

On the other hand, it is very probable that the chemical processes carried out in the preparation of all the other samples, removed practically all of the mesothorium contained in them. Thus the activity of a sample of thorium dioxide, made by ignition alone of sample A of nitrate, had an activity of 476 in Sept., 1907, while samples 1 to 4, made from the same sample of nitrate, had a mean activity of 418.

Summary

1. The specific activity of thorium in minerals was found to be 1009 (the unit being the activity of one sq. cm. of a thick film of U_3O_8) when measured under such conditions that all of the α -rays reach their maximum ranges in air.
2. The direct separation of radiothorium, from thorium by chemical processes is remarkably difficult, if not impossible. This question is being studied further in this laboratory.
3. The diminutions of activity of thorium, which we previously observed after certain chemical treatments, are completely explained by Hahn's hypothesis of an intermediate product, mesothorium, between thorium and radiothorium; which product is easily removed by the chemical treatments; in consequence of which the radiothorium decays with time and thus causes the observed changes of activity.
4. If all of the mesothorium be removed, at one time, in the process of preparation from a mineral of pure thorium dioxide, the activity of the latter will fall to a definite minimum. From the activity of a sample of thoria, supposed to have reached this minimum, the period of mesothorium was calculated to be 5.5 years.
5. The quantitative changes of activity with time, of a number of samples of thoria agreed well with the values calculated on the assumption of a period of 5.5 years for mesothorium.

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THE ATOMIC WEIGHT OF HYDROGEN.

BY WILLIAM A. NOYES.

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Some years ago the writer¹ carried out a series of determinations of the quantitative composition of water, from which the value 15.896 was calculated for the atomic weight of oxygen on the hydrogen basis. The opinion was expressed, in the paper, that the true value was probably within one part in a thousand of this number, and that it was rather below than above the value reported. Several years later Morley² pub-

¹ Am. Ch. J., 12, 441 (1890).

² Smithsonian Contributions to Knowledge, 1895 : Am. Ch. J., 17, 267 and 396 ; Z. physik. Chem., 17, 87.

lished an account of his elaborate determinations of the densities of hydrogen and oxygen, and of the composition of water by weight, which led him to the value 15.879 for oxygen, or 1.00762 for hydrogen ($O=16$). Meanwhile Richards¹ had shown that copper oxide retains occluded gases obstinately, a fact which was partly known to me at the time of my work, but which was not as carefully considered as it should have been. There was obtained in each of my experiments, at the end, a small amount of gas which was assumed to be nitrogen on the basis of one or two rather imperfect analyses of the earlier samples. The weight of this gas, calculated as nitrogen, was subtracted from the weight of the hydrogen, giving, on the average, a correction of about one part in a thousand. Several years after the publication of Morley's results it occurred to me that this gas came, very probably, from the copper oxide and that its weight should be subtracted from the weight of the oxygen instead of from that of the hydrogen. On applying the correction in this manner the value 15.879 (or 1.00765) was found.

While this agreement with Morley's value was gratifying and the fact was stated to a few personal friends, it did not seem proper to publish a statement about the matter until the surmise could be confirmed by new experimental evidence.

In addition to the desire of confirming or refuting the above explanation of my earlier results, several reasons have made it seem worth while to undertake a new determination of this constant. Hitherto our accurate knowledge of the composition of water has rested on Morley's work alone. He secured so high a degree of concordance in his results, and he exercised such an extraordinary degree of care at every point that the results obtained by all other observers must be considered as having only confirmatory value in comparison². It seemed worth while, if possible, to secure a similar order of accuracy by a different method.

Richards and Wells³ have recently given us a very accurate determination of the ratio between silver and chlorine, but the exact value for the atomic weight of chlorine is still in doubt because the ratio between silver and oxygen is not satisfactorily known⁴. A determination of the ratio between hydrogen and chlorine has been carried out at this Bureau, and by using hydrogen generated in the same manner for that determination and for the determination of the composition of water, a very direct comparison between oxygen and chlorine has been secured. As the atomic weights of more than forty elements have been determined in their relation to silver or the halogens, or both, the fundamental importance of the ratios of chlorine and silver to oxygen is apparent.

¹ Pr. Am. Acad., 26, 276 (1891).

² This will be discussed further in a later paper.

³ This Journal, 27, 459.

⁴ Guye and Ter Gazarian: Compt. rend., 143, 411.

