

AN EXAMINATION OF THE ELECTROLYTIC  
METHOD FOR THE SEPARATION OF ISOTOPES.

by

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AN EXAMINATION OF THE ELECTROLYTIC  
METHOD FOR THE SEPARATION OF ISOTOPES.

In 1913, instead of writing "elements chemically identical and non-separable by chemical methods", Soddy<sup>(1)</sup> coined the name isotope, signifying the same place, to express the nature of the elements which occupied the same place in the list in the light of Moseley's new interpretation of the periodic law. This idea fitted in nicely with two others of that same year: (1) Thomson's parabola method of determining the masses of gaseous ions showing that ordinary, non-radioactive elements may be mixtures of the isotopes; (2) The new conception of atomic structure given by the Bohr theory<sup>which</sup> provided an explanation for isotopes.

According to the Bohr theory, certain outer electrons determine the chemical properties of an element. A marked success for Bohr's theory was the prediction of the way nuclei of varying masses would affect the behaviour of these chemically reacting electrons. For example, the difference between the wavelengths of the hydrogen lines of the Balmer series and alternate members of the Puppis series of helium was accounted for. Since that time many exact investigations have been carried out in order to find a difference in some chemical properties of isotopic elements/

elements. By 1931, no such research had been accepted as definitely successful.

At the beginning of 1931, Professor Kendall suggested that I should try to confirm an electrolytic separation of the isotopes of mercury, which he and Malcolm Haring had obtained in 1924. Haring electrolyzed out a small fraction of the mercury from a solution of a mercury salt. The density of this electrolytically deposited mercury was found to be nineteen parts per million less than the density of common mercury.

In his dissertation,<sup>(2)</sup> Haring gives a review of previous attempts at isotopic separation. A more recent review has been given by Jokowlew<sup>(3)</sup>.

The work on the chemical properties of isotopes will be briefly reviewed here.

Soddy's definition of an isotope as an element having identical chemical properties with another element was based on the careful work done in the years 1907 to 1913 by such investigators as Boltwood, Marckwald and Keetman, Hahn, von Auerbach, Svedberg, von Hevesy, Fajans, Russell, and Fleck.

Only the heavy radioactive isotopes of the radium, actinium, and thorium series were investigated.

The development of Thomson's parabola method, particularly by Dempster and Aston, led to the discovery/

discovery of many isotopic elements among the common, non-radioactive elements. These discoveries stimulated many new and varied methods for their separation. In general, these methods may be classified as physical or chemical.

The physical methods that have given a separation make use of a physical property that depends upon the mass of the atom, with the exception of the radioactive isotopes, where different half-life periods make automatic separations. Three successful physical methods are:

- I. The deflection of the ion in an electric field.
- II. Diffusion.
- III. Irreversible vaporization.

Some other similar experiments have not been successful as yet:

- I. Molecular dissociation and recombination.
- II. Migration velocities.
- III. The action of centrifugal forces.

Other experiments suggested but not yet tried are:

- I. Thermal diffusion.
- II. Gravity.
- III. Electron impacts.

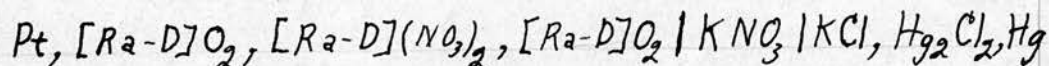
The chemical methods are those that depend upon the properties of the valence electrons. The following have/

have been unsuccessful:

- I. Recrystallization.
- II. Selective chemical reaction.
- III. Selective excitation of a photochemical\* (3A) reaction by light of different wavelengths.
- IV. Electrolysis.

The history of the electrolytic method will now be considered in greater detail.

The early work was done with the radioactive isotopes. Paneth and Hevesy<sup>(4)</sup> showed that in the electrolytic deposition of RaE, the decomposition voltage is altered by the addition of Bi to the same extent as required by Nernst's theory had the same quantity of Ra E been used instead of Bi. Similar results were obtained in the case of Th B and its isotope Pb. An attempt was also made to measure the electrode potentials of two isotopes by a direct experiment. Radium emanation was allowed to decay in a quartz vessel and the radium-D obtained was deposited electrolytically on platinum in the form of the dioxide. In this way  $10^{-5}$  mg. of lead produces a clearly visible and electrochemically active deposit on a fine platinum wire. The following galvanic chain was set up and found to have the potential, - 0.884 volt.



By substituting for the radium-D peroxide electrode a similar one prepared with ordinary lead, the potential was - 0.888 volt. The increase was not large enough compared with the experimental error to be definite.

More accurate experiments were made with solutions of isotopes. The addition of Pb ions to the solution of Ra-D produced the same change in E.M.F. as would be required by the Nernst equation for the same concentration of Ra D. From this it was concluded that in the Nernst equation,

$$V = \frac{RT}{nF} \lg \frac{C}{c}$$

the ionic concentration,  $c$ , should refer to the sum of the isotopic ions, and, hence, electrolytically, isotopic elements may fully replace one another.

Klemensiewicz<sup>(5)</sup> made a direct experiment upon the solution pressures of isotopes. An amalgam of lead and its isotope Ra B or Th B was washed with an acid mercurous salt solution. In this way successive fractions of the mixed isotopes were removed. No difference in the distribution ratio of the isotopes in these fractions was observed, although 0.5% could have been detected. With the aid of the Nernst equation the conclusion was drawn that the normal electrode potentials of Ra B and Th B are equal to that of Pb within  $2 \cdot 10^{-5}$  volt.

Lindemann, <sup>(6)</sup> from a consideration of the theoretical relations, found that isotopes should have different melting points, vapour pressures, and chemical properties. In the case of lead, he found that the discharge potentials of the two isotopes 206 and 208 would not differ by more than 0.001 volt, but would more probably differ by less than 0.0001 volt.

Mulliken <sup>(7)</sup> dissolved mercury electrolytically in K CN solution. It was hoped that the complex ion formed would be so stable that irreversible conditions could be obtained at the mercury-solution boundary. No separation was obtained.

#### THE ELECTROLYTIC PROCESS.

At the start of this work, the chief factor for consideration was the choice of a suitable electrolytic process for the isotopes to be tried. The process will be briefly described. The Nernst equation for the equilibrium potential,  $E_m$ , of a metal in a solution containing the corresponding metal ions at concentration  $c$  is given by,

$$E_m = E_{m_0} + \frac{0.058}{n} \log c$$

where  $E_{m_0}$  is the normal electrode potential,  $n$  is the valence and  $c$ , the concentration of the ion.

Ions may be removed from such a solution by electrolytic/

electrolytic deposition, a process analagous to chemical reduction except that in electrolysis the electrons affecting the reduction are obtained from an external source of direct current. Electrolysis has the advantage that it may be controlled and measured by means of its supply of electric current. If electrons are supplied to the electrode at a potential greater than  $E_m$ , the equilibrium potential, ions will take up an electron and plate out upon the electrode. The rate at which ions are removed is thus accurately controlled by regulating the supply of electrons. The point to be emphasized here is the way the concentration ratio of two elements having different normal electrode potentials may be varied by the deposition. For example, let us take a solution normal with respect to each of two monovalent ions which differ by 0.348 volts in their normal electrode potentials. If ions are removed from this solution at an equilibrium potential, Nernst's equation may be used to calculate the concentration ratio of the two elements deposited. As the normal potential of one is 0.348 greater than the other, its concentration, to give the same equilibrium potential, is given by the equation,

$$- 0.348 = .058 \log c$$

Thus  $c$  is  $10^{-6}$ , a concentration which is negligible for/



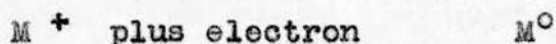
for most chemical purposes.

When this process is adapted to determinations of normal electrode potentials, the limit to the difference of potential measured is determined by the exactness with which the concentration ratios can be estimated. Thus if the concentration of one element is found to be changed by deposition to one tenth, it should differ in normal potential by .058 volts. Similarly for a concentration ratio of 1.1 the potential difference need be only 0.0024 volt and for the ratio 1.01, 0.00024 volt.

In practice various complications come in. As the actual mechanism of the process is little understood, it is difficult to predict just how each of these may affect the separation as for example:-

- (1) The potential is not such a direct function of concentration as given by the Nernst theory. Experimental values are expressed as the thermodynamic ion concentration or activity.
- (2) The process is not reversible. A potential which is in some cases considerably greater than that for equilibrium must be applied.
- (3) Even though the electrode potential, activity, and overpotential may all be favourable to a separation, still the separation obtained may be entirely offset if the process reverses itself with sufficient speed. The cathode process,  
if/

if perfectly reversible, is expressed by the equation,



(7)

Mulliken appreciates this difficulty so fully that he says, "It is probable that all attempts to separate isotopes by solution or precipitation processes, whether physical or chemical, involving the transfer of molecules or ions across the boundary between two condensed phases are doomed to fail, because of the difficulty of obtaining irreversible conditions at such a boundary".

Summing up, the conditions for the most successful operation of the process, which depends for a separation upon the difference in normal electrode potentials are:-

- (1) Low current density,
- (2) Irreversibility,

The factors considered in the choice of isotopes for separation were:-

1. The ratio of the mass of the electron to the mass of the nucleus.
2. The "isotopic moment"
3. The sensitivity and precision of the method of determining the distribution ratio.
4. Chemical properties suitable for electrolysis.

As/

As the isotopes of hydrogen had not yet been discovered, the next isotopic element in the series was lithium. The advantage of lithium over the other isotopes considered is shown by a table.

For Hydrogen	$\frac{M \text{ (electron)}}{M \text{ (nucleus)}}$	$\frac{1}{1840}$	
Lithium	"	$\frac{1}{1840 \times 6}$	$\frac{1}{11000}$
Tin	"	$\frac{1}{1840 \times 118}$	$\frac{1}{217,000}$
Hg	"	$\frac{1}{1840 \times 200}$	$\frac{1}{368,000}$
Pb	"	$\frac{1}{1840 \times 206}$	$\frac{1}{379,000}$

Aston<sup>(8)</sup> introduced the idea of "isotopic moment" as a factor in isotope separations. "The relative importance of an isotope in shifting the mean mass number is clearly, (abundance) x (distance from the mean mass number on the mass scale). The sum of such products for all the isotopes is a constant, of considerable interest, which may be termed the "isotopic moment" of an element. It will clearly be zero for a simple element and one for a complex element/

element (such as bromine) which consists of two equally abundant isotopes two units apart. This number is not only roughly proportional to the error to be expected in an atomic weight calculated from the mass-spectrum but is an accurate measure of the ease with which the atomic weight may be altered, per unit, artificially by such methods as diffusion or free evaporation".

The isotopic moments for the elements considered are:-

Lithium	0.11
Tin	1.77
Mercury	1.40

As the amount of the radioactive isotopes used with lead is very small, probably about one in  $10^{10}$  lead atoms, the isotopic moment is nearly zero.

The method considered most suitable for detecting a change varied in each case. For lead the radioactive indicator method used by Klemensiewicz<sup>(5)</sup>, and Paneth and Hevesy<sup>(4)</sup> would appear at first sight to be very exact. The method becomes complicated because the radioactive indicator is a member of a whole series which are decomposing simultaneously. If the  $\alpha$ -ray activity is measured with a leaf electroscope, the accuracy does not easily exceed 5%.

Since the atomic volumes of isotopes are the same/

same, Haring<sup>(2)</sup> used a density determination as the easiest and most precise means of investigating mercury. With a suitable pycnometer, balance, and temperature bath, densities can be measured to one part in one or two millions. Haring worked with a pycnometer of such small volume (0.44 cc.), that his accuracy was much less.

For lithium a direct atomic weight determination as worked out by Richards<sup>(9)</sup> offered exactness. Richards titrated a weighed amount of LiCl with silver, determining the end point with a nephelometer. The chief errors feared here were impurities in the LiCl such as Na, Br, or water. Richards obtained the atomic weight to one thousandth of a unit. Other methods considered were: (1) Density of a saturated salt solution. (2) Band spectra. (3) Atomic line spectra.

Two atomic weight methods were suitable for tin. Briscoe<sup>(10)</sup> titrated Sn Cl<sub>4</sub> with silver obtaining the atomic weight 118.69. Baxter and Starkweather<sup>(11)</sup> deposited in a mercury cathode the tin from a solution of Sn Cl<sub>4</sub> obtaining the value 118.703.

Mercury, lithium, and tin isotopes could also be determined with a mass-spectrograph.

The electrolysis of lead, tin, and mercury is easily accomplished in aqueous solution. Lithium, however, presents a difficult problem. Two ways of solving/

solving it were tried.

(1) Deposition in a flowing mercury cathode  
from an aqueous solution.

(2) Deposition from non-aqueous solutions.

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THE EXPERIMENTAL WORK WITH TIN AND LITHIUM.

Tin was easily deposited from a solution of the chloride in HCl solution. At a low current density, the tin grew out from the cathode as rectangular crystals. At higher current densities the cathode "treed" very badly. A mercury cathode was found to dissolve a large amount of the deposited tin. The mechanism of deposition in mercury should probably be a simpler process than the deposition on growing crystals.

It was found that lithium could be deposited as an amalgam in a mercury cathode. In order that the lithium ion will be reduced at the cathode in preference to the hydrogen ion, three conditions were necessary:

(1) The concentration of lithium ions must be large. For this purpose a concentrated LiCl solution was used.

(2) The concentration of hydrogen ions must be small. To affect this the electrolyte was kept saturated with lithium carbonate.

(3) The surface of the mercury must be clean in order to make use of the high overpotential necessary for the discharge of a hydrogen ion at a mercury surface.

