inverted vertical engine; in another, a three cylinder Willan's engine.

The working fluid is the vapor generated from petroleum spirit. The boiler consists of about 30 ft. of 1 in. copper tube worked into a double spiral coil, one of the coils being right and the other left handed. The coils are covered by a sheet iron case terminating above in a chimney. The petroleum spirit is forced by a feed pump into the coil, evaporated, and the resulting vapor or petroleum steam is used in the engine precisely like steam. The exhaust vapor passes into two copper pipes lying along the garboard stakes of the hull. These terminate in a small, strong tank in the bows of the boat, which is the equivalent of a hot well, and from which, by another pipe, the spirit condensed in the two submerged tubes is led back to the feed pump.

The entire arrangement is so simple and obvious that it will be understood without further description. The furnace is supplied, not with petroleum spirit, but with the ordinary safe oil used in so-called paraffin lamps. This paraffin oil, as we shall term it for the sake of distinction, is carried in a small circular tank, the top of which may be seen in our engraving just in front of the engine.

This tank is quite air tight, and is fitted with a small hand pump, by which air may be forced in on top of the petroleum in the tank. The pressure thus set up forces the paraffin out of a very ingenious sprayer, the paraffin being first highly heated and gasified; the flame thus produced is as smokeless as that of a Bunsen burner, and plays on the copper coils containing the petroleum spirit, which, as we have said, is converted into vapor and drives the engine. The working pressure is about 60 lb. above the atmosphere.

Not the least advantage about the system is that steam can be got up in about five minutes. No coal is carried to make dirt. There are no ashes, or cinders, or smuts to fall about. The boiler once started requires no further attention, so that one man can steer and take charge of the engine. For pleasure boats it far excels anything that has yet been brought before the

public in convenience. It possesses all the advantages of electricity, while the fuel used can be bought at any oil shop.

renew the supply in the tank, as it would readily take fire and burn the boat. But inasmuch as the same spirit is used over and over again for long periods, and the whole quantity carried for the use of a 5 horse engine does not exceed some two or three gallons, this can scarcely be regarded as a risk worth taking into account.

We may now turn to the question of economy, and the results actually obtained by Mr. Yarrow are very curious and interesting. It is laid down by all writers on thermodynamics that the efficiency of a heat engine is entirely independent of the nature of the fluid or other working substance, and is measured solely by the well known formula $E = \frac{T-t}{T}$, where E is the efficiency of the engine, T the absolute temperature at which it receives the working fluid, and t the absolute temperature at which it rejects it.

This is no doubt true when we deal with the working of the fluid, so to speak; but it is open to question if it be true when we have to deal with the making of the fluid as well. Thus it would be true of a hot air engine, for the apparatus does not make the air, but it is not quite satisfactorily proved that it would also be true of a steam engine and boiler combined, in which we have to make the fluid—steam—first and to use it afterward.

In order that it may apply, it is essential that the volumes of a vapor shall vary in the same ratio as their latent heats. Let us, for example, suppose that we have two liquids, one of which we shall call A and the other B. If the latent heat of the vapor of A is one half the latent heat of the vapor of B, then the volume for the same pressure of vapor produced by A will be one half the volume of that produced by B, so that although a pound of coal might evaporate 20 lb. of A and only 10 lb. of B, yet an engine driven by the vapor first of A and then of B would make only the same number of strokes in each case.

The question which presents itself for solution here is, Is this true of petroleum spirit? The only answer

The most crucial test is, however, that supplied by the Zephyr launches to which we have referred. These engines can be worked with water or petroleum spirit; with the latter they indicate about 4 to 5 horse power, with water about 1 or 1½ horse power, the consumption of paraffin oil as fuel being the same in both cases. —The Engineer.

[AMERICAN CHEMICAL JOURNAL.]

ON THE COMBUSTION OF WEIGHED QUANTITIES OF HYDROGEN, AND THE ATOMIC WEIGHT OF OXYGEN.

By E. H. KEISER.

THE atomic weight of oxygen is the foundation upon which the entire system of atomic weights rests. It is unquestionably one of the most important constants in chemical science. At the present time the opinions of chemists differ as to its most probable value. While many accept 15.96 as the mean result of all the more trustworthy determinations, others are inclined to believe that the whole number 16 approaches nearer to the truth. Both numbers lie between the maximum and minimum values that have been obtained by the best methods heretofore employed in determining this constant. As all the other atomic weights, with few exceptions, depend upon that of oxygen, it follows that two values may be obtained for each element accordingly as one or the other of these numbers is made the basis of the calculation. As a result of this, all the atomic weights are uncertain to the extent of about one quarter per cent. of their values. It is very desirable for this reason, as well as for others of a more speculative nature—as, for example, the question of the validity of Prout's hypothesis—that the atomic weight of oxygen should be redetermined with the very greatest care.