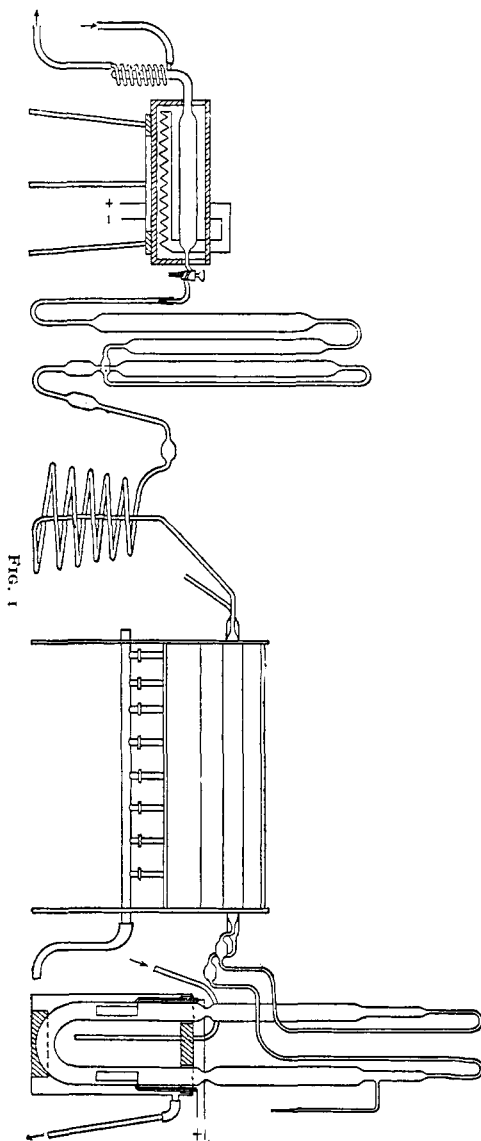
Finally, it seemed possible to so carry out the work as to secure some evidence with regard to the question of change of weight in a chemical reaction in which a large amount of energy is dissipated. This phase of the problem was suggested to me while considering the claim made by Prof. S. M. Babcock some years ago that ice loses weight when it melts. He proposed the theory that the loss of weight was intimately connected with the gain of energy by the ice as it melts. If this were true, hydrogen and oxygen should gain weight when they combine to form water. It may be said, at once, that the results to be given are not conclusive on this point. So far as they have any bearing on the question they indicate a loss rather than a gain in weight when hydrogen is converted into water.

Apparatus.—The apparatus used in the work was, in part, very similar to that used in the previous investigation.¹ Five series of determinations have been carried out. In the first four of these the hydrogen and oxygen were obtained by the electrolysis of dilute (15 per cent.) sulphuric acid. In the last series the gases were generated by the electrolysis of a six to eight per cent. solution of barium hydroxide.

The purifying train will be easily understood from the figure. In the first three series of experiments and in all but the last three determinations of the fourth series, the hydrogen was passed at first through a tube of common glass filled partly with platinized asbestos and partly with copper gauze, and the oxygen was passed through a similar tube filled partly with platinized asbestos, partly with asbestos mixed with lead chromate. These tubes were heated to 300°–350°. In the last three experiments of the fourth series hard glass tubes were substituted for the common glass, so that a higher temperature could be used, and in the fifth series hard glass tubes filled with platinized quartz were used. The platinized quartz was prepared by moistening the quartz, which had been heated and quenched in water, with a solution of chlorplatinic acid and reducing the latter in a current of hydrogen. Each gas then passed through a serpentine tube about four meters in length and of 8 mm. internal diameter. These tubes contained a fifteen per cent. solution of potassium hydroxide, in which was dissolved a small amount of lead oxide. Sulphur compounds present in the hydrogen were reduced to hydrogen sulphide as the mixture passed over the platinized asbestos and copper, and the sulphur of the hydrogen sulphide was retained by the lead as lead sulphide. Only a very small amount of lead sulphide was deposited during the passage of more than 1,000 liters of hydrogen through the asbestos. When the barium hydroxide was used as an electrolyte, the serpentine tubes were replaced by bulbs to collect the condensed water and the solution formed by the deliquescence of the potassium hydroxide.

¹ Am. Ch. J., 12, 441.

The union between the hard and soft glass was made by grinding the joint and then melting in it a very small amount of Khotinsky cement. Ample evidence is given below that these joints were perfect.