An/

An arrangement was devised for continually circulating the mercury cathode. A small Erlenmeyer flask was fitted with a syphon outlet tube blown into the centre of its bottom. It was adjusted so that when the mercury layer on the bottom of the flask became greater than 5 mm., the excess would overflow through the syphon. A rubber stopper was fitted to the flask to carry the anode lead, the lithium carbonate supply tube, and the jet for dropping the mercury. The mercury jet was backed with a good pressure of mercury so that myriad numbers of very fine drops were formed. These falling drops did not unite with the mercury surface immediately beneath them, but raced across to the edge of the flask, where they piled up and coalesced. The mercury of the cathode was thus constantly replaced. As the amalgam formed it was covered with fresh mercury which made less probable any reversal of the deposition process. The dilute lithium amalgam then dropped from the syphon into a concentrated HCl solution, which was contained in a flask equipped with an overflow syphon similar to the electrolysis flask. As the overpotential for hydrogen was so high that the amalgam was not attacked by the acid, a platinized cathode was dipped into the HCl solution and connected to the amalgam thus forming a cell with hydrogen given off at the platinized cathode. This did not remove all the lithium, so/



so the amalgam was then dropped from a fine jet through a long column of  $\text{HgNO}_3$  solution. The circulation of the mercury was made automatic with the help of a water jet vacuum pump. By fitting an air inlet into the small 3 mm. suction tube which dipped into the mercury, alternate bubbles of air and mercury were formed which could easily be sucked up a height of ten feet. (This method of circulating mercury is described in L. Dunoyer's "Vacuum Practice") (12)

At the same time experiments were made with the non-aqueous solvents, acetone and pyridine. Acetone was tried first without much success. A solution of  $\text{LiCl}$  in acetone was made from fused  $\text{LiCl}$  and acetone. An excess of the fused  $\text{LiCl}$  was used so that it would thoroughly dehydrate the solution. An electrolysis with small platinum electrodes was tried. The cathode became covered with a black deposit while the anode was surrounded by a brown solution, which was thought to be a chlorination product of the acetone. The resistance of the cell was greatly increased, making impossible a successful electrolysis. When the black coated cathode was dipped into water the resulting effervescence indicated that metallic lithium had been deposited.

A similar electrolysis was then tried with pyridine as the solvent of the  $\text{LiCl}$ . The pyridine used was redistilled. After the first distillation it was shaken with a lithium amalgam for thorough drying/

drying and purification. An electrolysis with small platinum electrodes as before gave very much the same results. Although some small silvery trees of metallic lithium grew out from the cathode, the anode was covered with a brown solution very much the same as that in the acetone solution.

Kallenberg<sup>(13)</sup> (J. Phys. Chem. 3, 601 (1899) ) reports the successful deposition of metallic lithium on an iron cathode using a carbon rod as anode and an electrolyte of LiCl dissolved in pyridine. A carbon rod anode and an iron cathode were tried. With a current density of 2 m.a. per sq. cm., the first sign of a reaction in the cell was the appearance of small bubbles of gas at the cathode. Then a silver grey coating spread across the cathode while the gas evolution lessened. The gas may have been hydrogen obtained from traces of water. No gas was evolved at the anode, the solution did not become brown, nor did the current fall off at first, but after a few hours the solution became brown and the cathode deposit appeared fluffy. An explanation of this may be that the carbon anode absorbed the first of the chlorine liberated.

Therefore it seemed as if the electrolysis could be carried on in pyridine if a method could be found for disposing of the chlorine evolved at the anode. Several/

Several methods were considered. An absorbent like active charcoal might absorb the chlorine or a chlorine compound might be formed as with a silver electrode, while much the best method would be a lithium anode. Therefore an iron rod was coated with a little lithium by the above method and was made the anode in a cell with a mercury cathode. The potential of the cell formed in this way was sufficient to maintain a moderate current. As pyridine is not a pleasant solvent to work with, a new experiment was made with acetone, this time with the carbon anode. Silvery lithium was deposited on an iron cathode, but with a mercury cathode, a troublesome skin formed. At last, when it seemed as if two independent methods of depositing lithium would be available, the whole situation was changed completely by the announcement of the discovery of a hydrogen isotope of mass two with the possibility of another of mass three.

#### HYDROGEN.

The discovery of the hydrogen isotope followed upon its prediction by two independent methods. Birge and Menzel<sup>(14)</sup> (Phys. Rev. 37, 1669 (1931) ) suggested the possibility of a heavy isotope from a consideration of atomic weights. In July, 1929, R.T. Birge<sup>(15)</sup> summarized the "Probable Values of the General/

General Physical Constants" in the first number of the Physical Review Supplement. For the derivation of certain constants, he considers the "probable values" for the atomic weights of H, He, N, Ag, I, C, and Ca. At this time some of Aston's<sup>(16)</sup> mass spectrograph determinations had reached such great refinement as to be considered preferable to the chemical values. However, Birge points out that since the discovery of the oxygen isotopes by Giaouque and Johnston,<sup>(17)</sup> it is only permissible to use Aston's values as an indication of the relative abundance of  $O^{18}$  and  $O^{16}$ , and not as an atomic weight determination. As the values for the chemically determined atomic weights for H, He, N, and I agreed within the limits of accuracy with the mass-spectrograph values of Aston, it implied that in ordinary oxygen,  $O^{16}$  is more than one thousand times as abundant as  $O^{18}$ . This estimation was confirmed later by Babcock<sup>(18)</sup> with an estimation of the ratio as 1: 1250, and by Naude<sup>(19)</sup> as 1: 1075.

However, in 1931, Mecke and Childs<sup>(20)</sup> made a careful quantitative investigation of the A and A' bands of oxygen in the atmospheric absorption spectra and conclude that the relative abundance of  $O^{16}$  to  $O^{18}$  is 630 to 1. Aston's values based on  $O^{16} = 16,0000$ , are thus made 2.2 parts in ten thousand too large and the agreement with chemical values is lost. In 1931, Birge<sup>(14)</sup> reconsidered the atomic weights with/

with this correction.

Birge selected the atomic weights of C, N, He, F1, and H as most suitable for a comparison of the chemical and mass-spectrograph values. Thus in the case of carbon the most probable value is 12,0025. Aston's mass  $C^{12}$  is 12.0036 which becomes 12.0010 on division by 1.00022 in order to reduce to the chemical scale. The best chemical value for nitrogen is 14.008. Aston finds 14.008 which reduces to 14.005. The best chemical value for helium appears to be 4.0018. Aston finds 4.00216 or 4.00127 on the chemical scale. The discrepancy is within the published limits of error. The best chemical value for fluorine is  $18.995 \pm 0.005$ . Aston obtains 19.000 which reduces to 18.996 on the chemical scale, a perfectly satisfactory agreement. The chemical value for hydrogen is  $1.00777 \pm 0.00002$  (probable error) as compared with Aston's,  $1.00778 \pm 0.00015$  (limit of error). Aston's value reduced to the chemical scale becomes 1.00756, which appears to be outside the limits of error.

As there were no discrepancies with helium and fluorine, and since the discrepancies in the case of carbon and nitrogen were removed by the recent discovery of their heavy isotopes  $C^{13}$  and  $N^{15}$  by the methods of molecular spectra, Birge postulated that the discrepancy in the hydrogen determinations could be/

be removed by an isotope of mass 2 with a relative abundance of  $H^1/H^2 = 4,500$ .

The existence of the isotope of mass 2 was also called for by several systematic arrangements of nuclear species. Guido Beck<sup>(21)</sup> leaves a place in his table for  $H^2$ ,  $H^3$  and  $He^5$ . Johnston<sup>(22)</sup> has question marks in his table for  $H^2$ ,  $H^3$ ,  $He^5$ , and  $Li^5$ . Urey's<sup>(23)</sup> proton-electron plot of atomic nuclei calls for the the three isotopes,  $H^2$ ,  $H^3$ , and  $He^5$ .

In a letter to the Physical Review, Urey, Brickwedde, and Murphy<sup>(24)</sup> reported the discovery of an isotope of hydrogen of mass 2 by means of its atomic line spectrum. The letter gave a brief description of their experimental work. They calculated the vapour pressures of the molecules  $H^1 H^1$ ,  $H^1 H^2$ ,  $H^1 H^3$ , in equilibrium with the solid phases, and found the ratio of the vapour pressures  $P_{11} : P_{12} : P_{13} = 1 : 0.37 : 0.029$ . Although the theory of the liquid state was not sufficiently well known to permit a calculation, they believed that the differences in vapour pressure of these molecules should be large enough to make possible a rapid concentration of the heavier isotopes in the residue. Two samples of liquid hydrogen were prepared. The first sample tested for the enrichment of  $H^2$  was collected from the end portion of six litres of liquid evaporated at atmospheric pressure, and the second sample from four/

four litres evaporated at a pressure only a few millimeters above the triple point.

Their description of the spectrum analysis is as follows:-

"These samples were investigated for the atomic spectra of  $H^2$  and  $H^3$  in a hydrogen discharge tube run in Wood's so-called 'black stage' by using the second order of a 21 foot grating with a dispersion of 1.31 A. per mm. With the sample evaporated at the boiling point no concentration so high as had been estimated was detected. We then increased the exposures so that the ratio of the time of exposure to the minimum required to get the  $H^1$  lines on our plates was about 4,500 : 1. Under these conditions we found in this sample as well as in ordinary hydrogen faint lines at the calculated positions for the lines of  $H^2$  accompanying  $H_D$ ,  $H_F$ ,  $H_g$ . These lines do not agree in wavelength with any molecular lines reported in the literature. However, they were so weak that it was difficult to be sure that they were not ghosts of the strongly overexposed atomic lines.

The sample of hydrogen evaporated near the triple point shows these lines greatly enhanced, relative to the lines of  $H^1$ , over both those of ordinary hydrogen and of the first sample. The relative intensities can be judged by the number and intensity of the symmetrical ghosts on the plates.

The/

The wavelengths of the  $H^2$  lines appearing on these plates could be easily measured within about 0.02 A. The following table gives the mean of the observed displacements of the lines from those of  $H^1$  and the calculated displacements.

Line	$H_{\alpha}$	$H_{\beta}$	$H_{\gamma}$	$H_{\delta}$
Calc. displacement	1.793	1.326	1.185	1.119
Obs. displacement.				
Ord. Hydrogen	-	1.346	1.206	1.145
1st sample	-	1.330	1.199	1.103
2nd sample	1.820	1.315	1.176	-

The  $H^2$  lines are broad, as is to be expected for close unresolved doublets, but they are not as broad and diffuse as the  $H^1$  lines probably due to the smaller Doppler broadening. Although their intensities relative to the ghosts of the respective  $H^1$  lines appear nearly constant for any one sample of hydrogen, they are not ghosts for their intensities relative to the known ghosts are not the same in the case of ordinary hydrogen and of the 1st sample. They are not molecular lines for they do not appear on a plate taken with the discharge tube in the "white stage" with the molecular spectrum enhanced".

We trusted that the conclusions reached in this letter/



letter were correct and considered the advantages which hydrogen offered for our purpose. As hydrogen is the lightest element, it has the smallest value of the mass ratio, electron: nucleus, and, therefore, the nucleus may be expected to have the greatest effect on the electron. The spectroscopic method of examination offered great advantages for only a small amount of hydrogen would be required, and even this small amount could be readily purified. The electrolytic production of hydrogen seemed to offer no such difficulties as did lithium. The only disadvantage was the very small proportion of the isotope. It was realized that if the lighter isotope came out first the spectroscopic analysis would be difficult. However, as the heavier isotope has the lesser vapour pressure, it might also have the lesser deposition potential. If this were the case, we should be able to carry out the spectroscopic analysis as Urey had. The small amount of the heavy isotope means that the "isotopic moment" of hydrogen is very small (about 0.0005).

THE/

THE EXPERIMENTAL WORK WITH HYDROGEN.

In practice, however, the spectroscopic examination offered many difficulties. The spectroscope must have a very large dispersion to separate such close lines and the source of light must be very brilliant to bring up the weak  $H^2$  line.

A two glass prism spectroscope was tried first. The dispersion was obtained by photographing the standard iron arc lines. In the region of  $H_B$  the dispersion was 0.13 mm. per angstrom. Then for the 1.33 A. displacement of  $H_B^2$ , the separation of the lines on the plate would be 0.15 mm.

The first method tried for exciting the hydrogen was an electrodeless discharge. This method is especially effective in exciting the atomic spectrum in preference to the molecular, and also offers the advantage of not contaminating the gas with a metallic electrode. With the "electrodeless" discharge the electrodes consist of metal foil wrapped around the glass tubing containing the excited gas. The electric current used for exciting the gas is of sufficiently high voltage and low amperage that it readily passes through the glass. A discharge tube was made of soda glass. One centimeter tubing was used for contact with the foil electrodes, but a 5 cm. length/

length of 2 mm. diameter capillary was joined between these two wide electrode pieces so that the current would be more concentrated. A transformer capable of giving 50 m.a. at 10000 volts, fed a condenser and spark gap which discharged through the primary of a small Tesla, which gave the high voltage necessary.

A convenient method of purifying hydrogen is diffusion through hot Palladium. A small palladium tube, closed at one end with gold solder, and also soldered with gold at the other end to a piece of platinum tubing for sealing into glass, was fitted up for admitting hydrogen to the discharge tube. In order to heat the palladium up to a red heat, at which temperature hydrogen diffuses through it readily, it was fitted with an electrical heater made by winding resistance wire around a silica tube. A large tube with a ground joint at the top fitted over this furnace, carrying in its closed bottom the palladium electrode, from which the hydrogen was emitted on heating. A stopcock allowed this tube to be evacuated before heating. The other end of the discharge tube ran through a stopcock and a liquid air trap to a Gaedé two stage mercury vapour pump which was backed with a Hyvac rotary oil pump. The taps and ground joints were lubricated with Apiezon grease, which was supposed to have a vapour pressure of  $10^{-7}$  mm.