In a preliminary paper* I called attention to a new method of determining this atomic weight, by means of which, it seemed to me, more accurate results could be obtained than by the older methods. Briefly stated,

PETROLEUM LAUNCH ZEPHYR.

we can give is that very little is known on the subject, and that Mr. Yarrow's direct experiments go to show that it is not true. In the first place, it is difficult to say what the precise composition of petroleum spirit is; but assuming it to be very nearly the same as benzene, its latent heat is about one-fifth of that of steam; its boiling point is, however, much lower than that of water; at 274 deg. Fah. it has a pressure of about 50 lb. on the square inch above the atmosphere, that of steam of the same temperature being 30 lb.

According to the text books, its vapor volume would be about one-fifth that of steam, or possibly less. The direct experiments, however, made by Mr. Yarrow do not confirm this view. Thus it would appear that the latent heat is much less than one-fifth, for by repeated experiments it has been ascertained that a given weight of fuel—coal gas—will evaporate in an open vessel, under atmospheric pressure, nine times as much petroleum spirit as water. There are corrections to be made, possibly, but the figures cannot be very far from the truth.

The experimental land engine fitted up by Mr. Yarrow has a small vertical boiler traversed by coils of copper pipe. This engine is provided with duplicate sets of condensing apparatus and a small Prony brake, a counter, apparatus for taking diagrams, etc. Steam being raised from water in the boiler, a certain number of revolutions is got by the consumption of a given number of cubic feet of gas burned under the boiler to make steam. Everything else being left unaltered, steam is shut off and petroleum spirit pumped into the copper coils in the hot water in the boiler. The pressure of the steam falls to 30 lb. from 50 lb., that of the petroleum spirit vapor generated in the coil becomes 50 lb., and the engine is then run with it instead of steam, until the same number of cubic feet of gas has been burned.

Dozens of experiments gave the same result. The engine always made at least twice as many revolutions with the spirit as it did with steam. In another experimental engine the spirit was pumped direct into the water in the boiler; the result was about the same—two to one in favor of the spirit; but it was also found that in all cases about twice as much spirit had to be vaporized per minute as water, that is to say, twice as large a feed pump was needed with the spirit as would suffice with the water.

As to the vapor unmixed with air exploding if ignited, that is a physical impossibility. It could no more explode, or even burn, without air than coal gas can. Consequently, if one of the boiler coils were to be split by excessive pressure, the spirit vapor as it rushed out would take fire and flare up the chimney; but the chances of a true explosion resulting are about as remote as would be the case if water were used.

The principal precaution necessary is to take care that none of the spirit is spilled when it is necessary to

it consists in burning weighed quantities of hydrogen by passing the gas over heated copper oxide, and weighing the water formed. From the weight of water obtained by the combustion of a known weight of hydrogen, the atomic weight of oxygen may be readily calculated.

It is evident that the accuracy of the results obtained by this method must depend to a large extent upon the purity of the hydrogen that is used and upon the correctness with which it is weighed. It is, however, extremely difficult to weigh accurately any considerable quantity of hydrogen in the gaseous state. If Regnault's method of compensated glass globes be used, it would require very large and heavy vessels to weigh comparatively small quantities of hydrogen, and in weighing such large globes errors may arise from many different sources. Lord Rayleigh has recently pointed out a source of error in this method which appears to have been overlooked by all who had previously used it. He has shown that the volume of a glass globe is larger when it is full than when it is empty, and that the weight of the gas contained in it is not equal to the difference in weight of the full and empty globe.

In order to be able to weigh hydrogen accurately, I have taken advantage of the beautiful discovery made by Thomas Graham in the year 1866. Metallic palladium, as he has shown, has the power at ordinary temperatures of occluding many hundred times its own volume of hydrogen gas. The palladium hydrogen which is thus formed is stable at ordinary temperatures, and the metal retains the hydrogen even in a vacuum. If, however, the temperature be raised above 100°, then the gas will be expelled in a slow and regular current. Under atmospheric pressure nearly all of the hydrogen can be driven out at temperatures below 200°. By inclosing a quantity of metallic palladium in a glass vessel from which the air has been removed, and saturating it with pure hydrogen, a large volume of the gas may be condensed into a small space. If now the temperature be raised gradually, the gas will be driven out slowly and regularly. If the vessel be weighed before and after the heating, the loss in weight will equal the weight of hydrogen that has been ex-

public in convenience. It possesses all the advantages of electricity, while the fuel used can be bought at any oil shop.