The gases passed next through the tubes containing potassium hydroxide in the form of sticks and then through two or three tubes 15 mm. in diameter and 25 cm. long, filled with phosphorus pentoxide which had

been sublimed in a current of oxygen. When not in use these tubes were always sealed and great care was exercised to avoid the entrance of moist air from the exits where the gases were delivered for use. If the phosphorus pentoxide were to become moist on that side, there would be danger that the gases might carry some of the moisture away with them.

The electrolytic apparatus containing the sulphuric acid or solution of barium hydroxide consisted of a U-tube with platinum electrodes. The limbs of the tube were about 35 mm. in diameter and 55 cm. long. It was filled about two-thirds full at first and when the solution became too concentrated, water, recently boiled and cooled out of contact with the air, was introduced through the small tube shown on the oxygen side of the apparatus. It was easy to do this without allowing any air to enter, but after each filling a considerable amount of the gases were generated before further use of them for a determination. The water used for preparing the original solution and for subsequent dilutions was purified by redistilling distilled water with the addition of an alkaline solution of potassium permanganate and collecting the portion that was free from ammonia.

The resistance of the sulphuric acid in the apparatus was 4-5 ohms, while that of the solution of barium hydroxide was considerably greater. It was necessary to cool the electrolytic apparatus with a pretty rapid current of water through the jar containing it. The electrical current used had a pressure of 120 volts, and was reduced by means of a rheostat placed in series with the electrolytic cell. With the sulphuric acid electrolyte a current up to 15 amperes could be used, giving six liters of hydrogen an hour. With the barium hydroxide it was not considered safe to go beyond four liters an hour, because of the greater resistance and consequent heating of the solution.

Copper Oxide.—In the first three series of experiments copper oxide was used to convert the hydrogen into water. In the first three experiments copper oxide prepared by precipitating copper sulphate with a hot solution of sodium hydroxide was used. The precipitate was washed by decantation until it became colloidal, and then thoroughly on a Büchner funnel. This oxide retained a trace of sulphate, which was reduced by the hydrogen to sulphur dioxide and the latter was found in small amount in the water obtained. Only two determinations were made with this oxide. Seven determinations were made with a sample of copper oxide purchased as pure from Kahlbaum. It contained arsenic and other impurities. As these determinations formed a part of the first series, the results of which are rejected for reasons to be given below, they need not be discussed further here. The copper oxide for the remainder of the first and for the second and third series was prepared by precipitation of a hot solution of copper sulphate, Rochelle salt and

sodium hydroxide with glucose. The cuprous oxide obtained could be washed indefinitely and all sulphates were very completely removed. After ignition in a current of oxygen the oxide retained a very small amount of carbon dioxide, but as this appeared as a gas at the end of the experiment and the amount could be determined, no serious error can have arisen from this source. The same copper oxide was used repeatedly and after several determinations the carbon dioxide nearly disappeared.

Balance and Weights.—The balance used was made by Ruprecht, of Vienna, and was designed to carry a maximum load of one kilogram on each pan. The air of the balance case was dried by means of a rapid current of air blown through two wash bottles containing concentrated sulphuric acid and a little chromic anhydride. The spray of sulphuric acid carried by the current was removed by passing through two tubes, the first containing glass wool and the second cotton wool. The current of air was stopped ten to twenty minutes before the weight was determined. During the last series of experiments the balance case was enclosed in a larger glass case and the air within the latter was dried by means of large dishes of calcium chloride set on top of the inner case. For determinations in which the weight of the hydrogen was involved, the weight was always determined twice at an interval of one-half hour or more and with the current of air passing into the case during a part of the interval. In 100 pairs of weights taken from the notebook at random, the average difference was 0.05 mg., and the maximum difference 0.12 mg.

Weights.—The weights used were carefully calibrated by Mr Pienkowsky, of this Bureau, at the beginning of the work, a second time after they had been in use for ten months, and a third time at the completion of the investigation, a little more than two years after it was begun. The largest change observed in any of the weights used was 0.04 mg.; while none of the platinum weights changed more than 0.01 mg. The aluminum rider gained 0.014 mg. A recalculation of the amounts of hydrogen in the last series showed that the use of the new corrections caused no change exceeding 0.14 mg. in the weight of the hydrogen for any experiment of that series, while the algebraic sum of the changes for the five experiments of the series was 0.09 mg. or one part in two hundred and fifty thousand of the weight of hydrogen used.

