-thirds that of hydrogen divided by the numbers 16 and 14 respectively.

The behaviour of the gas evolved from the electrodes indicates that it is not a mixture but a pure gas and that its molecular weight is 4 or some multiple.

In the present paper the nature of this gas is further examined. The first point was to see if the gas was helium.

The spectrum was the familiar one always obtained when a new spectrum tube is exhausted and the electrodes heated with a discharge, and consisted of hydrogen and the secondary spectrum of hydrogen together with faint indications of the strongest bands of carbon dioxide. The gas was subjected to the action of calcium volatilized by an electric furnace in the manner recently described by one of us (Soddy, Proc. Roy. Soc. vol. lxxviii. A. p. 429, 1907), and was found to be completely absorbed leaving no trace of helium.

The quantities of the unknown gas obtainable are too small for ordinary analysis, so it was attempted to identify it by its electrical behaviour, taking the values of p^2V for a variety of different substances in the hope of finding one giving a value one-fourth that of hydrogen.

The experimental arrangement was similar to that used before. The current was obtained from an 8-plate Wimshurst machine producing nearly half a milliampere when at full speed, so that the independence of discharge potential on the current could be verified within a larger range than formerly, in fact up to the point where the tube became perceptibly heated. The potentials were measured directly by a Kelvin electrostatic voltmeter.

In the search for the unknown gas the most valuable hint given by earlier results is the fact, that for mixtures p^2V is not constant, so that pure gases only have to be tried. But it was found advisable again to ascertain this point by trying several mixtures, between the components of which chemical action was excluded, special care being taken that the mixtures did not change during the investigation. The results are given in the following tables :—

I. 50 parts N ₂ + 32 parts H ₂ .		
<i>p</i> .	V.	<i>p</i> ³ V.
56. 10 ⁻³ mm.	1100 volt.	3449. 10 ⁻³
46	1900	4020
40	2800	4480
36	3800	5280
32	5600	5732
29	6700	5948
27	8800	6416
26	10400	7028
II. 24 parts N ₂ + 29 parts H ₂ .		
64	1100	4504
52	2100	5676
44	3300	6388
38	4600	6640
33	8000	8384
26	12800	8652
III. 16 parts N ₂ + 42 parts H ₂ .		
84	1200	8467
66	2300	10020
56	3400	10660
50	4800	12000
46	6000	12696
42	8000	14112
IV. 52 parts He + 48 parts H ₂ .		
196	1200	46096
158	2450	53704
132	3600	52580
114	4400	57180
110	5000	60500
105	6000	65148
92	9100	77020
80	13200	84480

At the end of series IV. the gas at a pressure of .08 mm. was subjected to volatilizing calcium. A residue of .042 mm. was left, corresponding to 52.5 per cent. of helium, which is very nearly the original composition.

To compare with these results, the values given by the unknown gas (taken in another tube) are given within a wider range than previously tested (p. 782).

The constancy of *p*³V here as compared with the inconstancy in the case of mixtures make it extremely probable that the unknown gas is a definite chemical body.

p .	V .	p^2V .
26	15000	10140
28	13000	10192
32	10000	10240
34	8000	9288
40	6000	9600
26	5000	10180
51	4000	10404
Mean value		10292
Hydrogen value		38120

The second indication given by earlier results is the probable connexion of the p^2V values with the molecular weights. But as this regularity mainly rests on the comparison of hydrogen and nitrogen, more gases ought to be tested. Unfortunately, the members of the argon family, which seemed best suited for this purpose, show the peculiarity that their behaviour is extremely dependent on very small impurities present (Strutt, *Phil. Trans.* vol. cxci. p. 377, 1900; Soddy, *loc. cit.*). Helium was tried and gave p^2V values much higher than hydrogen.

Several compound gases were then tried, choosing such bodies, the occurrence of which seemed possible for one reason or another. These gases are :—

Water vapour,
Carbon dioxide,
Methane,
Acetylene,
Cyanogen,
Hydrocyanic acid.

None of these gases could stand the discharge without changing; water vapour, methane and hydrocyanic acid split up into their components, the carbon compounds forming a thin carbon deposit on the glass near the cathode. Acetylene and cyanogen begin by polymerizing, the latter forming paracyanogen, which is deposited on the cathode, the former probably benzene. On the other hand, a partial decomposition sets in, the equilibrium altering with every change of pressure or potential. Carbon dioxide is less quickly decomposed, but is not stable enough to give satisfactory p^2V values. Moreover, it shows an anomaly otherwise not observed, the bulb becoming suddenly non-conducting with a small decrease of pressure, so that no readings could be taken above 5000 volts.