Two very important questions have, however, to be considered. Is the new motor safe? Is it economical, seeing that paraffin oil at 7d. a gallon is a very much more expensive commodity than coal? We shall deal first with the question of safety.

Rock oil is an excessively complex hydrocarbon. It is possible to distill from almost any sample as many as twenty products, each with a different specific gravity and flashing point. Petroleum spirit may be said to stand midway between the highly volatile benzoles and the safe paraffins. Its vapor is, however, of course very inflammable and explosive if mixed with a sufficient quantity of air.

In Mr. Yarrow's launch, however, the spirit is hermetically sealed up in the boiler and condenser tubes. The only places where leakages can take place are at the stuffing boxes. These are fitted with lantern brasses; from each lantern a small tube is led to the condenser, so that leakage into the atmosphere cannot well take place. Even if it did, however, no evil consequences could ensue in an open launch, as the vapor would be too largely diluted to burn.

As a matter of fact, in the experimental shed fitted up in the first instance by Mr. Yarrow, leakages used to take place to such an extent that those in the room could scarcely breathe; but naked gas jets were burning all the time, and no approach to an explosion ever occurred. Whether petroleum spirit could be used in a closed engine room with safety must remain a matter of opinion. We believe that it could. But this is quite beside the question, because there is nothing in common between an open boat and a closed stoke-hole.

As to the vapor unmixed with air exploding if ignited, that is a physical impossibility. It could no more explode, or even burn, without air than coal gas can. Consequently, if one of the boiler coils were to be split by excessive pressure, the spirit vapor as it rushed out would take fire and flare up the chimney; but the chances of a true explosion resulting are about as remote as would be the case if water were used.

The principal precaution necessary is to take care that none of the spirit is spilled when it is necessary to

* Ber. d. chem. Ges. 20, 2323. † Chem. News, 57, 73.

pelled. It is possible, therefore, with an apparatus of small dimensions to weigh comparatively large volumes of hydrogen. Preliminary experiments showed that 100 grammes of palladium foil will readily absorb from 0.6 to 0.7 gramme of hydrogen, and that with an apparatus having a volume of about 150 c.c. and weighing 130 grammes, it is possible to weigh, with great accuracy, an amount of hydrogen which in the gaseous state would occupy a volume of from 7 to 8 liters. A glass globe that could hold the same quantity of gas would be much heavier than the tube containing the palladium; and such a globe, owing to its much greater volume, could not be weighed with nearly the same degree of accuracy.

There is, however, another and no less important advantage gained in weighing hydrogen in the condition of palladium hydrogen. It is necessary that the hydrogen which is weighed and burnt for the purpose of determining the atomic weight of oxygen should be absolutely pure. The greatest difficulty connected with the preparation of pure hydrogen is to get rid of all traces of air. Other impurities may be avoided by starting with chemically pure materials for the preparation of the gas, and by using appropriate absorbing and drying reagents for purifying it. If air is present, the oxygen of the air may be removed by passing the gas over heated copper. Water will be formed, and this may be absorbed by means of phosphorus pentoxide. But there is no way of removing the nitrogen. Palladium, however, has not the power of absorbing nitrogen. If the hydrogen used for saturating the palladium contains nitrogen, the hydrogen will be occluded, the nitrogen will remain unacted upon; and, after the palladium has been saturated, the nitrogen may be removed from the palladium tube by means of an air pump.

Thomas Graham,* who first studied the behavior of palladium toward gases, found that hydrogen was the only constituent of illuminating gas that possessed the power of penetrating palladium foil. Wohler† has shown that palladium cannot absorb ethylene, and that at high temperatures it decomposes hydrocarbons into carbon and hydrogen. Wilm‡ has also observed that at high temperatures palladium can decompose hydrocarbons, and he has shown that the hydrogen is absorbed by the metal, while the carbon is left on its surface in an extremely finely divided condition. Hempel§ has found that from a gas mixture containing hydrogen, marsh gas, and nitrogen, the hydrogen may be completely absorbed and separated from the other constituents by means of metallic palladium.

PRELIMINARY EXPERIMENTS.