Metallic palladium has the peculiar property of occluding/

occluding large volumes of hydrogen (25) (26). The amount absorbed from the gas may be as much as 950 volumes, but when the palladium is made the cathode of an electrolysis, a greater amount may be taken up. The palladium electrode seemed to offer a convenient way of depositing a small amount of hydrogen at low current densities. The mechanism of the reaction taking place was not sufficiently well known to make a definite prediction concerning reversibility. Nevertheless in spite of uncertainties it was decided to try palladium.

A piece of palladium foil about 15 x 10 cms., weighing 0.9 grams, was available for use as cathode. A small electric motor was fitted with a shaft extension so that the palladium cathode could be rotated. A large beaker held the electrolyte,  $\frac{N}{10}$  HCl, and a platinized platinum anode. Although a platinum anode is attacked by chlorine, the effect was not serious at the current densities used, though it might have caused some trouble, for the dissolved platinum was deposited as black upon the cathode. As with this method air was stirred through the solution by the rotating cathode, the chief reaction was probably the oxidation of the hydrogen. Though such a reaction might or might not be favourable to a separation, it was tried to see if enough hydrogen was obtained in the/

the cathode for analysis. Later measurements indicated that about one twenty-fifth of the hydrogen reduced was retained by the palladium. An electrolysis was run for 15 hours with a current density of .2 m.a. per sq. cm. The electrode was then removed, washed, and dried with a towel, before placing in the palladium diffusion apparatus. The discharge tube was rinsed out several times with this source of hydrogen before a spectrogram was taken. It was considered that some separation of the isotopes might also be taking place in the diffusion through the palladium.

The first plate showed that the  $H_B^1$  line was recorded in about 15 seconds. An exposure of an hour showed no trace of the  $H_B^2$  line. Since an exposure of 15 hours would be necessary to bring up the  $H_B^2$  line in ordinary hydrogen, it was decided to construct a stronger light source. A new discharge tube was made so that the light could be collected by a long focus lens from an 'end-on' 40 cm. long discharge tube of about 5 mm. diameter. The lens was about 6 feet from the slit of the spectroscope.

The new light source recorded  $H_B^1$  in 10 seconds. An exposure of 5 hours showed no trace of  $H_B^2$ , but it was difficult to be sure of this as  $H_B^1$  had spread out so as partially to cover the  $H^2$  position. With an exposure of 10 hours, the position of  $H_B^2$  was blotted/

blotted out by  $H_B^1$ . As the dispersion of a glass spectroscope increases greatly towards the shorter wavelengths, further experiments were tried with  $H_\gamma$  but no better results were obtained.

About this time Kallmann and Lasereff<sup>(27)</sup> reported that in their analysis of hydrogen with a mass-spectrograph the amount of  $H^2$  found was less than one tenth part of the concentration reported by Urey. If this value were correct it would mean that instead of an exposure time of 10 hours, 100 hours would be needed. It was, therefore, decided to try better equipment to see if Urey's work could be confirmed.

Permission was obtained to use the Rowland 21 foot concave grating at the Royal Observatory. The grating had been set up in an Eagle<sup>(28)</sup> mounting and was being used in the third order for measurements of the sun's rotation. The dispersion in the third order was 0.70 Angstrom per mm. Since the dispersion of a grating does not fall off in the red as that of a glass prism does, the Balmer line  $H_\alpha$  would now give a much larger separation of the isotope lines than  $H_B$  or  $H_\gamma$ .  $H_\alpha$  is also considerably more intense than the other members of the series. The disadvantage of  $H_\alpha$  is that photographic plates are less sensitive in that region than in the  $H_B$  region. However, as the spectroscope was set up for work near the/

the H region, it was decided to try H . The separation of the isotope lines on the plate would be  $1.82A - 7A = 2.6$  mm. This is a tremendous advantage over the dispersion of the glass prism instrument, which was seventeen times less. The enormous value of this dispersion may be realized by noting that the visible spectrum is spread out over some seventeen feet.

Since our large hydrogen discharge tube and pumps could not be conveniently carried to the Observatory, preliminary experiments were made with a small capillary discharge tube<sup>(29)</sup> having internal aluminium electrodes. The production of the atomic lines was enhanced by a condensed discharge. The difficulty in producing atomic lines in such a discharge tube with a continuous current is that so much heat is produced as to melt the glass. A condensed discharge gives the high current necessary for exciting atomic lines as a sharp burst of current, which is followed by a rest period while the condenser is recharging.

With the maximum current possible through such a capillary discharge which was placed end on directly in front of the slit, the line  $H_{\alpha}^1$  was just recorded in three minutes. With this arrangement about a week's exposure would be necessary to bring up the  $H_{\alpha}^2$  line! This great extension of exposure time over/

over that necessary with the glass prism spectroscope was to be expected for a grating wastes most of the light given to it.<sup>(30)</sup> Only a small fraction of the light passing through the slit falls on the 6 x 2 inches of the ruled grating which is 21 ft. from the slit, and this small amount is then further split up into the several orders of spectra on each side of the central image. Also the image formed by the grating is very astigmatic. Though the length of the slit may be only 1 cm., the line formed on the plate is many times this. Since the several orders overlap, a filter is required in order to select any particular region. For example,  $H_{\beta}$  in the fourth order spectrum falls very close to  $H_{\alpha}$  of the third order. The filter used was a 22 Wratten and Wainwright.

For any practical work with the grating a tremendously strong light source would be necessary. This problem had been taken up by R.W. Wood,<sup>(31)</sup> when he was engaged in photographing the Balmer series. In experiments with long discharge tubes, Wood found that the atomic spectrum might be fifty times stronger in the centre of the tube than in regions near the electrodes. The atomic spectrum was especially strong when the hydrogen contained a trace of oxygen. The best results were obtained by continually pumping fresh/



fresh moist hydrogen through the discharge tube. As the result of a conversation with Longmuir, Wood gave an explanation of these phenomena. The atomic lines come from the hydrogen atom which is difficult to obtain in a discharge tube for the walls of the tube and the metal electrodes may catalyse its recombination to molecular hydrogen, a reaction which liberates 100, 000 calories. The trace of oxygen added is supposed to stick to the walls and thus poison their catalytic action for atomic recombination. By placing the electrodes at the ends of long sidearms (about 70 cms.), the catalytic effect of the electrodes was made negligible in the 40 cm. long central portion. When producing the molecular spectrum the tube glows with a white light, but when giving the atomic spectrum, the light is of a rich fiery purple colour. If the purple central portion is viewed with a direct vision spectroscopie only the four visible lines of the Balmer series will be seen, the space between them being perfectly black. Wood calls this condition of the tube the "black stage" as distinguished from the "white stage", when the molecular spectrum fills up the spaces between the atomic lines with the enormous number of molecular lines. This molecular spectrum is also called the secondary or the many lined spectrum. Thus a Wood's tube in the "black stage" is much more efficient than a capillary tube for/

for the production of atomic lines. Since the recombination of the atoms is not catalysed, much lower current densities suffice.

An attempt was made to duplicate Wood's apparatus. Wood made his original tube without any ground joints or stop cocks. Hydrogen from an electrolytic generator passed through a capillary to the discharge tube, from which it was continually removed with a Gaede pump. Grease and waxed joints were found to introduce impurities which destroyed the atomic spectrum. As convenient apparatus for circulating the gas was not available, it was decided to try stop cocks and standard ground joints for easy handling of the gas, since the new apiezon grease should have a low enough vapour pressure to be negligible. As Pyrex equipment was not at hand, soda glass was substituted.

Since the soda glass would require water cooling for operation at high intensities, a tube was designed which would fit into a copper box. The central portion, from which the light was collected, had an internal diameter of 6 mm. and was about 50 cms. long. A small bulb was blown on the end for a window. The front sidearm was joined to this about 5 cms. from the window, so that a rubber stopper could be cemented around the tube for making a watertight gasket connection to the copper box. The sidearms of the tube were made of 12 mm. tubing. In order to make them as long/

long as possible they were bent around and extended to the other end of the box, where they joined a piece of 25 mm. tubing which bent upwards at right angles and held the electrodes in the vertical position. The electrodes were hollow pieces of aluminium tubing about 12 cms. long. Above the water surface the 25 mm. tubing was joined to smaller 12 mm. tubing for connecting the stop cock and a side arm with pinch seal of borated copper wire for the electrode connection.

Wood's electrolytic hydrogen generator was copied. A U-tube of 15 mm. tubing was fitted with sealed-in platinum electrodes about half way up each limb. To the cathode limb was fitted a capillary tubing for controlling the flow. The capillary was made by fusing a short section of 5 mm. tubing and then quickly pulling it out to arms' length. This gives a highly flexible capillary of about a hair's thickness. Several attempts were necessary before the right size was obtained for a flow that would keep the gas in the discharge tube at its proper pressure (0.6 mm.) while the pumps were evacuating at the other end. The electrolyte used was dilute phosphoric acid. The gas bubbling off from this contains the slight trace of moisture so favourable to the atomic spectrum. Sufficient voltage was applied to/

to the electrodes to ensure that the hydrogen was always produced faster than could be pumped off through the capillary. The result was a handy automatic generator for it shut itself off as the hydrogen pressure built up and drove the electrolyte back from the cathode. A small 9 volt grid bias battery supplied sufficient current for a long time. The hydrogen capillary was joined to the discharge tube with a standard ground joint so that it could be conveniently replaced with other hydrogen sources.

With internal electrodes only a moderate voltage is necessary. A transformer wound with a 230 - 10,000 ratio with a capacity of 5 K.V.A. was available and was found to provide ample power. The primary current was controlled with a tapped resistance wire which could carry 20 amperes.

The tube was connected up for trial in the chemistry department. When the current was first switched on, the white molecular spectrum was obtained, which was replaced after a few minutes run by the intense fiery purple of the "black stage". The tube was disconnected from the hydrogen generator and pumps so that it could be conveniently moved to the Observatory.

An achromatic long focus lens of about 10 cms. diameter was used for collecting the light from the end/  
end/

end on discharge tube. The lens was about two meters from the slit.

The photographic plate used was an Ilford Soft Panchromatic of H. & D. Speed, 700. The plates were backed to cut down halation. They were handled and developed only in absolute darkness. The metol-quinone developer was used according to the directions given on the box for dish development. The temperature and time recommendations were closely followed. A large excess of developer was used and the developing dish was rocked continuously, in order to avoid as far as possible the reversal effects caused by developer dilution and bromide formation in the region of strong blackening<sup>(32)</sup>

With the new light source,  $H_{\alpha}^I$  was recorded in two seconds. An exposure of two and one half hours failed to bring up any  $H_{\alpha}^2$  line. An exposure of 5 hours brought up a faint line, which was believed to be the  $H_{\alpha}^2$  line. Although too faint for careful measurements, it was definitely closer to  $H_{\alpha}^1$ , than the separation given by Urey. Our measurement suggested a difference of 1.76 Å while Urey reported a separation of 1.820 Å. The difference amounts to nearly a tenth of a millimeter on our plate measurements. When an attempt was made to obtain a better plate, the discharge tube cracked. The glass seemed to/

to be affected by the discharge, becoming somewhat more brittle and taking on a light purple shade.

Urey had used the concentrated  $H^2$  sample to assure himself that he was dealing with an atomic line. As diffusion of hydrogen through palladium might possibly give an enrichment of  $H^2$ , an experiment was planned to try this.

A second hydrogen discharge tube was built similar to the first. Since it was necessary to arrange our apparatus at the Observatory so that it could be moved out of the way when observations on the sun's spectrum were in progress, we designed the tube for mounting on a sliding table (See photograph). The copper water box and the projecting lens were mounted on a teak board and the diffusion apparatus fitted above them. Wood's experiments on the catalysis of the atomic hydrogen recombination suggested a new means of heating the palladium diffusion tube. Wood heated small wires to incandescence by putting them in the path of the atomic discharge. A discharge tube was constructed with the palladium tube projecting down a side arm into the path of the discharge. With a condensed discharge from the  $\frac{1}{2}$  K.V.A. transformer, the heating was a great success for the tube was heated up to a bright red heat in a few moments.

An all-glass Bourdon pressure gauge was attached to/

to the spectroscopic discharge tube. The new hydrogen discharge tube was tried out in the chemistry building. It was run first without any water cooling so that the hot walls would vaporize all impurities. This time the black stage was not obtained even after a long run with a high current. The heat at last caused one of the electrodes to crack off, so the tube was taken down and more carefully cleaned. The tube was first rinsed out with a chromic and sulphuric acid mixture and then with dilute caustic soda. A final careful rinsing was given with distilled water. The carefully cleaned tube gave the black stage almost immediately.

The two discharge tubes were filled with a sample of the electro-deposited hydrogen, and the whole apparatus mounted on the teak board was moved up to the Observatory. During the removal, a connecting tube cracked, and the resulting high air pressure coming on the Bourdon gauge smashed it. The sample of hydrogen in the discharge tube was not affected, so the apparatus was set up for testing this. During the preliminary adjustments the tube cracked again and the electrolytic sample was lost.

