found desirable to make an experiment on an iron salt at great dilution. Solutions of iron alum, $\text{Fe}_2.3\text{SO}_4.\text{K}_2\text{SO}_4.24\text{H}_2\text{O}$, having strengths in the salt of 1 in 100,000 and 1 in 1,000,000, were made up, and the absorption ratios were respectively .679 and .924. The latter solution is 1-20th the strength in salt of the weakest of the four principal constituents, and thus it is evident that a number of such impurities are quite likely to be able to bridge over the gap between the natural and made-up tap-water.

5. From the above it might be concluded that the absorption of ultra-violet light might be a delicate enough test to distinguish between different kinds of distilled water. But I have been unable to detect any difference. The specimens of distilled water available in the laboratory gave identical results, within the limits of experimental error, with two specimens of greater purity. One of these was of conductivity $.8 \times 10^{-6}$, and was also sterilized.

It need hardly be said that no mathematical formula can be given for the form of the curves in fig. 1. Apart from the fact that the non-homogeneity of the source of light prevents the simple exponential law of intensity from holding, it has been shown by Griffith * that in any case the intensity of the transmitted light is not proportional to the electrometer deflexion.

During the experiments I have been much helped by the advice of Professor Dreyer, and he has been kind enough to sterilize some of the solutions. Mr. D. H. Nagel has very kindly furnished me with some very pure distilled water. Lastly, I have to offer my thanks to Professor Townsend, in whose laboratory the work was performed, for his encouragement and suggestions during its progress.

LXVI. *The Dissociation of Water Vapour.*

By ALFRED HOLT, Junr.†

TWO years ago the author published in this Journal a short account of some experiments on the dissociation of water vapour by an incandescent platinum wire (Phil. Mag. 1907, p. 630). The percentage decomposition at a temperature of about 1000° (abs.)‡ was in close agreement with the values previously published by Nernst and Wartenburg (*Göttingen Nachrichten*, 1905), and Langmuir (Journ.

* I. O. Griffith, Phil. Mag., Aug. 1907.

† Communicated by the Author.

‡ All temperatures mentioned in this paper are absolute, unless stated to the contrary.

Amer. Chem. Soc. 1906, xxviii, p. 1357), but at 2000° the percentage was 1/7 the amount obtained by these authors.

The present communication contains an account of a repetition of the author's previous experiments.

It has not been found possible to determine the dissociation of water vapour with any accuracy for temperatures above 1650°, as it then becomes very difficult to calculate the temperature of a platinum wire from its resistance. The author's already published numbers for temperatures above this point are therefore of little value.

The errors in the determination below 1650° arose almost entirely from the fact that at the time the work was being carried out the author did not realize that the temperature-resistance curve for platinum approximated to a straight line above 1300°, and could not be calculated from the Heycock and Neville formula.

It will be seen from the following table that if the old temperatures are recalculated the values for the percentage decomposition do not greatly differ from those of other experimenters. The variation that remains results from a number of minor causes which have been corrected in the present research.

Old Temp.	Recalculated Temp.	Per cent. decomp. at 760 mm. determined experimentally.	Per cent. decomp. at 760 mm. calculated for new temp.
1220°	1220°	0·00108	0·001
1350	1318	0·00175	0·003
1500	1435	0·00887	0·0102
1540	1465	0·015	0·0158
1560	1480	0·0158	0·018
1630	1530	0·01842	0·027
1640	1540	0·0246	0·031

Although the method adopted by the author in the present and the previous research resembles that of Langmuir in that the decomposition of the water vapour in both is brought about by an electrically heated platinum wire, yet it differs in one important feature, namely, the wire is heated in a known volume of vapour at low pressure until equilibrium is established, instead of in a current of steam at atmospheric pressure.