While it thus appears from a study of the literature of palladium that this metal has not the power of absorbing nitrogen or marsh gas, ethylene, and other hydrocarbons, it, nevertheless, seemed necessary to determine by careful preliminary experiments whether, under the conditions under which the palladium was to be used for occluding hydrogen, it might not be able to take up minute traces of nitrogen or oxygen. For this purpose several pieces of palladium foil, weighing together 140 grammes, after being carefully cleaned and rolled into the shape of a cylinder, were placed in a wide glass tube which was closed at one end. The open end was drawn down to a small diameter and fused to a three-way glass stop cock. The tube was exhausted with a Geissler air pump and the metal heated to a temperature of about 400° in the vacuum. The glass tube was protected from the flame by a wrought iron trough containing a layer of magnesia. After the metal had been heated for some minutes in the vacuum, the lamp was removed. Pure dry nitrogen gas was then admitted by means of the three-way stop cock, and the metal was allowed to cool down slowly and to remain for several hours in an atmosphere of nitrogen. The tube was thereupon exhausted with the pump and, after a vacuum had been obtained, it was again heated. Not the minutest trace of gas was given off. If only a small fraction of a cubic centimeter of nitrogen had been driven out of the palladium, it would have been detected, because the pump was kept in constant operation. The experiment was repeated several times, but the result was always the same. In one experiment the palladium tube was exhausted and weighed. It was then heated in the vacuum and treated with nitrogen as above described. After being again exhausted, the weight was found to be the same as before. It appears, therefore, that under these conditions palladium has not the power of absorbing nitrogen; but these are the conditions that were found to be the most favorable for the occlusion of hydrogen. After the metal had been heated in a vacuum, it was allowed to cool in an atmosphere of hydrogen. The gas was absorbed in large quantities. When perfectly cold, the tube was exhausted and weighed. It was found to be nearly a gramme heavier than it was before the hydrogen had been occluded. The hydrogen was held so firmly by the palladium that, when the tube was exhausted with the air pump, the palladium hydrogen showed but a very slight tension. On warming it, however, the gas was given off in large quantities. Other experiments made with oxygen showed that this gas also, under the conditions described above, is not absorbed by palladium.

Experiments were now made for the purpose of determining what the effect would be of treating palladium with hydrogen containing a small percentage of air. The metal was heated in a vacuum and then allowed to cool in an atmosphere of hydrogen containing air. The hydrogen was rapidly absorbed, but at the same time a minute quantity of moisture was deposited on the interior surface of the tube. When no more gas was absorbed, the palladium tube was connected with a weighed phosphorus pentoxide U tube and heated. As the gas escaped from the palladium tube, the film of moisture gradually disappeared. The U tube was weighed again after the hydrogen in it had been displaced by air. It was found to have increased in weight, thus showing that when palladium is treated with hydrogen containing air, the oxygen is converted into water. The idea suggested itself that perhaps hydrogen dioxide might also be formed, and that the palladium hydrogen in the presence of nitrogen might cause the formation of ammonia. The

palladium was therefore treated again with hydrogen containing air, and after the metal had been saturated the palladium tube was connected with a Geissler potash bulb containing Nessler's solution. The gas was thereupon driven out of the palladium tube by heating, and although more than six liters of hydrogen were passed through the Nessler's solution, not the faintest reaction for ammonia was obtained. The experiment was repeated, but in this case, instead of using Nessler's reagent, the gas from the palladium tube was led through a solution of potassium iodide and starch paste to which a small quantity of ferrous sulphate had been added. No reaction for hydrogen dioxide was obtained.

Another experiment was made for the purpose of determining whether palladium itself is not volatilized when palladium hydrogen is decomposed. A quantity of palladium foil was carefully weighed and then saturated with hydrogen. The hydrogen was then completely removed by heating in the presence of air. On weighing the foil again, its weight was found to be unchanged.

The conclusions drawn from the results of these preliminary experiments are as follows: Palladium at temperatures below 400° cannot occlude oxygen or nitrogen. If palladium be treated with hydrogen containing a trace of nitrogen, the hydrogen will be occluded, but the nitrogen will remain unabsorbed, and it may be removed from the vessel containing the palladium hydrogen by means of an air pump. If the tube containing the palladium hydrogen be heated, pure hydrogen will be expelled, and the weight of the gas thus driven out may be determined from the loss in weight of the palladium tube. If palladium be treated with hydrogen containing traces of air, the hydrogen will be occluded, the nitrogen will remain unabsorbed, but the oxygen will be converted into water. By means of an air pump the nitrogen and a portion of the water may be removed from the tube containing the palladium. On heating the tube, the hydrogen which is driven out will carry with it traces of moisture. The weight of the hydrogen and moisture thus expelled may be determined from the loss in weight of the palladium tube, and the amount of moisture present in the hydrogen may be determined by passing the gas through a weighed phosphorus pentoxide U tube. Lastly, palladium itself is not volatilized when palladium hydrogen is decomposed.