Further experiments with a soft glass tube were considered hopeless, so pyrex equipment was ordered. During the delay in delivery a small Pyrex tube was constructed of the light walled tubing at hand and a Pyrex/

pyrex-glass ground joint was made for connection to the glass stop-cocks available. This pyrex tube was found to work well, and it was decided to try out a diffusion experiment.

The U tube electrolytic hydrogen generator and a Hyvac pump were moved up to the Observatory. The hydrogen generator was joined on to the diffusion discharge tube. The Hyvac was connected with a two-way stop cock so that it could pump either through the discharge tube or through the diffusion tube. However, when the current was turned on to heat up the palladium, the palladium refused to heat. However, by greatly increasing the current, the heat of the discharge became just sufficient to let 7 cc. an hour diffuse through the 3 cm. x 2 mm. palladium tube. When about 100cc. had passed through the one cc. residue was tested for  $H^2$ .

For this trial we were fortunate to obtain some faster photographic plates. The new Ilford Hyper-sensitive Panchromatic plates were rated with an H. & D. speed of 2,000 to daylight and 4000 to half-watt lighting. Unfortunately, they were sent unbacked, as the Ilford company said their great sensitivity made the backing process too difficult. They also suggested that the double coating should make backing unnecessary. When the plates were tried out, the halation from  $H^1_{\alpha}$ , i.e. the light reflected/



reflected from the back of the plate, completely filled up the  $H^2$  region. Ways of backing the plates were therefore sought. Ordinary black paper stuck on with gum arabic was tried successfully. Another method used was a suspension of lamp black in glycerine which was spread in a thick coating over a piece of black paper and plastered over the back of the plate. This was very successful and was used for these experiments.

The hydrogen residue seemed somewhat stronger in  $H^2$  but it was not sufficient to be definite. The displacement of the line showed no signs of increasing.

However, we were reassured about the existence of  $H^2$  by Urey's article<sup>(32)</sup> giving further details of his work. In a note he says that an error was made in the calculation of the  $H^2$  displacement. The correct value for the one plate measured at that time was 1.778 A. In a table he lists the correct value of the  $H^2$  displacement as 1.791 A. He gives no other details regarding the accuracy with which this was measured. As his new values were scarcely outside the limits of error of our measurements, it seemed certain that we had found the atomic line of  $H^2$ .

Further diffusion experiments with the palladium tube were impossible, for the tube had sputtered in the/

the discharge and coated the glass walls of the tube with a mirror of metallic Pd. This made negligible any heating due to catalytic effect on the palladium tube and the rate of diffusion fell off.

A two foot length of palladium tubing was obtained for a better diffusion experiment and an apparatus was designed for use with compressed electrolytic hydrogen supplied in cylinders by the British Oxygen Company.

The tube was to be heated this time with an electric current. Preliminary measurements showed that the resistance of the tube was about 0.2 ohm. A 25 volt transformer was tried as a source of current and the tube was found to become red hot at 20 amperes. The palladium tube was bent in the form of a U, with the two ends joined to small lengths of platinum tubing. The diffusion vessel selected was a 5 litre long-necked Pyrex flask. A large rubber stopper was bored to carry the two glass connections to the U tube, the two electrical leads for the heating current, and the inlet and outlet connections for hydrogen. In order to remove any oxygen present as an impurity, the hydrogen was passed through a U tube containing palladised asbestos heated to 200°, and then through a column of Ca Cl<sub>2</sub>. With the exception of a short length of rubber tubing for the connection/

connection to the cylinder, all joints were glass seals. A pressure escape valve for the system was made by dipping the open end of a 100 cm. glass tube into a bottle of mercury. When the pressure was reduced the mercury rose in the tube to its barometric height, while when the pressure became greater than atmospheric the hydrogen escaped into the bottle, from which it passed off into the air through a gas meter. Connection was made to the diffusion vessel through a long capillary tube so that no hydrogen from the flask would diffuse back and bubble away.

The plan proposed for diffusing the hydrogen was to send through the tube a large volume of gas and then remove the small final residue by means of palladium black, cooled in liquid air. On heating the palladium black the hydrogen could be driven off into a reservoir. When sufficient hydrogen had been collected in this way it could be refractionated.

It was desirable to keep the vacuum as perfect as possible on the outlet side of the palladium diffusion tube, so that any back diffusion would be negligible, i.e. the process should be as nearly irreversible as possible. The pumping system consisted of a Gaede two-stage mercury diffusion pump backed by a Hyvoc. A convenient means of making connections to the Gaede pump was designed, making use of "Tombac" flexible copper vacuum tubing.

The/

The head of the pump had been threaded so that it could be used with a mercury seal cup. A piece of iron pipe was threaded to fit this, and the other end of the pipe was brazed onto the "Tombac" tubing. The other end of the "Tombac" was soldered to a piece of brass tubing for making a waxed joint to the glass tubing of the diffusion apparatus.

A mercury manometer was attached for measuring pressures, and a small sulphuric acid U tube manometer, having a stop cock for closing one limb of the U, was used for measuring small changes in pressure. The sulphuric acid level was read on the scale of a small telescope. This was very useful in testing the apparatus for leaks, as 0.01 mm. of mercury pressure change could be easily detected.

The various parts were assembled. When 20 amperes were sent through the palladium tube in the hydrogen gas, the tube did not get very hot. The "accommodation coefficient" and the heat conductivity of hydrogen are much greater than is the case for air. As 20 amperes was the limit of the transformer, another similar transformer was connected in parallel. The tube became red hot with somewhat over 30 amperes. At this temperature about 2 litres an hour diffused through the palladium, and at this speed the pumps maintained a vacuum at the ends of the palladium tube of less than 0.5 mm. After 50 litres had been diffused/

diffused the rate of diffusion became much less. The supply of hydrogen was cut off and the diffusion continued 5 hours longer. The pressure reached a minimum at about 25 cms. and refused to go any lower. The residue was then opened up to the palladium black, but this did not make a measurable decrease in pressure. In order to find out what the residue consisted of, a side tube was fitted on and a small discharge tube attached. A small direct vision spectroscope showed that nitrogen and hydrogen lines were present as well as a great many other lines which were not recognized.

The tube holding the palladium black was fitted with a stop cock and standard ground joint so that it could be easily moved to the Observatory for testing its  $H^2$  concentration. Since most of the residual gas in the diffusion flask seemed to be nitrogen, the hydrogen would only be a small fraction of the total diffused and might be enriched in  $H^2$  if the process was especially effective. The method of testing this sample was as follows. The tube was filled with gas from the small electrolytic generator for a standard run. Exposures of 1, 2 and 3 seconds were made to record the strength of the strong  $H^1$  line. An exposure of 1 minute would just bring up the first pair of ghosts, which served as a further test/

test of the main line. An hour's exposure was then necessary to bring up the  $H_{\alpha}^2$  line. The discharge tube was then filled with the gas for testing at what was judged to be the same pressure, and run under exactly the same conditions. When the sample from the palladium black was introduced, there were some of the unknown gases of the residue present. These gases destroyed the atomic spectrum and made it impossible to photograph  $H_{\alpha}$ . A liquid air trap was attached for purifying the hydrogen admitted to the discharge tube. It was perfectly successful. The hydrogen, however, showed no enrichment.

Another similar diffusion was run and an attempt made to extract the last litre of hydrogen from the residue with the palladium black. Although the palladium black had been well activated by alternate oxidation and reduction<sup>(25)</sup>, and had shown its ability to absorb pure hydrogen, it refused to take up the hydrogen from this residue either because of poisoning or because of poor mixing. It seemed also as if poisoning could explain best the very slow diffusion obtained when the impurities collected.

It was decided to build a Sprengel pump for collecting a pure sample of the hydrogen diffused through the palladium which could then be used for further diffusion. The Sprengel pump was built with an/

an automatic mercury lift worked from a water jet pump. (12) Especial care was taken to see that no air could be carried over with the mercury on the way to the fall tube. The mercury falling from the suction lift passed down and up a U tube, sprinkled itself through an evacuated space at the top of this U-tube, and then passed down and up another U tube before reaching the fall tube. The fall tube of 2 mm. bore was about 150 cms. long. The Sprengel was connected in back of the two stage Gaede pump which worked with an 8 mm. backing pressure. A 5-litre flask was connected on for a gas reservoir to be filled by the Sprengel.

A litre of hydrogen was collected from the residue of 50 litres. Unfortunately, when a second similar litre was collecting the platinum glass joint of the diffusion tube developed a leak and the pure sample became contaminated with the foreign residue gases. Several attempts at mending this joint were unsuccessful. The heat from the hot palladium tube made a considerable strain on the joint. With the help of Everett wax, a joint was made which held up for a time. The two impure litres in the reservoir were pumped into the diffusion flask and taken down to a small residue. It became tremendously difficult to get the last traces of hydrogen through the palladium tube. The pump was run for two days, but a residue/

residue of hydrogen was still left. This last residue was collected for testing by admitting oxygen to the flask, heating up the palladium to catalyse the hydrogen oxidation, and then pumping out the flask through a liquid air trap.

The liquid air trap containing the small residue of water was connected by means of a standard ground joint so it was readily removed to the Observatory for testing. As water vapour itself works very well in the discharge tube, the liquid air trap was connected directly to the tube. The first gas coming off contained those unknown foreign gases which had formerly wrecked the atomic spectrum. The tube was fortunately left running while a new method of solving this problem was sought. In this case the liquid air trap would not do, for it would remove the water vapour as well as the unwanted gases. The problem solved itself for the gases disappeared after the tube had run for about 20 minutes. This sample also showed no enrichment of  $H^2$ .

Further experiments were undertaken to assure that we were working with the genuine atomic  $H^2_{\alpha}$  line, and not with lines emitted by the molecule. When the tube has run for a time the molecular spectrum often becomes stronger. Several of these lines occurred near  $H^2_{\alpha}$ , and it was found that their strength/



strength could be very much increased while the ratio of our  $H^2$  to  $H^1$  remained the same. The  $H_B^2$  line was photographed in the fourth order, and was found to have the displacement given by Urey, though careful measurement could not be made as it was partially overlapped by a 'ghost'. The supposition that the  $H^2$  line was a strong line in another order which was only weakly transmitted through the filter was disproved by a photograph without the filter.

#### CONTEMPORARY WORK ON $H^2$ .

At this time Walter Bleakney announced further results which he had obtained with the mass-spectrograph. In his first work<sup>(34)</sup> he used a sample of the enriched hydrogen prepared by Brickwedde. The results showed a large increase in ions of mass 3 over ordinary hydrogen, and this increase, moreover, varied linearly with the pressure. Since the intensity of the triatomic ion,  $(H^1 H^1 H^1)^+$ , varies as the square of the pressure, it is assumed that the linear part is due to  $(H^1 H^2)^+$ . Bleakney estimated the abundance of the  $H^2$  in the enriched sample as 1 : 1,100, in contrast with Urey's value of 1 : 800. At the Boston meeting of the Physical Society, Bleakney announced that his results for ordinary hydrogen indicated an abundance ratio of 1 : 30,000. This is a marked disagreement with Urey's estimation of/

of 1 : 4000.

In a letter to the Physical Review<sup>(35)</sup> Urey accepts Bleakney's figure. He explains the error in his estimations as due to a selective absorption of the  $H^1$  line in the long discharge tube. He found that by photographing the tube from the side rather than end on, the intensity of  $H_B^2$  was decreased relative to  $H_B^1$ ; decreasing the current density produced the same effect.

Washburn and Urey announced<sup>(36)</sup> that the electrolyte from a hydrogen generator which had been operated continuously for two years was considerably enriched in  $H^2$ .

About this time we heard that the Mond Nickel Company was engaged in the electrodeposition of palladium. A small amount of hydrogen should be deposited simultaneously with the palladium and should be irreversibly trapped as more palladium was deposited on top of it. The palladium was deposited with a 98% current efficiency. The Mond Nickel Company very kindly provided us with samples for analysis. The palladium was dried before shipment at  $100^{\circ}$ .

The volume of gas in the palladium was measured by collecting the gas from the heated palladium with a Toepler pump<sup>(12)</sup>. Less than 1 cc. was obtained from an ounce of the palladium.

Half an ounce of palladium was taken for a test  
of/

of  $H^2$ , and gave off just enough hydrogen to fill the discharge tube. The plate indicated that  $H^2$  was certainly not more intense but perhaps less. Unfortunately, when the tube was being thoroughly evacuated for rinsing, so good a vacuum was obtained that it was non-conducting, and, when the current was turned on to test the pressure, the pyrex tube punctured.

A new tube was built after the same style except that heavy walled Pyrex tubing was used. The inside diameter of the central discharge portion was increased to 8 mm., which was an improvement. The tube was cleaned by rinsing only with water and A.R. acetone. The black stage was readily obtained.

An interesting catalytic effect was noticed with this tube. A few small particles of broken glass lodged in the window which extended outside the copper water bath. Although there was no glow from the discharge in this part of the tube, the small glass particles were heated red hot, presumably because they catalysed the recombination of atomic hydrogen. The particles danced about extremely vigorously and it was indeed curious to watch the red-hot particles bouncing around in a cold glass vessel.

Improved plates were obtained from the Ilford Company. These were rated with an H. & D. speed of 8,000 for half-watt lighting and at our request they were supplied backed. Washing the plates was still somewhat/

somewhat difficult, for the top coating peeled off very easily. The plates were usually washed with several successive rinsings of distilled water. No other ways of hardening the film were tried other than the regular acid fixing bath.