On the whole, all these gases were found altogether unlike the unknown gas, and small chance seems to be left to find it among the class of chemically compound bodies.

The only *positive* indication obtained is the following :— It was found impossible to obtain any gas out of the bulbs made in England, which always showed a marked absorption under the same conditions as those in which the bulbs obtained in Germany were generating the unknown gas. Comparing this with the fact previously noted, that the effect could not be obtained with copper nor with iron electrodes, it seemed reasonable to attribute this difference in behaviour to a difference in the aluminium employed. This view proved correct. When the electrodes were interchanged, those from the German tube gave gas when remounted in the new English tube. It is therefore probable that this aluminium contains an impurity responsible for the observed effect. Among the admixtures liable to be found in aluminium, the most likely are carbon, nitrogen, and sodium. The two first-mentioned elements suggested the examination of the cyanogen compounds, and to test the latter possibility one of the English aluminium electrodes was alloyed with sodium on its surface. This electrode now showed a behaviour very similar to the one exhibited by the German electrodes. On applying the coil much gas appeared, the cathode showing a marked scintillation. After a short time this action reversed, the induction current now absorbed gas. But on applying the steady current given by the Wimshurst machine, a continuous slow production set in, gradually ebbing down as in the case of the old electrodes. The p^2V values of this gas neither became really constant nor did they reach entirely the quarter of hydrogen value, but they came very near in both these respects. The following table gives a series of final values :—

p .	V .	p^2V .
28	12000	9408
31	9600	9224
36	8000	10368
38	7000	10708
44	6000	11616

The hydrogen value of the tube was 53,000. The values obtained in the beginning of the experiments were much lower and showed a much more decided slope. It is considered as consistent with these results, that the electrode alloyed with sodium behaves like the one made of German aluminium, with the difference that it is polluted by sodium carbonate, decomposing under the influence of the electric discharge, so that the unknown gas is only obtained in an impure state. This result, without solving the question as to the nature of this gas, changes the direction of the research in pointing to the electrode metal as a field of investigation.

It is improbable that the sodium plays more than an indirect part in the generation of the gas. The following suggestion seems at least probable. The presence of a trace of sodium in aluminium renders it, as is well known, capable of decomposing water, so that an electrode of such metal becomes charged with hydrogen, probably chemically combined as hydride, by mere exposure to air. The unknown gas may be a modification of hydrogen like ozone is of oxygen, capable of withstanding the discharge of an influence machine, but decomposed by the discharge of a coil. This theory is being investigated.

The question of the quality of aluminium used for the purposes of electrodes is of great practical importance. Of old, aluminium was manufactured by a process which rendered the presence of sodium unavoidable. A trace of sodium is, however, a very undesirable impurity technically on account of the metal being attacked by moisture, and the most strenuous efforts of recent years have been directed to increasing the purity of the metal for technical purposes, with the result that the aluminium to-day differs entirely from that first made. It is a very unsuitable material for the construction of electrodes, the discharge passing with difficulty and irregularity. Too great purity of the British aluminium may serve to explain some of the difficulties besetting the X-ray bulb manufacturers in this country.

We are indebted to the Carnegie Trust for the provision of the instruments used in this investigation.

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The University, Glasgow.

LXXVII. *Gradual Modification of the First Linear Spectra of Emission of Mercury. Preliminary Note by Prof. ENRICO CASTELLI* *.

[Plate XVII.]

THE recent discoveries made by Sir W. Ramsay on the transformation of several elementary substances, which were lately mentioned at the Congress at Parma of the Italian Association for the Progress of Science, have recalled in my mind a fact I observed about a year ago, in studying the luminous spectra of mercury.

I had found that in taking (with a Steinheil spectrograph, fitted with three quartz prisms) some spectrophotographs of the electric arc in the vapour of mercury, contained in a Uviol lamp, the spectrum lines (amounting only to 16, on account of the limited dispersion of the apparatus), while remaining constant in position, showed in time a gradual variation of their photochemical action: the lines corre-

* Communicated by Sir Wm. Ramsay, F.R.S.