The calibration of the weights was, of course, to a vacuum standard. Since the substances to be weighed were always enclosed in a glass apparatus whose volume remained constant and which was counterpoised by another glass apparatus of very nearly the same volume and weight, no vacuum correction in the ordinary sense was required. For our present purpose it is most convenient to assume the brass weights in air as standard. If we do this, the platinum weights will appear too heavy be-

cause they displace less air in proportion to their weight. This requires a correction of 0.087 mg. which must be added for each gram of platinum weights used. For convenience, a table was prepared which included this correction for the platinum weights with the other corrections as determined in the comparisons of the weights.

Purity of the Gases Used.

As with all atomic weight determinations, the value of the present investigation depends in very large measure upon the purity of the substances weighed—in this case, hydrogen, oxygen and water. The impurities which might be present were: in the hydrogen:—nitrogen, oxygen, water, phosphorus pentoxide and compounds of sulphur; in the oxygen there might be the same impurities with hydrogen in place of oxygen; in the water:—sulphur dioxide or carbon dioxide.

Nitrogen.—In the former series of determinations there was obtained at the end of each experiment a small amount of gas which, when calculated as nitrogen corresponded to about one one-thousandth of the weight of hydrogen used. It was found quite early in the present investigation that when the water is removed from the apparatus containing reduced copper it carries with it a small quantity of hydrogen, probably hydrogen which has been occluded by the copper. The gases were analyzed in a narrow eudiometer of such length that when the amount of gas was small, the column of mercury in the eudiometer was 600-650 mm. in length so that the gas was under a pressure of only about one-seventh of an atmosphere. In this way quantities of nitrogen as small as 0.02 mg. could be measured.

As will be seen below, it was possible to secure copper oxide so pure that only very small amounts of nitrogen were found at the close of experiments in which it was used. But the best evidence of the freedom of the hydrogen from nitrogen was obtained in the last series. From 22.6 grams of hydrogen and the equivalent amount of oxygen there was obtained only 0.59 mg. of nitrogen. This includes all of the nitrogen in the oxygen as well, and all of the leakage of the stop-cock during seven weeks. If we assume that two-thirds of this nitrogen came from the hydrogen it is only one part in 57,000 by weight, or one part in 800,000 by volume. On the basis of this evidence it is assumed that all of the hydrogen used was free from nitrogen and no correction has been made for the small quantities found in each experiment. It is not believed that the error from this source can be so great as one part in 20,000.

Incidentally these experiments have demonstrated the possibility of using, without leakage, ordinary, well ground and carefully lubricated stopcocks under such conditions that they are subjected to atmospheric pressure with a vacuum inside of the apparatus for days together. The

well known rubber lubricant was used. It was made by heating a mixture of 16 parts of vaseline, 8 parts of pure rubber and 1 part of paraffin to a temperature of 350°-400° for several hours until it was thoroughly homogeneous. For warm weather, or for a stopcock liable to become warm, a little more paraffin was added.

Oxygen.—After the investigation had progressed so far that it was evident that the results differed from Morley's by a much larger amount than can be accounted for by accidental errors, it was feared that the hydrogen contained a trace of oxygen which escaped conversion into water as the gas passed over the platinized asbestos and copper gauze, especially as the latter were heated to only about 350°. To test this possibility the purified and dried hydrogen was passed through a hard glass tube containing platinized asbestos heated to dull redness and then through a phosphorus pentoxide tube. The latter was closed with stopcocks and was weighed each time filled with hydrogen and with the use of a counterpoise. The earlier experiments gave appreciable amounts of water (1 mg. from 1 g. of hydrogen) which was in part, at least, from the asbestos, and even after the asbestos had been heated almost daily for six weeks some water was still obtained (1.1 mg. from 2.74 g. of hydrogen)¹.

But when some of the same hydrogen was passed over strips of palladium heated to 360° in an electrical airbath, 3.78 g. of hydrogen gave a change of weight of -0.08 mg. It still seemed possible that a trace of oxygen mixed with *dry* hydrogen might pass the palladium without change. To test this a small T-tube was introduced between the hydrogen generator and the palladium tube in such a manner that the lower arm could be filled with dry oxygen. This would then find its way into the hydrogen by slow diffusion. The amount of oxygen retained in the arm of the T-tube was found in two experiments to be 1.68 and 1.94 mg. respectively, while in three experiments in which similar amounts of oxygen were allowed to diffuse into the hydrogen before it entered the palladium tube there were found 2.29, 2.21 and 2.58 mg. of water. While the conditions were such that an exact quantitative agreement could not be expected, the experiments demonstrated that minute quantities of oxygen can be readily detected by this method.