APPARATUS FOR PREPARING AND WEIGHING THE HYDROGEN.

The construction of the palladium tube that was used for weighing the hydrogen in the atomic weight

with phosphorus pentoxide. The joints of the apparatus were made of thick walled rubber tubing; they were all wired securely and coated with varnish.

The method of charging the palladium with hydrogen was conducted as follows: The palladium tube, resting upon a trough of sheet iron and protected from contact with the iron by a layer of magnesia, was connected with a Geissler air pump and exhausted.

After the palladium had been heated to a temperature of about 250° for fifteen minutes in the vacuum, the stop cock, *b*, was closed, and, while the tube was still warm, the end, *c*, was connected with the U tube, *h*, as shown in Fig. 2. Meanwhile all the air in the hydrogen generating apparatus and the wash bottles had been expelled, as the evolution of gas was begun more than one half hour before the palladium tube was attached. For several minutes more the hydrogen was allowed to escape from the downward branch of the stop cock, to which a straight glass tube dipping in mercury was attached, to insure that all the air had been displaced in the tube connecting the palladium vessel with the U tube, *h*. The stop cock was then turned carefully so as to allow a slow stream of hydrogen to enter the warm palladium tube. Under these circumstances the metal absorbs the hydrogen so rapidly that it is necessary to open the stop cock very cautiously, otherwise the gas will pass too rapidly through the wash bottles.

While the hydrogen is being absorbed the metal cools down very slowly, because considerable heat is evolved in the formation of palladium hydrogen. When the absorption of gas had become very slow—and from two to two and a half hours sufficed for saturating 140 grammes of palladium—the stop cock was closed and, after being again attached to the Geissler pump, the tube was exhausted. By this means nitrogen, if it should have been present in the hydrogen used for saturating the palladium, was removed. Palladium hydrogen gives off hydrogen very slowly in a vacuum, so that, if the pump be kept in operation for some time, all traces of nitrogen in the palladium tube and in the pump itself may be completely carried out by means of this slow evolution of gas. After the removal of the nitrogen the tube was closed and disconnected from the pump. It was then thoroughly cleaned and placed in the balance room.

A short beam analytical balance, made by Becker Brothers, New York, was used for all the weighings. It could carry safely 225 grammes in each scale pan, and was adjusted so that a load of one milligramme caused a deflection of twelve divisions of the ivory scale. All weighings were made by the method of vibrations. In weighing the palladium tube and the tubes used for

determinations is shown in Fig. 1. The expanded portion, *a*, contained 140 grammes of palladium foil that had previously been thoroughly cleaned, and which, before being placed in the tube, had been heated to a bright red heat in a vacuum. The three-way glass stop cock, *b*, was fused to *a*, and its construction will be readily understood from the cross section drawing, *b'*. The end, *c*, was ground to fit accurately into the phosphorus pentoxide tube, *d*, shown in Fig. 3. The diameter of *a* was 3 cm. and its length 14 cm. The total length of the tube, including the stop cock, was 26 cm.; its weight, including that of the palladium, was 204.5 grammes. The first six determinations were made with a somewhat smaller tube, which contained only 100 grammes of palladium and weighed 160 grammes.

The hydrogen that was used for saturating the metal was prepared by the action of pure dilute sulphuric acid upon chemically pure zinc, free from arsenic. The apparatus for generating and purifying the gas is shown in Fig. 2. The zinc was placed in *e*, and it was acted upon by the dilute sulphuric acid contained in *f*. The vessel, *f*, was supported by a shelf, and was connected with *e* by means of glass tubing, as shown in the figure. After leaving the generating apparatus, the hydrogen passed through four wash bottles. The first one contained a solution of lead hydroxide in concentrated caustic potash; the second one, a concentrated solution of potassium permanganate, acidulated with dilute sulphuric acid; the third one, an alkaline solution of potassium permanganate; and the fourth one, pure concentrated sulphuric acid. To the fourth wash bottle was connected the combustion tube, *g*, which contained metallic copper. The copper was obtained by the reduction of the chemically pure oxide in a current of hydrogen. A small gas furnace supported the combustion tube, and while the gas was being generated the tube was kept at a bright red heat. After having passed over the heated copper, the gas was conducted through the U tube, *h*, which was filled