#### ELECTROLYSIS USING PALLADIUM CATHODE.

A large sheet of palladium (10 x 10 cms.) had been obtained and an electrolytic cell was set up using this foil as cathode. The sheet was coiled in a circle around the syphon tube leading to the anode. The electrolyte, a solution of  $\frac{N}{10}$  HCl, was carefully boiled out and sealed off from air. The electrolysis was allowed to continue for a week with a current density of .01 amp. per sq. cm. No bubbles were given off at any time by the cathode. The electrode removed for testing, was dried with a towel and dropped into a pyrex tube which was connected by means of ground joints to the discharge tube. A good deal of hydrogen could be pumped off from the palladium without heating. A sample of this was tested using exposures of 1, 2, and 3 seconds, one minute, and one hour. The  $H^2$  seemed to be of the usual strength. When no more hydrogen could be obtained with pumping, the palladium was heated in an oil bath. At  $110^{\circ}$  there was a tremendous rush of hydrogen. Upon testing this/



this the  $H^2$  line did not come up in the hour's exposure.  $H^2$  was obtained with a two hour exposure and seemed definitely weaker in comparison with the ghosts of the  $H^1$  line. The gas coming off at  $140^\circ$  was very similar. A five hour exposure was necessary to bring up the  $H^2$  line definitely. Another sample was tried at  $250^\circ$ . The oil bath was replaced by an electric furnace and the temperature of the palladium raised to  $500^\circ$ . Just enough hydrogen was obtained to work the tube. Strangely enough the  $H^2$  seemed to be back to its usual strength.

Further tests were then made with hydrogen from a large sample of the Mond Nickel electrolysed palladium. Very similar results were obtained.

Several different causes were suspected. The rate of diffusion or desorption from the palladium might be different for the two isotopes. The presence of water vapour on the palladium foil and its Pyrex holder might alter the ratio of  $H^2$  in the gas tested or it might alter the character of the discharge.

The desorption rate from palladium was tried out by absorbing a 100 cc. of hydrogen in the 2 oz. palladium sample and then pumping it off as before. No marked change in  $H^2$  was noted.

Factors that might affect the discharge tube were studied more closely. A source of oxygen was provided by a small U-tube electrolytic generator similar/

similar to the hydrogen generator described before. A tiny pipette for admitting the oxygen was made by blocking the hole in the key of the stop cock. A sensitive pressure gauge was made of similar design to the  $H_2SO_4$  manometer mentioned earlier, except that it was filled with a light oil obtained from the Shell Co. The vapour pressure of the oil was supposed to be less than  $10^{-7}$  mm. Hg., and it was found to work very successfully. As the oil was light the gauge was especially sensitive, A 0.001 mm. of Hg. might have been measured.

These indications that the light isotope is deposited first started considerations for an apparatus that would enable us to test the residue left from a prolonged electrolysis. A tremendous amount of current is necessary to decompose very much water; for instance 30 amperes flowing for an hour decompose only about 10 cc. of water. As this high current density is incompatible with our demands for a separation due to different electrode potentials, the design of a suitable apparatus for a reasonably quick electrolysis is difficult.

While the discharge tube was being fitted up with more exact controls, another electrolysis was run with the palladium sheet. A new electrolytic cell was made from a couple of vacuum dessicator tops.

An/

An inverted top held the HCl electrolyte in which the palladium sheet was stretched out flat on a small glass table with legs, so that it was held about 7 or 8 cms. above the syphon tube which led to the anode. The other top fitted this and carried a two hole rubber stopper for bringing in the electrode lead and the evacuating tube. The ground glass surfaces of the two tops were lubricated with vaseline and a vacuum tight joint was formed. Both anode and cathode gases were evacuated continuously by means of a water jet pump. A current density of about 0.5 - 1.0 milliamperes was used. The gas was allowed to bubble off the cathode for about three days.

The cathode was removed and dried as before, but this time the containing vessel was evacuated immediately. It was hoped that this would more effectively remove any moisture remaining on the palladium. The evacuation was thorough, as the Gaede Mercury vapour pump was used. The vessel was then carried immediately up to the Observatory. However, by this time enough hydrogen had diffused out from the palladium to fill the discharge tube. A comparison with the standard hydrogen was made on the same plate. A 15 minute exposure with this sample shows the  $H^2$  line, while a 15 minute exposure with the standard does not; (see photograph). The ghosts of the  $H^1$  line appear to/

to have about the same strength in both exposures. This indicates that the light hydrogen was escaping more readily from the palladium electrode allowing the heavy isotope to collect.

Effect of Current-Density on Relative Intensity of Lines.

The characteristics of the tube were studied further. The effect of the current density in the tube is considerable. (see photograph) A high current density brings up the  $H^2$  line with a greater intensity as compared with the ghosts of  $H^1$  than a low current density does. This was mentioned by Urey<sup>(35)</sup>.

In earlier experiments the pressure of the gas in the discharge tube had been estimated by observing the nature of the striae and of the glow around the electrodes. The new pressure gauge showed that this method was very accurate, the estimations being correct to about the 0.01 mm. of Hg. However, when oxygen was admitted, the pressure characteristics of the glow were changed very greatly. Instead of being a pure function of pressure alone, the nature of the glow was also a function of the oxygen content. The addition of oxygen also lowered the resistance of the tube, thus giving rise to a greater current density. Since/



Since the increase was only 10%, it did not seem sufficient to account for the increased intensity of  $H^2$  in the first and last fractions of the electro-deposited hydrogen coming off from the palladium. However, in these fractions there might well have been oxygen present, for moisture from the palladium and the walls of its containing vessel could have appreciably contaminated the very small volumes of gas making up the end fractions, while the large volumes of gas making up the middle fractions would not have been affected.

It was thought that the Mond Nickel Company's palladium might have lost some of its hydrogen when dried at  $100^{\circ}$ . A new sample was supplied which had been dried in a desiccator, but the new sample contained even less hydrogen. A couple of plates were tried and the  $H^2$  concentration was found the same as our standard.

The  $H^1$  line was causing considerable trouble in these measurements of weak  $H^2$  lines, because it would spread out during a long exposure and gradually cover the  $H^2$  line. Earlier attempts had been made to block out the strong  $H^1$  line with a small black shutter which was adjusted so as just to cover the position of  $H^1$  on the plate. At this time it was thought that the spreading was due to halation, a consequence of imperfect backing. The shutter did not/

not stop the spread, which indicated that the great width was not a fault of an imperfect plate, but an essential property of the  $H^1$  line in these circumstances.

This spreading of the  $H^1$  line made quantitative estimates of  $H^2$  very difficult, for the blacking of the plate was a function of two factors. In order to obtain a better understanding of what the photographic plate was recording, an attempt was made to find out some of the plate characteristics.

The same photographic effect is not obtained by reciprocal variations of light intensity and exposure time. (52) (57) If the blackening were a function of the total amount of energy falling on the plate, the effect of the light could be expressed as the product of the intensity and the time of exposure.

Thus

$$S = f(I.t)$$

where  $S$  is the blackening;  $I$ , the intensity; and  $t$ , the time of illumination. Schwarzschild has shown that the action of the photographic plate can be better represented by the equation,

$$S = f(I.t^P)$$

The index,  $P$ , has become known as Schwarzschild's constant.

An attempt was made to determine the Schwarzschild constant for the plates. A rotating sector, which/

which had been used in earlier work at the Observatory, was tried out as a method of cutting down the intensity of the light source by a known amount. The value of Schwarzschild's constant could then be determined from the time factor necessary to bring the blackening back to its original strength. For example, if the light intensity is cut down to a sixth, the time of exposure would only need to be multiplied by six to produce the same blackening according to this simple reciprocity law; but experiment may show that the time of exposure must be multiplied by ten, a result which is expressed by means of Schwarzschild's formula.

Since light of the same wavelength must be used and the measurements made over the same intensity range to avoid the variations in Schwarzschild's constant with intensity, it was decided to use the spectroscope arranged in the usual way with the rotating sector placed in front of the slit in order to cut down the strength of the hydrogen light source. When the sector was rotated, a dark shadow passed periodically across the slit. This must have been a stroboscopic effect produced by a periodic extinction of the light sent out by the hydrogen tube. The light from the hydrogen tube had no-visible flicker. It was not unlikely that the periodic flicker was caused by the 50-cycle alternating current, but this was/

was not definitely determined. The speed of the rotating sector was adjusted to reduce the shadow effect as much as possible and the required exposures were made. Unfortunately, the shadow wrecked any confidence in the accuracy of the determination. However, the constant,  $P$ , was found to be 0.8, which is a usual value and was expected.

It is interesting to note how this constant would effect  $H^2$  estimations. If a line that has such an intensity as to be just recorded in one second, is to be compared with another line that is four thousand times weaker, the time of exposure would simply need to be multiplied by four thousand according to the reciprocity law; but with a Schwarzschild constant of 0.8, the length of exposure must be multiplied thirty thousand times. Likewise if the intensities should have the ratio 1: 30,000, the exposure time must be multiplied by four hundred thousand in order to bring up the weak line. The importance of Schwarzschild's constant thus becomes much greater when faint and strong lines are being compared.

Meanwhile, other work on  $H^2$  was published. Rank<sup>(38)</sup> photographed the  $H_y^2$  line using a spectro-scope made of six glass prisms, which were arranged in the Littrow form and were, consequently, equal to twelve prisms. The dispersion at  $H_y$  was 1.09 A. per mm. The separation of  $H_y^2$  from  $H_y^1$  was found to be/

be 1.211 Å in substantial agreement with Urey, Brickwedde, and Murphy's value. The source of light was a Wood's tube 220 cms. long, which was observed through 40 cms. of the central portion. The source of flowing hydrogen was an electrolytic generator and capillary similar to Wood's<sup>(31)</sup>. An estimation of the abundance of  $H^2$  was made by determining the exposure times necessary just to record the  $H^1$  and the  $H^2$  lines. With 190 m.a. through the tube, a two and a half hour exposure did not record the presence of the  $H^2_y$  line, although a one second exposure recorded  $H^1_y$  with about five times the intensity necessary to make it visible on the plate. Upon increasing the current to 310 m.a. the  $H^2_y$  line appeared with a 35 minute exposure. It was concluded from these results that the ratio of  $H^2$  to  $H^1$  is not more than one part in 80,000, if the reciprocity law held for the photographic plate. Owing to the failure of the law, Bleakney's results are accepted as more reliable.

Bainbridge<sup>(39)</sup> determined the mass of the  $H^2$  atom with great accuracy by means of a mass-spectrograph. He mentions that the concentration of  $H^2$  is increased by the process of effusion through the slits of the instrument.

At one time it had been thought that a similar separation had been taking place in the capillary supplying/

supplying our standard hydrogen. A series of photographs indicated that a slight separation did take place but it did not seem great enough to interfere seriously with our standard.

Roy,<sup>(40)</sup> at St Andrews, showed that the presence of oxygen has a selective effect on the intensity of the Balmer series. The intensity of the whole series is increased, but the higher members of the series show a greater increase in intensity than the lower members. This was explained by the theory of collisions of the second kind between oxygen atomic ions or molecular ions and hydrogen atoms. The difference in the energy transferred determines the probability of such collisions occurring. It is shown that the energy to be transferred should thus favour the production of the higher members.

Rao and Badami<sup>(41)</sup> found an anomalous distribution of intensity among the members of the Lyman series. The enhancement of the 10th and 11th members was associated with the presence of arsenic vapours. The explanation suggested was the transfer of energy by collisions of the second kind between metastable arsenic atoms and the atoms of hydrogen.

This collision mechanism was of very great interest, for it seemed the best explanation of the inconsistent operation of the discharge tube during long exposures. At the commencement of a long exposure/

exposure, just after it has been rinsed out with moist electrolytic hydrogen, the tube is in a good "black stage". After about a half to two hours' run, the tube becomes definitely whiter. Our earlier experiments with the impurities in the diffused sample of tank hydrogen had shown how a foreign gas could destroy the atomic spectrum, i.e., the "black stage". The new pressure gauge on the discharge tube showed that the pressure increased as the tube went white. A black deposit formed in the dead end of the tube which extended out a short distance beyond the joint to the sidearm. As the tube went white a great number of lines appeared in between the atomic hydrogen lines. It was not known whether these were due to the hydrogen molecular spectrum or to a foreign gas. Anderson<sup>(42)</sup> has shown that a silica discharge tube may be decomposed by the action of the discharge. He found that oxygen was set free and a black deposit of silica was obtained. By operating for some weeks 135 cc. of oxygen were collected. It therefore seems likely that the white stage produced by long exposures is caused by a gas resulting from the decomposition of the discharge tube. The foreign gas may act either by destroying the "poison" effect of the oxygen on the walls or by acting as a third body in a triple collision with which the hydrogen atoms can recombine.

Of course, with uncontrollable variations in the intensity/

intensity of the atomic spectra, the method of estimating intensities by the time taken for the initial appearance of the line is worthless for accurate work. However, the estimations of  $H^2$  made by comparing the  $H^2$  line with the ghosts of the  $H^1$  line should not be affected. Experiment showed that any change in the intensity ratio of  $H^2$  to ghosts was not very great. The atomic spectrum becomes weaker in the white stage just as if the current intensity through the tube had been decreased. The  $H^2$  ghost intensity ratio changes in such a way that the ghosts become stronger with weaker currents. The variation with the condition of the discharge tube was no more than the variation with current density.

#### OTHER ESTIMATIONS OF ABUNDANCE.

An estimation of the abundance of  $H^2$  was made by Hardy, Barker, and Dennison using a different method. At this time the various estimates of the abundance of  $H^2$  in natural hydrogen varied widely. Urey's estimate of the abundance as 1:4000, and Rank's estimate of 1:80,000 were both considered less accurate than Bleakney's value of 1:30,000. Our work has shown that the factors which might cause this disagreement are: (1) Selective absorption as suggested by Urey. (2) The value of Schwarzschild's constant/



constant for the photographic plate. (3) The current density in the discharge tube. (4) The effect of foreign gases on the nature of the discharge. (5) Rate of capillary diffusion.