The advantage of using water vapour at low pressure is that the amount of decomposition increases rapidly as the

pressure of the vapour diminishes, and as one of the experimental difficulties is the estimation of the electrolytic gas produced, it follows that the larger the amount the smaller the error in its estimation. The percentage decomposition was calculated for atmospheric pressure by the following formula :—

$$D_1 = D \times \sqrt[3]{\frac{P}{760}},$$

where D is the percentage decomposition at a water-vapour pressure P , and D_1 the decomposition at atmospheric pressure (760 mm.).

The results obtained between 1220° and 1640° are in good agreement with those of other experimenters, and, once the apparatus is set up and calibrated, the experiments can be performed easily and with expedition.

The apparatus is shown in fig. 1. It is essentially the

Fig. 1.

same as that previously described, but has various minor improvements in order to minimise possible errors.

The large glass bulb A had a capacity of 3948 c.c. at 15° C., and was connected by a ground-glass joint to the bulb D, which contained distilled water and a thermometer. The platinum wire EF was heated by the current led in through the mercury leads LM, but the resistance was only determined for the distance GH in order to avoid the error due to the cooling of the ends of the wire by the thick leads.

A thermometer was hung inside the globe A to determine the temperature of the vapour.

Each experiment was carried out as follows:—The whole apparatus being evacuated, the tap B was closed and the bulb A allowed to fill with water vapour. The tap C was left open until the water in D and the vapour in A had assumed the same temperature, and this had been noted. Then the tap C was closed and the wire heated to the required temperature until equilibrium was reached.

The wire was then allowed to cool, and the taps B and C being opened, the gases in the bulb A were pumped out through the condenser K surrounded by a freezing-mixture in order to condense water vapour.

The electrolytic gas was collected by a pump and analysed by explosion.

The platinum wire EF was about 7 cms. long and 0.5 mm. diameter, and gave a value for $\delta = 1.54$. At the ends it was welded to short pieces of thick platinum which communicated with the mercury leads LM. Extremely fine platinum wires, which would produce hardly any cooling effect, were welded on to it about 2 mm. from each end at G and H, and the resistance was determined between these two points.

The temperature of the wire up to 1300° was calculated from the resistance by the Heycock and Neville formula

$$\theta = \frac{R_t - R_0}{R_{100} - R_0} 100$$

$$t - \theta = \delta \left\{ \left(\frac{t}{100} \right)^2 - \frac{t}{100} \right\},$$

where θ is the temperature on the platinum thermometer, and t the temperature on the air thermometer.

But for higher temperatures, since the temperature-resistance curve becomes asymptotic to a straight line, the formula proposed by Langmuir has been employed:—

$$T(\text{abs.}) = 344.4 \frac{R_t}{R} - 247.$$

The resistance of the wire at 0° C. and 100° C. was determined from time to time during the course of the research, but it remained practically constant unless the wire was heated above 1670°. The irregularities in the resistance determination which begin about this temperature are due either to the volatilization of platinum, or to changes in the wire itself. On one occasion a wire was heated to 1760° for a short time and then examined, when it was found to have become brittle, and apparently crystalline.

It was noticed by Langmuir that when a wire was heated to a very high temperature in water vapour, the amount of apparent decomposition (*i. e.* volume of electrolytic gas collected) rapidly diminished, but that if the glass surfaces surrounding the wire were cleaned, the decomposition at once increased to the normal amount. He explained this on the supposition that platinum was sprayed on to the glass from the wire, and that it caused recombustion of the electrolytic gas. Platinum was undoubtedly deposited on the walls of the large bulb used by the author, but a number of experiments on this point showed that the amount of electrolytic gas which was caused to recombine was negligible, as, owing to the size of the bulb, the platinum deposit did not get heated sufficiently to exert a strong catalytic effect. Practically the same values were obtained before and after cleaning the globe.

The electrolytic gas resulting from the decomposition of the water vapour was collected and analysed in a vessel of the shape shown in fig. 1.