condensing and absorbing the water, each tube was compensated by a similar one, of the same external volume, constructed of the same material, and having nearly the same weight. The weights were also made by Becker Brothers; the smaller ones were of platinum, the larger ones of brass. One of the ten-gramme weights was selected as the standard, and the relative values of all the others were determined by the well known method of adjustment. All atomic weight determinations were made on days when the weather was clear and dry; and, as a combustion including the weighings could be made in four hours, the barometer, temperature of balance room, and the humidity of the air remained practically constant during each determination.

METHOD OF BURNING THE HYDROGEN.

The arrangement of the apparatus that was used for burning the hydrogen is shown in Fig. 3. The palladium tube was connected by means of a ground glass joint with the weighed phosphorus pentoxide tube, *d*. The latter tube served to determine the amount of moisture in the hydrogen that was expelled from the palladium tube. The tube, *d*, was connected by means of another ground glass joint with the combustion tube, *g*, which contained copper oxide. For the purpose of obtaining pure copper oxide, the chemically pure granular oxide of commerce was reduced in a current of pure hydrogen, and the metallic copper thus obtained was heated to a bright red heat in a vacuum. All volatile matter having been removed in this way, the copper was oxidized with pure oxygen. In each determination the reduced copper was again oxidized to copper oxide, so that the condition of the combustion tube was the same at the beginning and end of the combustion. The copper oxide that was used in the determinations recorded below had been repeatedly reduced and oxidized in preliminary determinations. The combustion tube was 90 cm. in length and had an internal diameter of 15 mm. It was filled to within 10

* Ann. Chem. (Liebig) Supp. Band 5, 61.

† Ber. d. chem. Ges. 14, 874.

‡ Ann. Chem. (Liebig) 184, 129.

§ Ber. d. chem. Ges. 12, 636.

cm. of the open end, and it contained so much copper oxide that there was never more than one half of it reduced in any determination. The object of this large excess was to insure the complete combustion of the hydrogen. The water formed by the combustion of the hydrogen was condensed in the bulb apparatus, *p*, and the U tube, *r*. When not connected with the combustion tube, *p* was closed by means of ground glass plugs. A tightly fitting rubber stopper was used to connect the bulb apparatus with the combustion tube. During the combustion the bulbs were kept cool by being surrounded with cold water placed in a glass dish. The U tubes, *r* and *s*, contained phosphorus pentoxide, and *s* served to protect *r* in case air should be drawn backward into the combustion tube. To the downward branch of the stop cock of the palladium tube was attached the three-way glass stop cock, *m*, by means of which either oxygen or nitrogen could be passed through the apparatus. The oxygen before entering was conducted through concentrated sulphuric acid, concentrated caustic potash, and over phosphorus pentoxide. The nitrogen was purified by passing through concentrated sulphuric acid, concentrated caustic potash, over red hot copper to remove the oxygen, and then over phosphorus pentoxide.

The combustion of the hydrogen was conducted in the following manner: In the first place, the copper oxide was heated to a bright red heat in a current of dry air, so as to remove hygroscopic moisture. The U tube, *d*, the palladium tube, and the tubes, *p* and *r*, after having been carefully weighed, were connected as shown in Fig. 3. The tube, *s*, and the stop cock, *m*, were then attached, and a stream of nitrogen was allowed to pass through the apparatus for from 20 to 30 minutes to expel the air, thus avoiding the possibility of an explosion when the hydrogen was admitted. The palladium tube was thereupon warmed gently, and, after its temperature had risen to a little above 100°, the stop cock, *b*, was turned slowly so as to cut off the current of nitrogen and to allow a slow stream of hydrogen to pass through *d* into the copper oxide tube. In warming the palladium tube the flame never came in contact with the glass. The tube was always supported by an iron trough, and the glass was protected from contact with the iron by a layer of magnesia. The rate at which the gas was expelled and burnt could be easily regulated by raising or lowering the temperature of the palladium tube. After the greater quantity of hydrogen had been burnt and the current of gas had become very slow, the stop cock, *b*, was turned to its original position, thus closing the palladium vessel and readmitting the stream of nitrogen. The palladium tube was then allowed to cool; in so doing the metal reabsorbs the gaseous hydrogen that is present in the tube, and at the end of the operation the pressure in the interior of the tube is the same as at the beginning. After the nitrogen had carried all of the hydrogen into the combustion tube, oxygen was admitted through *m*, and the reduced copper was converted into copper oxide. The oxygen was then displaced by a stream of dry air, and the copper oxide was allowed to cool.* The tubes were then disconnected and, after being cleaned, were taken to the balance room. They were allowed to stand a sufficient length of time to acquire the temperature of the room, and were then weighed.