Hardy, Barker, and Dennison used the methods of molecular spectra for their work. The fundamental absorption band due to HCl molecules was obtained in the region of 4.8  $\mu$ . Nineteen lines were measured in the band of  $H^2 Cl^{35}$ , and seventeen in the band of  $H^2 Cl^{37}$ . The abundance of  $H^2$  relative to  $H^1$  was estimated as 1 : 35,000. However, an enriched sample was measured which was of interest to us. Following a suggestion of Prof. Urey, a sample of the electrolytic residue was taken from cells making commercial hydrogen and the concentration of  $H^2$  was found to be about ten times increased.

While the characteristics of our discharge tube were being more carefully determined for long exposures, a letter from G.N. Lewis appeared in the J. Am. Chem. Soc.

"With the aid of Dr R.T. Macdonald I have been attempting to isolate various isotopes. Less than a month ago we turned our attention to the isotope of hydrogen. Our first experiments, employing a difference in overvoltage suggested by the work of Washburn and Urey, were so promising that we at once planned a systematic series of concentrations which have just been completed. This yielded water of specific gravity 1.035, which means that the heavy isotope constitutes one-third of all the water present. The refractive index of this heavy water is considerably lower than that of ordinary water, but exact figures cannot be given until the concentration has been accurately determined.

The/

The separation of any isotope in sufficient quantity to permit investigation not only of its spectroscopic but also of its other chemical and physical properties suggests a wide range of interesting experiments but the isotope of hydrogen is, beyond all others, interesting to chemists. I believe that it will be so different from common hydrogen that it will be regarded almost as a new element. If this is true the organic chemistry of compounds containing the heavy isotope of hydrogen will be a fascinating study."

TEST OF COMMERCIAL ELECTROLYTIC RESIDUE.

This letter decided us to carry out a final experiment with a sample of the electrolytic residue from a cell making commercial hydrogen in the works of the British Oxygen Company. The electrolyte was three times distilled in order to remove all the sodium hydroxide from the water. The pure water was then allowed to evaporate directly into the discharge tube. Ordinary distilled water was used as a standard for comparison. Both spectra were recorded on one plate so as to avoid any possible errors due to variations in plate characteristics and development. The time necessary to record  $H^2$  was speeded up somewhat by using a wider slit. The speed of the plates was also somewhat improved. The discharge tube was rinsed with oxygen each time before a fresh sample was tried. This left the tube in an excellent black stage which lasted well throughout the exposures. Three exposures of each sample were made 7.5 minutes,

30/

30 minutes, and 15 minutes. The 30 minute exposure was taken between the two others so that any tube variations could be better estimated. With such short exposures the variations in the nature of the discharge were not large.

#### DENSITY DETERMINATION.

From the spectra photographed the enrichment of  $H^2$  in the sample was judged to be only  $1\frac{1}{2}$  times the amount in ordinary water. It was decided to determine the density of the water in order to check this, but more especially to see if there was any marked increase in the concentration of the heavy isotope of oxygen,  $O^{18}$ , which has an abundance compared with  $O^{16}$  as 1: 650.

We were fortunate in having placed at our disposal a pycnometer of especially accurate design and the skilled assistance of Professor W.C. Vosburgh. The two limbs of the 74 cc. pycnometer were bent around in order to bring them close together for reading. One limb had a zero mark while the other was calibrated. Since the inside diameter of the capillary ends of the limbs was only 0.3 mm., the volume was obtained very accurately. A large division on the calibrated limb could be easily estimated to a tenth of its whole value of 0.00046 cc. The water bath, in which the/

the pycnometer was immersed while the volume was adjusted, maintained its temperature constant to a thousandth of a degree. Seven thousandths of a degree would be needed to produce a measurable change.

The balance was accurate to a tenth of a milligram. The counterbalance was of Pyrex and had the same overall volume as the pycnometer. When weights were used for balancing, the necessary vacuum corrections were made.

The water in the electrolyte was purified by distillation. After two ordinary distillations, the water was distilled from a long necked Pyrex flask which made a connection by means of a ground joint to a silica condensing tube.

The accuracy of the method was about one part in 500,000. An increase in density was found of one part in 50,000. The density of the water would be increased this amount by the presence of  $1\frac{1}{2}$  times the normal amount of  $H^2$ , provided that the normal concentration of  $H^2$  is taken as 1 in 30,000. Only one determination was made as time did not permit another.

Washburn has reported more recent results in a letter to the Editor of the "Journal of Chemical Physics". It was found that the "rise in specific gravity is accompanied by a rise in the freezing point and in the boiling point and by a decrease in the refractive index. Thus for water of specific gravity/

gravity 1.0014, the changes are; F.P., + 0.050°C;  
 B.P. + 0.02°C;  $n_D^{25}$ ,  $-(60 \pm 2) \times 10^{-6}$ .

No indication of approach to an electrolysis equilibrium has been found and there is every reason to hope that it will be possible to obtain the various isotopes of hydrogen and oxygen in a pure state, certainly in highly concentrated form".

### DISCUSSION.

The electrolytic method has been shown to be a successful method for the separation of isotopes. The only problem that remains is to determine just what part of the electrolytic mechanism is responsible for the separation. The various factors in the deposition process which might bring about a separation have been mentioned in the introduction. They were:

- (1) Normal electrode potentials, (2) Activities,
- (3) Overpotentials.

Urey and Rittenberg<sup>(46)</sup> have calculated some thermodynamic properties of the  $H^2$  atom including the electrode potential differences.

"These electrode potential differences at 298.10 are 0.00886 and 0.00195 volts in the cases of the hydrogen chloride and hydrogen iodide reactions respectively".

"These differences are so small that no separation of the hydrogen isotopes can be expected by fractional electrolysis insofar as this fractionation depends on the differences of electrode potentials. The discovery by Washburn and Urey<sup>(36)</sup> that such fractionation does occur in commercial hydrogen-oxygen electrolytic cells with KOH solutions as electrolyte and nickel electrodes is probably due to other/

other causes than the electrode potential differences, perhaps the rates of diffusion to the electrode surface or the rates of recombination of hydrogen atoms on the electrodes".

Urey and Rittenberg do not explain why no separation should be expected with a normal electrode potential difference of 0.00886. On the basis of the Nernst equation for normal electrode potentials, a measurable separation could be obtained. In his thesis<sup>(2)</sup> Haring discusses the work of Blum and Haring<sup>(47)</sup> who studied the electrodeposition of lead and tin. The electrode potentials of lead and tin differ by only 0.012 volt.

Eyring<sup>(48)</sup> has discussed the bearing which diffusion at the electrode surface and rate of recombination of the ions should have on the separation. The relation between diffusion and electrode overpotentials has been discussed by Gurney<sup>(49)</sup>. The question of the rate of recombination is considered in detail by Eyring. The effect of zero point energy on the rate is emphasized. This effect should permit separation by many reactions not involving electrolysis. In this connection, Eyring notes that "the intimate connection between the published data on separation by electrolysis and of desorption with the consequent necessity for different velocities of desorption, and therefore adsorption, of isotopes at electrode surfaces was also realized by H.S. Taylor who is arranging an experimental test of the possibilities of separation by such processes."

The scheme of simultaneous deposition of hydrogen and palladium is a process which should be accompanied by an extremely small overpotential. Since the ions may/

may maintain their status as ions in the palladium lattice<sup>(50)</sup>, the zero point energy effect on the rate of recombination does not come into consideration, though it would affect the rate of union with palladium. However, the palladium deposition process seems to offer the most direct means of determining the effect that different normal electrode potentials may have on the separation of isotopes.

Unfortunately, uncertain factors in the operation of the hydrogen discharge tube make it impossible to say with certainty that the evidence obtained for the preferential deposition of the lighter isotope is correct.

More exact experiments with the diffusion of gaseous hydrogen through palladium for comparison with the results obtained by ordinary diffusion methods might demonstrate any effect of the zero point energy on the rate of union with palladium.

If the separation is caused neither by the difference in normal electrode potentials nor by any factor in the reaction rates, it must be due merely to an ordinary physical diffusion process at the electrode sheath. It does not seem possible to decide the question by means of the experimental evidence available at present.

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SUMMARY.

1. The factors in the electrolytic separation of isotopes are discussed.
2. Methods for the electrolytic deposition of metallic lithium are described.
3. A thorough description of the construction and operation of a hydrogen discharge tube is given. The errors which may result in the determination of the abundance of  $H^2$  are carefully considered.
4. Experiments on the rate of diffusion of hydrogen through palladium have shown that there is no great difference between the diffusion rates of  $H^1$  and  $H^2$ .
5. Although spectroscopic evidence was obtained that the lighter isotope of hydrogen is preferentially discharged, a careful examination of the spectroscopic method of analysis showed that the results were not fully conclusive.
6. The enrichment of the heavy isotope in commercial electrolytic cells was demonstrated. A density determination of the residual water showed that the heavy oxygen isotope was not appreciably enriched in this water.



7. A discussion of the electrolytic mechanism points out the value of the palladium deposition process for the determination of the normal electrode potentials of the isotopes.

#### ACKNOWLEDGMENTS.

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To Professor Sampson, The Astronomer Royal, I owe the many facilities which were kindly given me at the Royal Observatory.

To Dr E.A. Baker and Dr J. Storey of the Observatory staff, I am grateful for their expert assistance.

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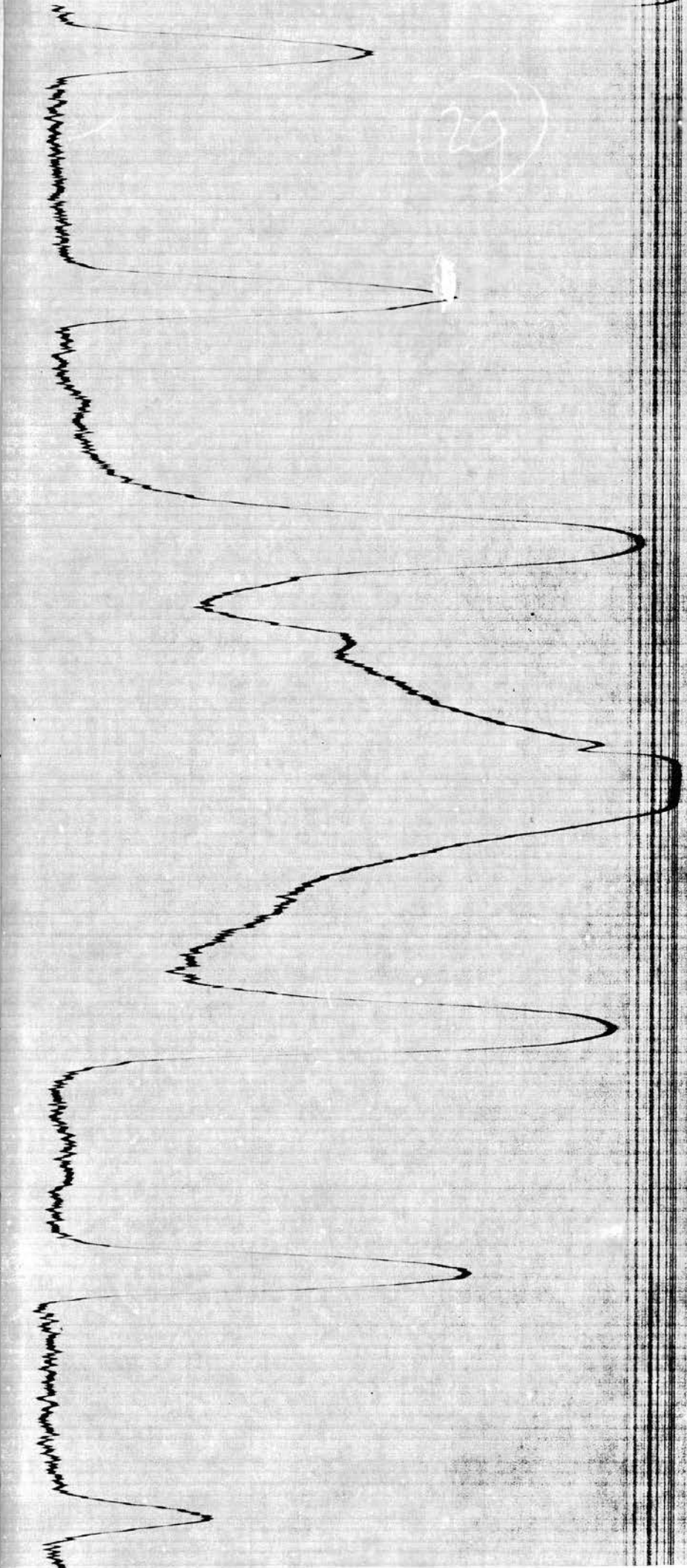
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MICROPHOTOMETER RECORDS.

The following microphotometer records of several plates were kindly prepared by Dr E.A. Baker of the Royal Observatory.