This gas-collector is a modified form of that previously used by Chapman and Lidbury (*J. C. S. Trans.* 1902, p. 1301), but it is specially suitable for the estimation of small quantities of gas, since the volume is determined by the weight of mercury displaced.

The collected gas always contained an excess of hydrogen. This varied considerably in amount, and did not seem to bear any direct relationship to the volume of electrolytic gas; sometimes it would be almost 30 per cent. of the total amount of gas, and at other times not more than 1 per cent. or 2 per cent.

A number of experiments undertaken to find the cause of the variations in the amount of this excess gave the following results:—

- (1) Moist oxygen is absorbed to a far greater extent than was imagined by the mercury in the fall tube of the pump. When the pump was working slowly,

or the volume of gas to be collected was very small, the percentage of oxygen absorbed was large, but if a considerable volume of gas was rapidly collected the percentage absorption diminished.

- (2) When the taps B and C were opened in order to pump off the gas and water vapour at the end of each experiment, the hydrogen, on account of its great power of diffusion compared with oxygen, passed rapidly through the condenser to the pump, leaving some of the oxygen behind condensed on the glass surfaces of the apparatus and dissolved in the water in the condenser. On carefully warming the glass this oxygen could be pumped out. The larger the amount of electrolytic gas produced the smaller the percentage of oxygen remaining on the glass surfaces. No perceptible quantity of oxygen was absorbed by the platinum wire, nor was hydrogen evolved from it when it was heated to incandescence.

This excess of hydrogen was always estimated and calculated as electrolytic gas.

The two following tables give the author's results.

The first consists of experiments carried out at almost constant temperature, and under as similar conditions as possible; the second gives the values obtained at a series of temperatures ranging from 1233° to 1637°.

TABLE I.

Temp. abs.	Percentage decomposition at 760 mm. pressure.	K.
1620°	0.05107	3.786
1621	0.05421	3.808
1620	0.04965	3.774
1620	0.04686	3.749
1620	0.05102	3.786
1620	0.05116	3.787
1620	0.04808	3.760
1620	0.04605	3.741
1620	0.05014	3.778
1620	0.05037	3.780
1620	0.05111	3.786
		Mean = 3.776

TABLE II.

Temp. abs.	Percentage decomposition at 760 mm. pressure.	K.
1233°	0·001087	3·768
1273	0·001864	3·783
1413	0·008366	3·768
1413	0·00906	3·803
1464	0·01658	3·857
1487	0·01612	3·753
1598	0·04992	3·849
1598	0·04963	3·844
1605	0·04719	3·802
1611	0·04996	3·806
1614	0·05263	3·818
1625	0·05855	3·830
1628	0·05716	3·809
1628	0·05628	3·803
1633	0·05825	3·805
1636	0·0591	3·797
1637	0·06118	3·810
		Mean=3·806

The third column in these tables contains the values for the equilibrium constant calculated from the percentage decomposition.

Three formulæ have been derived thermodynamically by Nernst and Wartenburg for calculating this constant K . The first was published in the *Göttingen Nachrichten* in 1905, and in a somewhat simplified form was used by Langmuir:—

$$\log \frac{2(100x)^3}{(2+x)(1-x)^2} = 11\cdot51 - \frac{25030}{T} + 2\cdot65 \log \frac{T}{1000} - 0\cdot00055(T-1000);$$

neglect x compared to 1, and divide by 3,

$$\log x = 3\cdot83 - \frac{8343}{T} + 0\cdot88 \log \frac{T}{1000} - 0\cdot00018(T-1000).$$

T is the absolute temperature, x the percentage decomposition. The constant K has therefore the value 3·83. At high temperatures it is necessary to substitute for x the value

$$\sqrt[3]{\frac{x}{\left(1 + \frac{x}{2}\right)(1-x)^2}}.$$

The experimental value for K determined by Langmuir from this formula is 3·79, which represents a difference of about 7 per cent. in the amount of decomposition from that

observed by Nernst and Wartenburg, for an alteration of 0.01 in the value of K makes 2.3 per cent. change in x .