The weight of water formed was determined from the increase in weight of *p* and *r*. To the weight of liquid water in *p* was added the weight of air which it displaced, thus its weight in vacuo was obtained. The weight of the tube, *d*, remained the same as at the beginning of the combustion, provided the hydrogen that had been used for saturating the palladium was free from oxygen. In this case the loss in weight of the palladium tube gave the weight of hydrogen that had been burnt. If, however, a small quantity of oxygen was present in the hydrogen used for charging the palladium, then the gas that was expelled from the tube contained a trace of moisture, and, in this case, the increase in weight of *d* had to be deducted from the apparent weight of hydrogen. In all carefully conducted atomic weight determinations, the increase in weight of *d* was never found to be more than a fraction of a milligramme.

ATOMIC WEIGHT OF OXYGEN.

The following results have been obtained by this method:

No. of Experiment.	Wt. of H burnt. Grammes.	Wt. of Water obtained. Grammes.	Atomic Wt. of Oxygen.
1	0.34145	3.06338	15.943
2	0.63394	6.14000	15.955
3	0.65529	5.88200	15.952
4	0.65295	5.86206	15.954
5	0.66664	5.98116	15.944
6	0.66647	5.98341	15.955
7	0.57967	5.20493	15.958
8	0.66254	5.94758	15.952
9	0.87770	7.86775	15.950
10	0.77215	6.93036	15.951
Total	6.55880	58.86263	[15.9492]

From these numbers the ratio of hydrogen to oxygen is found to be: H : O :: 6.55880 : 52.30383, or H : O :: 1 : 7.9746, and the atomic weight of oxygen = $7.9746 \times 2 = 15.9492$. Maximum value, 15.958; minimum value, 15.943. The result obtained from these determinations appears, in the author's mind, to furnish very strong evidence in favor of the view that the relative atomic weight of oxygen cannot be greater than 15.96, and that its true value is probably a little less than this number.

Several months after the appearance of my preliminary

*For the purpose of determining whether traces of hydrogen could escape combustion by this method, the following experiment was made: About one half of the copper oxide in the combustion tube was reduced with hydrogen, then a current of carbon dioxide was allowed to enter at *m*, so as to carry all of the hydrogen into the combustion tube. The gases after passing over the copper oxide were conducted through caustic potash, then over phosphorus pentoxide, and again over copper oxide contained in a second combustion tube. To this second combustion tube was attached a weighed phosphorus pentoxide tube. If any hydrogen should have escaped combustion in the first combustion tube, where it was diluted with a large excess of carbon dioxide, it must have accumulated in the caustic potash bulbs. Subsequently, when air was drawn through the apparatus, the hydrogen would have been carried into the second combustion tube in much more concentrated condition than it left the first one. In this tube it would have been burnt, and the phosphorus pentoxide tube would have increased in weight. Although the experiment was tried several times, the weight of the latter tube always remained constant.

inary paper, and while this investigation was still in progress, Prof. J. P. Cooke and Mr. T. W. Richards published the results of a redetermination of the atomic weight of oxygen by the same general method which I had proposed. They also have determined the quantities of water formed by the combustion of weighed amounts of hydrogen. But our work differs very much in the methods employed for weighing the hydrogen. Messrs. Cooke and Richards have weighed it in the gaseous state, and have used Regnault's method of weighing gases by means of compensated glass globes. Aside from the difficulties of weighing accurately such large glass globes, owing to air currents, changes of atmospheric condition, etc., and the fact that a comparatively heavy vessel must be used for weighing but a small quantity of hydrogen, this method is open to the objection that all impurities that may be present in the gas, such as traces of nitrogen or air, are weighed as hydrogen. Errors caused by impurities in the hydrogen tend to diminish the atomic weight of oxygen. On the other hand, Lord Rayleigh has pointed out another source of error which tends to increase the atomic weight. As mentioned above, the volume of a glass globe is not the same when it is full and when it is empty, and the difference between the full and empty weighings is less than the true weight of hydrogen.