(29)



Ghost lines

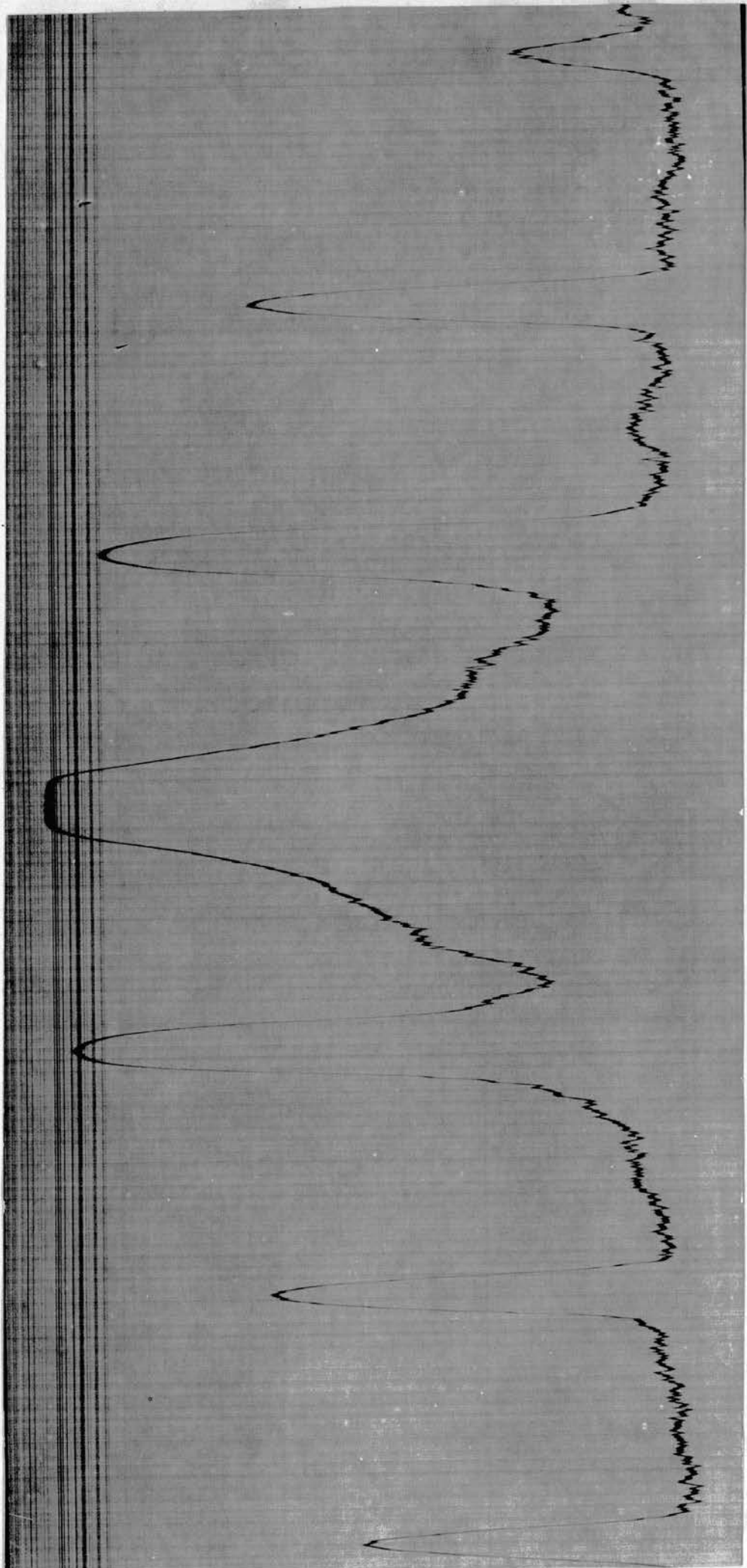
H<sub>2</sub>

H<sub>1</sub>

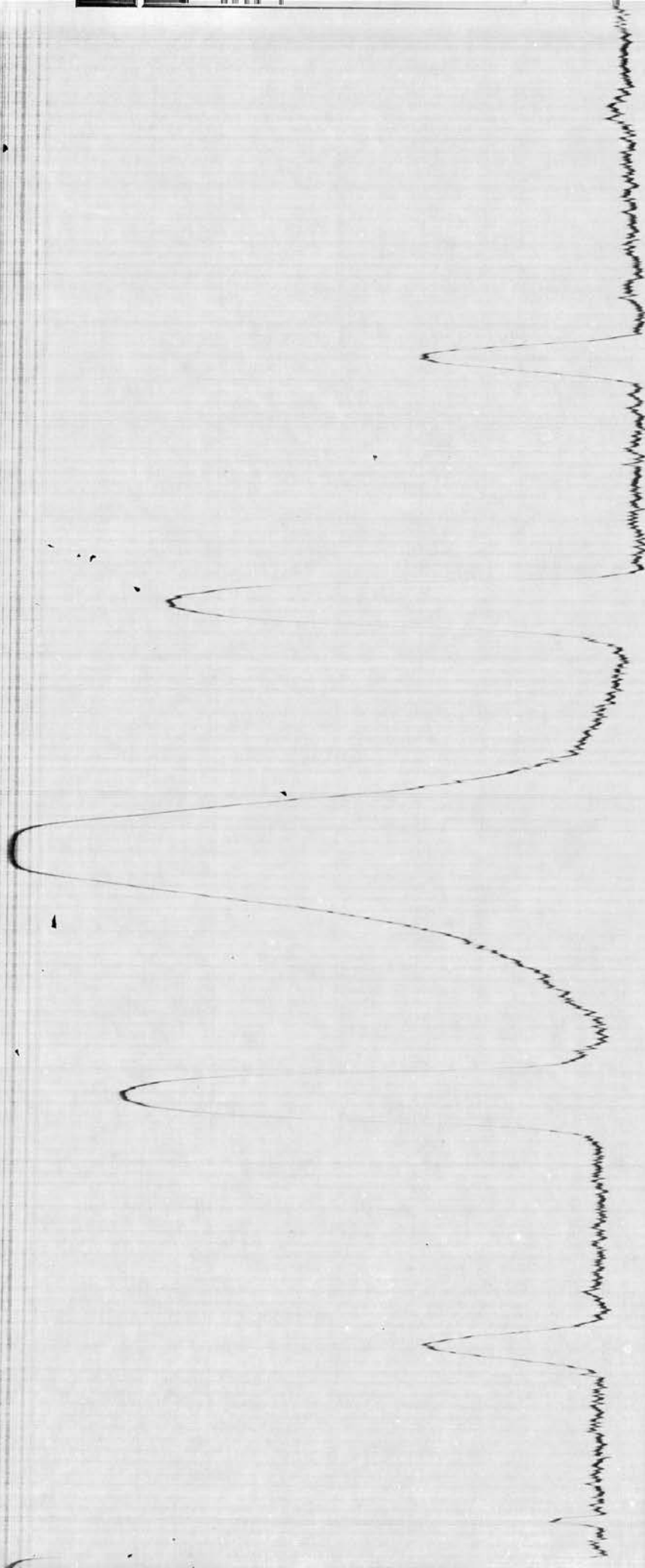
Ghost lines

Standard Hydrogen; Exposure 1 hr.; Prim. Current = 10 Amp.

Electrolytically Deposited Hydrogen; Exp. 5 hrs., Prim. Current = 10 Amps.

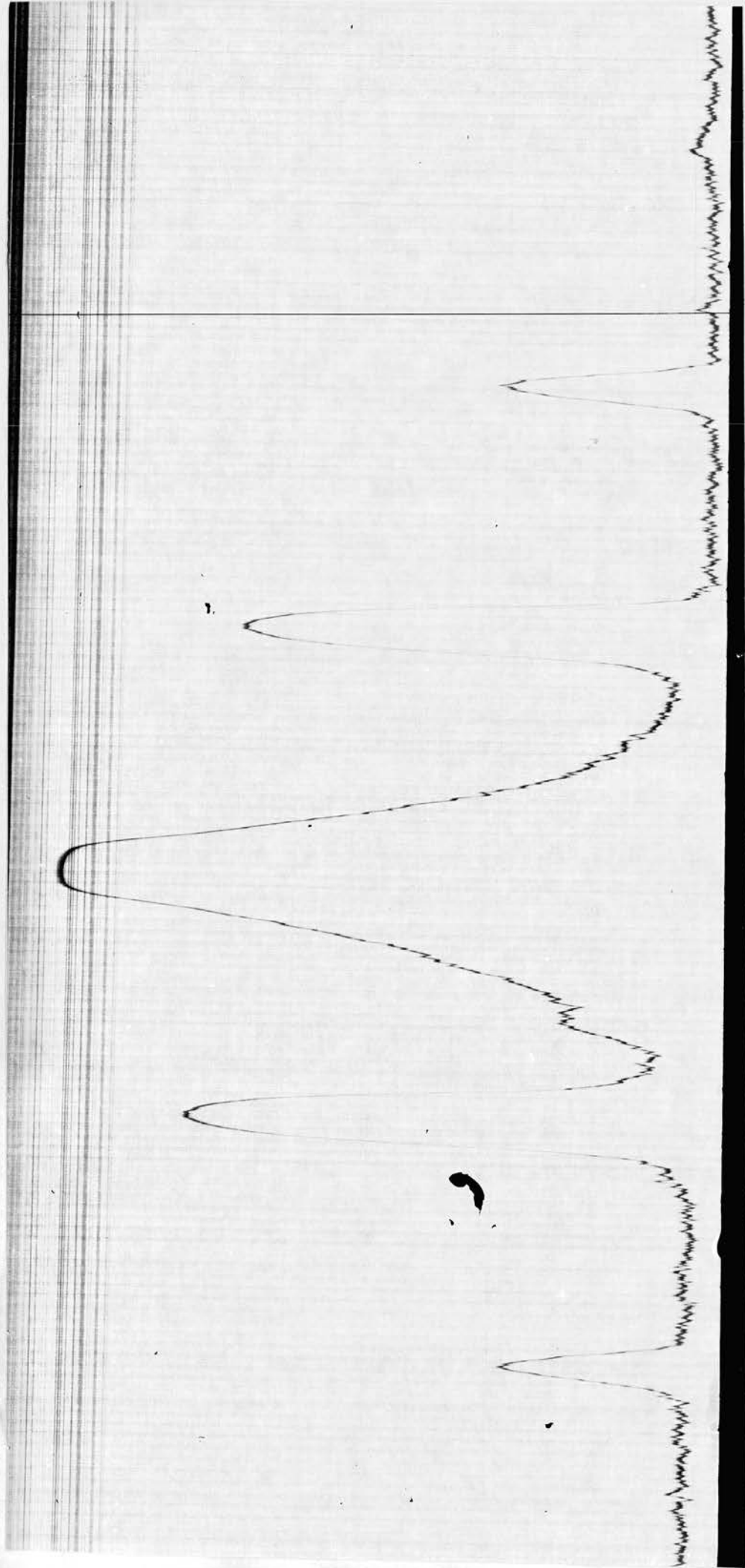






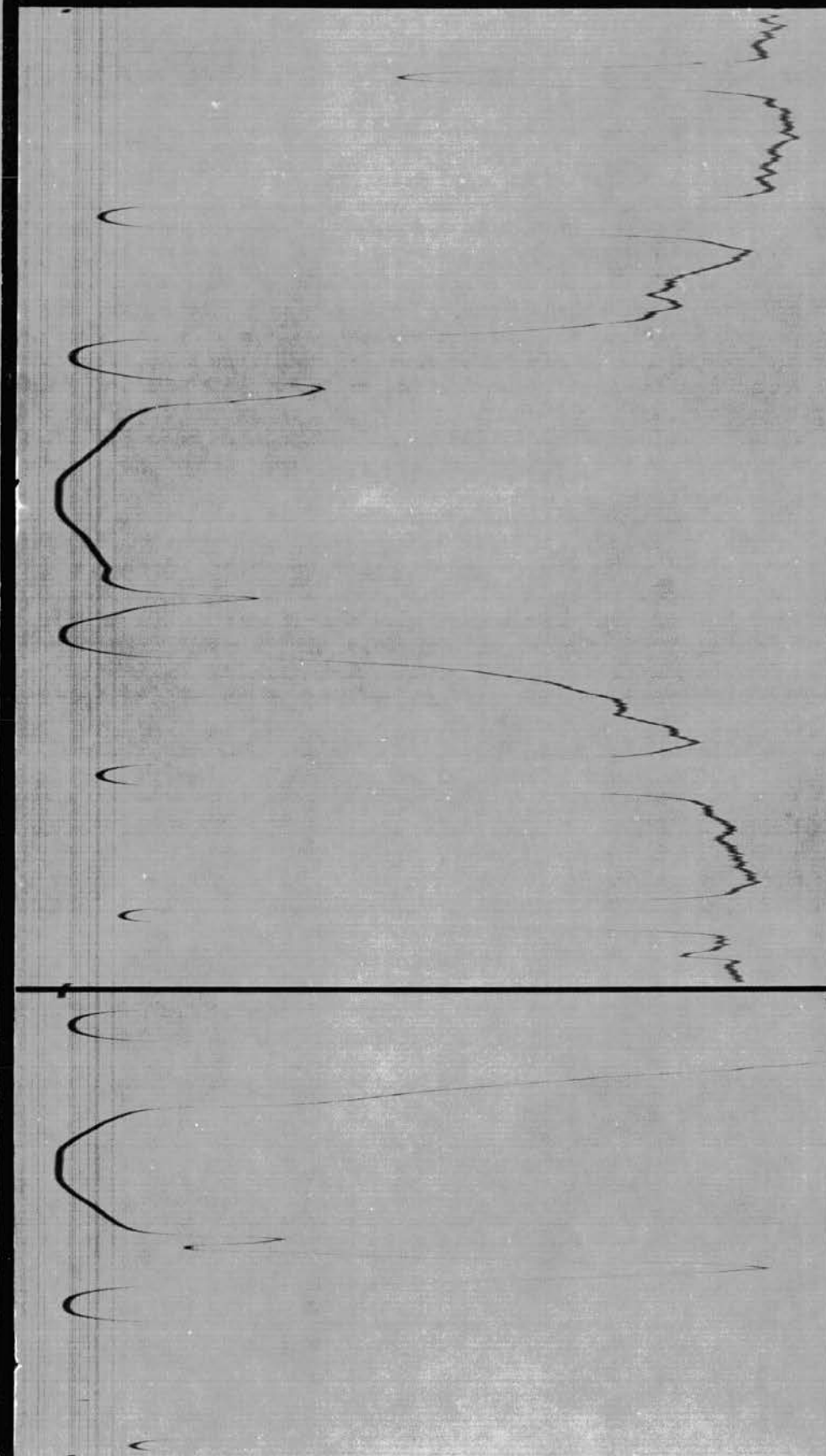
Ghosts  $H^{12}$   $H^1$  Ghosts  
 Standard hydrogen photographed on same plate  
 as the preceding. Primary current = 10 Amperes; Exposure 15'

Sample from Gassing Palladium Electrode. Exp. 15'; Prim. Current = 10 amps.