The author has employed the same formula in calculating his values for K , and obtained the mean value for all his experiments of 3.791, which is identical with that of Langmuir.

The values in Table II. are, however, probably more correct than those in Table I., since they cover a temperature range of 400°.

The two other formulæ proposed by Nernst and Wartenburg were published three years ago (*Zeit. Physik. Chem.* 1906, li. p. 534).

The first of these,

$$\log \frac{2x^3}{\left(2 + \frac{x}{100}\right)\left(1 - \frac{x}{100}\right)^2} = 11.38 - \frac{25030}{T} + 2.40 \log \frac{T}{1000} - 0.00016(T-1000),$$

gave results which, when compared with those obtained by their experiments, were somewhat too high at high temperature, but were in good agreement at 1370°.

The second formula,

$$\log \frac{2x^3}{\left(2 + \frac{x}{100}\right)\left(1 - \frac{x}{100}\right)^2} = 11.46 - \frac{25030}{T} + 2.38 \log \frac{T}{1000} - 1.38 \times 10^{-4}(T-1000) - 0.685 \times 10^{-7}(T^2-1000^2),$$

gave results which were too high at about 1370°, but became more and more in agreement with the experimentally determined values as the temperature increased. If in both these formulæ x compared to 1 is neglected, and then the whole formula is divided by 3, the constant K has the value 3.79 or 3.82; and as one of these formulæ gives too high results where the other gives too low, and *vice versa*, it is evident that if the experimental values of Nernst and Wartenburg are correct, the constant must lie between them. Their mean 3.805 will be seen to be practically the same as that from the experiments given in Table II.

The values obtained by Löwenstein (*Zeit. Physik. Chem.* 1906, liv. p. 715) for the decomposition of water vapour at very high temperatures (up to 1968° abs.) are in agreement with the values calculated for $K=3.80$.

As these experiments were performed in a totally different manner from those of Nernst and Wartenburg, or Langmuir,

they confirm 3.80 as the most probable value for the equilibrium constant of water vapour, hydrogen, and oxygen.

An attempt was made to determine the lowest temperature at which water vapour could be decomposed by a hot platinum wire.

For this purpose, the taps B and C were both opened and a steady stream of water vapour was drawn through the bulb A while the temperature of the wire was gradually raised. The wire was first heated to 770°, and then raised about 25° C., each half hour. No oxygen or hydrogen was collected by the pump until the temperature was between 1023° and 1043°, when very small quantities of electrolytic gas (containing an excess of hydrogen) were obtained.

At this temperature the percentage decomposition is only about 28×10^{-6} per cent., so the greater quantity of the electrolytic gas produced would dissolve in the condensed water.

The fact that it was found possible to collect gas at so low a temperature as 1023° shows that the decomposition of the water vapour must begin at a considerably lower temperature, probably a few degrees above that at which oxygen and hydrogen would combine under similar conditions.

The University, Manchester.

LXVII. *Condensation of the Radium Emanation.* By
E. RUTHERFORD, *F.R.S.*, *Professor of Physics, University of Manchester* *.

RUTHERFORD AND SODDY first showed in 1903 that the radium emanation condensed from the gases with which it was mixed at a temperature of about -150° C. At that time only small quantities of radium preparations were available, so that the partial pressure of the emanation with the gases with which it was conveyed was exceedingly small. Notwithstanding the very minute quantity of emanation present, the temperatures of complete condensation and of complete volatilization were found to be sharply marked, and did not differ from each other by more than a few degrees. Some evidence was obtained that the emanation had a vapour-pressure like an ordinary gas.

This property of condensation of the emanation in liquid air has proved invaluable in all later researches as a means of separating the emanation from the inactive gases with which it is mixed.

* Communicated by the Author. A preliminary account of the results was communicated as a letter to 'Nature,' Feb. 18, 1909.