The method which I have employed for obtaining weighed quantities of hydrogen seems to me to be free from these sources of error. By using palladium, a considerably larger quantity of hydrogen may be obtained from a very much smaller and lighter apparatus, consequently the gas can be weighed with greater accuracy. Impurities such as nitrogen and oxygen are eliminated, and as the pressure in the interior of the palladium tube is the same at the beginning and end of the determination, and as the vessel is of small dimensions, there can be no change of volume of the tube. Nevertheless, the value for the atomic weight of oxygen obtained by Messrs. Cooke and Richards agrees very closely with that obtained by this method. Value obtained by Cooke and Richards = 15.953. Value obtained by the palladium method = 15.949. That our results do not differ more is probably due to the fact that the errors in the method used by Messrs. Cooke and Richards are in opposite directions and tend to neutralize each other.

VERNON HARCOURT'S NEW PHOTOMETER.

The holophotometer has been designed in order to get rid of two difficulties connected with other methods of attaining the same object, viz., to measure the light emitted in every direction by any luminous source. These difficulties are: (1) The movement of the light to be measured or of the standard lamp, neither of which is desirable. (2) The errors caused in the measurement of lamps provided with reflecting fittings, by the assumption that the flame is the zero point from which measurements should be made, whereas, strictly speaking, the principal focus formed by the reflector should be taken as the zero point. Inasmuch, then, as this focus may be several inches away from the flame, and as the length of bar usually employed is 60 inches, it is evident that serious errors may be introduced by the difference between the real and the assumed zero point. To establish the existence of such an error, and to eliminate it, two things are necessary, viz., that readings should be taken with bars of various lengths and that the length of the bar should be very great

taining a graduated bar with movable disk (say of the Letheny pattern), and having a standard lamp fixed at the zero of the bar. The lamp to be measured is mounted upon or is in rigid connection with the movable table, and is therefore not moved during a series of readings.

The holophotometer consists of an axis working friction-tight in a collar supported by a vertical pillar. The axis is accurately fixed at the same height, and in a line with the center of the disk. At the end nearest to the disk is placed a large mirror with its center concentric with the axis, but so arranged that the plane of the mirror may be inclined and clamped at any angle to the axis. At the other end of the axis is fixed a telescopic arm carrying a smaller mirror, which is capable of being turned into any required position. The arm being rigidly fixed to the rotating axis of the instrument, to which is also attached the larger mirror,

it follows that the rotatory motions of the mirrors about the axis are identical. The angles of rotation are measured by the indications upon a divided circle attached to the moving axis, which are shown by a pointer fixed to the upright support.

The mirrors are adjusted in such a way that the light from the lamp to be measured falls upon the smaller mirror, thence is reflected on to the larger one, and, finally, along the axial line of the photometer disk. As both mirrors rotate together, it follows that if a horizontal beam is reflected correctly, all other beams will find their way along the axis of the photometer. If, therefore, the arm carrying the small mirror be moved through various angles, it will receive the light emitted from the lamp at those angles, and the light will at every angle be transmitted along the axis of the photometer. The divided circle is made large enough to serve as a complete screen of all direct light, and only the light falling on the small mirror can find its way to the disk. In order that absolute, as well as comparative, tests may be carried out, only one additional measurement need be made. The direct horizontal light is measured without the interposition of the holophotometer (which is mounted so as to be easily moved out of the direct line); then the mirrors are interposed, and a new measurement made. The additional path traveled by the light is allowed for in calculation, and thus the absorption of the mirrors is found once for all for the particular character of light under measurement. It is only necessary afterward to

compared with that between the real source of light and the focus formed by the reflector. Both these points are secured by the use of the holophotometer. The instrument is mounted upon a table capable of being moved nearer to or further from a fixed table con-

*Professor Cooke has recently determined the value of the error caused by the change in volume of the glass globe. He finds the corrected atomic weight of oxygen to be 15.869. This result, it seems to me, is undoubtedly too low. In my preliminary experiments (Ber. d. chem. Ges. 20, 2323), before the precaution was taken to remove traces of nitrogen by exhausting the tube containing the palladium hydrogen, nearly the same figure was obtained, viz., 15.872.

multiply subsequent values by this coefficient of absorption in order to obtain absolute measurements at various angles.

The employment of mirrors in photometry has sometimes led to serious errors; but it will be seen by the foregoing description that inasmuch as the relative angle of the mirrors is never changed, and as their absorption is easily calculated and allowed for, the only objections to their use have been guarded against and avoided.

In order to eliminate the second source of error men-