Series No. 12

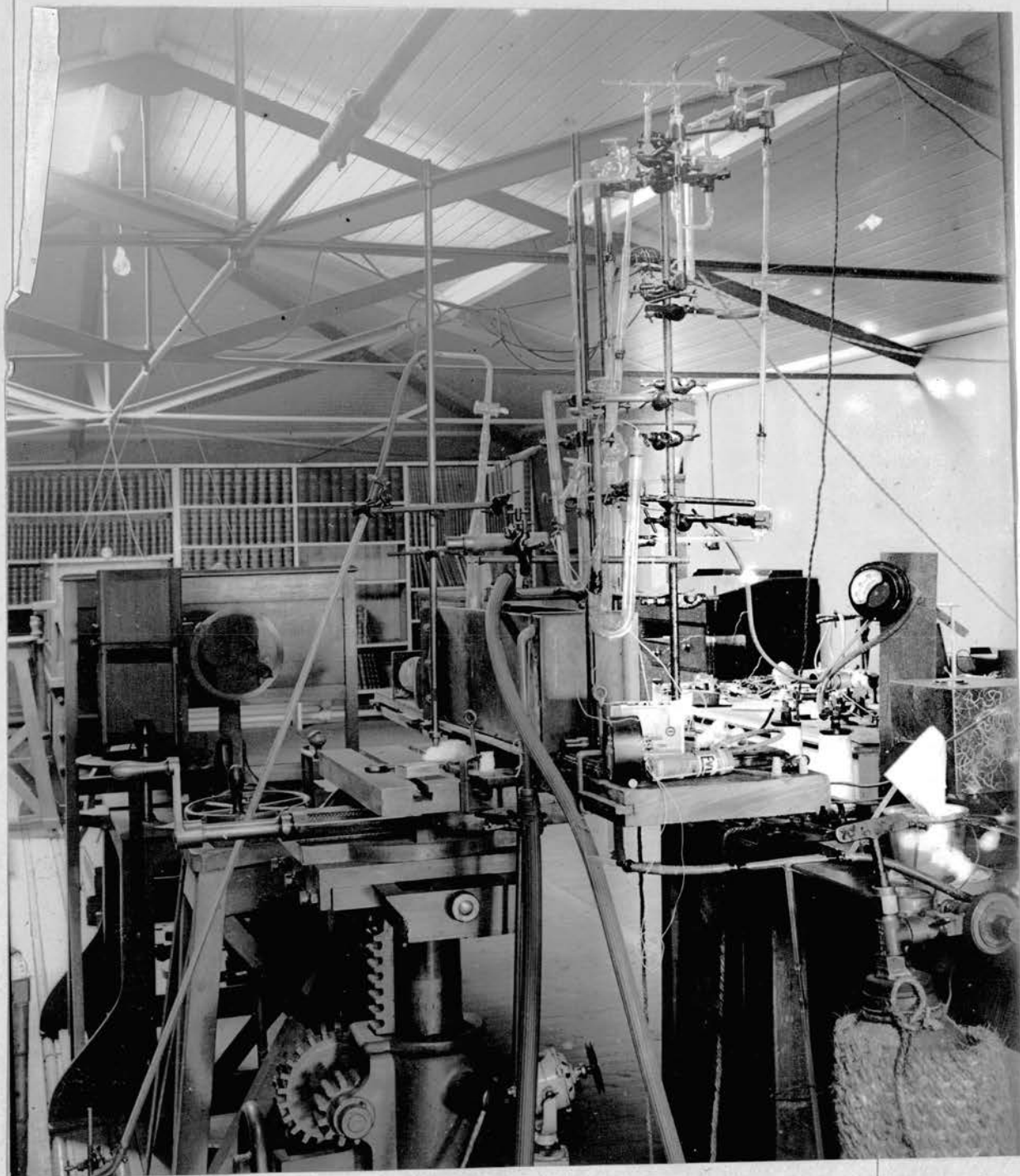
11 sweeps of 1000 cycles  
at 1000 cycles per second  
with 1000 cycles per second  
rate Dec. 15. Experiment 11.



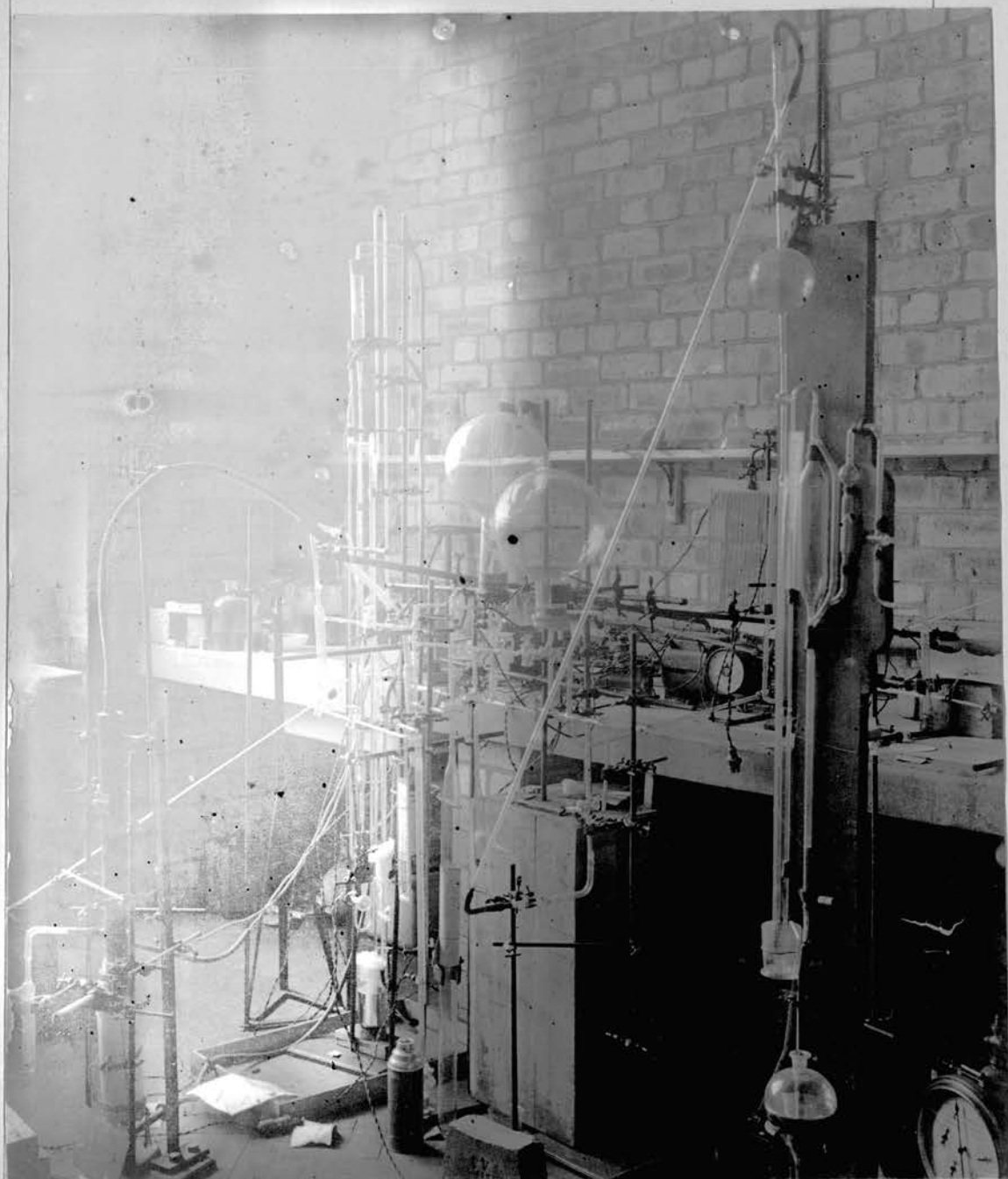
Labels on the right side of the page, connected to the waveforms by dashed lines:

- Ghosts
- $H_{\alpha}$
- $H_{\alpha}^2$
- Ghosts
- Ghost
- $H_{\alpha}$
- $H_{\alpha}^2$
- Ghost of the  $H_{\alpha}$  line

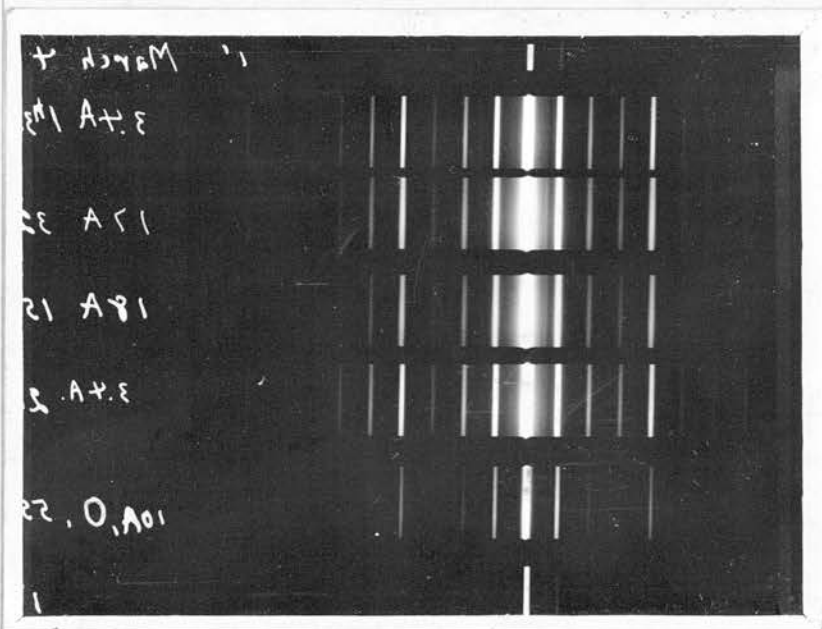
The Spectroscopic Equipment  
at the Observatory.



The Hydrogen Diffusion  
Apparatus



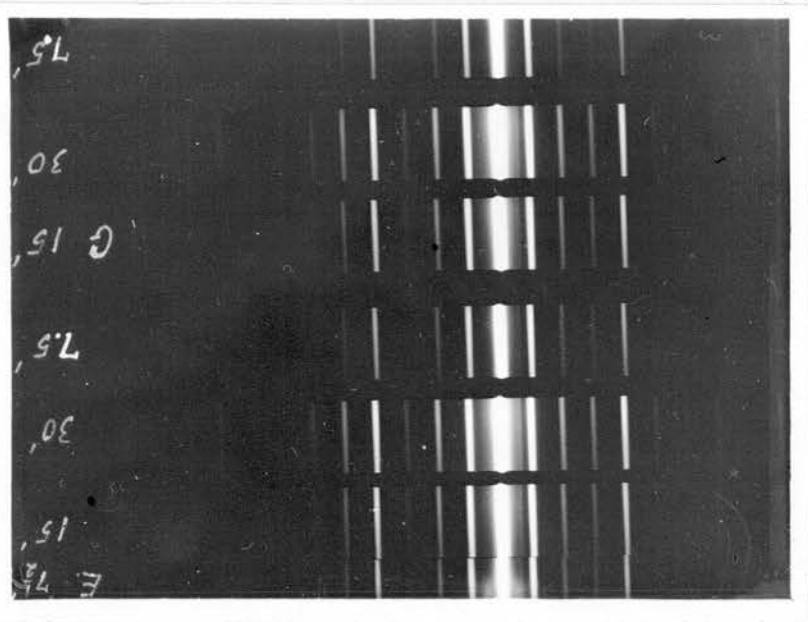
The Effect of Current Density  
on the Intensity Ratio between  
the  $H^2\alpha$  Line and the Ghosts of  $H\alpha^1$



Amps	Time
3.4	1'
3.4	1 <sup>h</sup> 32'
17.0	0 <sup>h</sup> 32'
18.0	0 <sup>h</sup> 15'
3.4	2 <sup>h</sup> 00'
Oxygen	. 1'

At the top and bottom are 1 minute exposures. The four exposures with varying current density have the values of the primary current and the time of exposure written at their right. Next to the bottom is an exposure with an excess of oxygen.

The Electrolytic Residue from  
the British Oxygen Company.



Exposure time

7.5'

30.0'

15.0'

7.5'

30.0'

15.0'

7.5'

The three upper exposures  
are standard hydrogen obtained from  
ordinary distilled water. The four  
lower exposures are the test sample.

A plate showing two samples  
of approximately the same  $H^2$   
concentration.