After the close of the last series of experiments the hydrogen was tested by passing it through the tube containing strips of palladium heated to 360° and then through the pentoxide tube. In these experiments there were passed 2.74, 2.92 and 2.92 g. of hydrogen respectively, while the changes in weight of the phosphorus pentoxide tubes were -0.44, +0.14

¹ It seems possible that this water may have passed through the walls of the red-hot tube during the five hours of the experiment. It seems not improbable that glass, as a viscous liquid, may dissolve a small amount of water and that such dissolved water might slowly diffuse through to the inner surface. This question is worthy of further study.

and +0.04 mg., quantities scarcely beyond the errors of weighing and insignificant in proportion to the weight of the hydrogen.

Water.—The experiments just described demonstrate the absence of water in the hydrogen used in the last series. After the close of the third series, hydrogen from the apparatus was passed through the phosphorus pentoxide tube at the rate of six liters an hour for five successive days, 12.6 g. of hydrogen in all. The changes in weight of the pentoxide tube were -0.01, +0.63, -1.06, -0.33, -0.14 mg.; in all a net loss of 0.76 mg., or one part in 17,000. At the close of the fourth series 3.78 g. of hydrogen were passed through the pentoxide tube at the rate of six liters an hour with a change in weight of -0.04 mg. and a similar amount passed through the tubes containing heated palladium, gave a change of weight of -0.08 mg.

It seems, therefore, that the phosphorus pentoxide used to dry the hydrogen retained its efficiency to the end. The first of these tubes showed considerable deliquescence, caused by the water still remaining in the hydrogen after it passed the sticks of caustic potash, but the last tube showed no sign that it was affected by the moisture.

Phosphorus Pentoxide.—Morley¹ has shown that one liter of a gas at ordinary temperatures carries with it only 0.00002 mg. of vapor of phosphorus pentoxide. This would correspond to 0.0002 mg. in one gram of hydrogen, an amount without any significance in comparison with the degree of accuracy now possible in determinations of atomic weights. It is believed that the crystalline phosphorus pentoxide obtained by sublimation, adhering as it did closely to the walls or the tube and fibers of glass wool, on which it was deposited, was much less likely to be carried on mechanically by the current of gas than the finely pulverulent pentoxide in its usual form would have been.

Compounds of Sulphur.—After the close of the third series a careful test for compounds of sulphur was made by bringing together the hydrogen and oxygen, delivered by the apparatus, in such a manner that they could be burned and the water collected. The hydrogen was evolved at the rate of six liters an hour, the most rapid rate used in the atomic determinations. The water obtained weighed 112.4 g. A little bromine water and 0.1 g. of sodium carbonate were added to it and it was evaporated to dryness in a platinum dish on an electric plate. The residue was acidified with hydrochloric acid, filtered from silica which came from the glass apparatus in which the gases were burned and the filtrate was tested with a solution of barium chloride. A trifling turbidity appeared slowly, estimated to be less than that occasioned by 0.1 mg. of sulphuric acid in a solution of similar volume and character. This would corre-

¹ J. Am. Chem. Soc., 26, 1171.

spond to one part of sulphur dioxide, by weight, in 250,000 parts of the hydrogen.

Purity of the Oxygen.—The experiment just described demonstrates the practical absence of sulphur in the oxygen. Tests for moisture also showed that no amount which could be of significance, was present.

Purity of the Water.—In the two experiments referred to above in which copper oxide prepared by the precipitation of copper sulphate with sodium hydroxide was used, some sulphur dioxide was found. When pure copper oxide was used no evidence of its presence was ever obtained. In all experiments in which the sulphuric acid electrolyte was used the water was tested with a dilute solution of potassium permanganate (1 cc. = 0.05 mg. available O) and with N/10 barium or sodium hydroxide, with phenolphthalein as an indicator. The amounts required never exceeded 0.1 cc. of the permanganate and 0.03 cc. of the N/10 alkali, to produce a coloration in from 20 to 40 cc. of the water. The water of the last two series, especially, was frequently tested for hydrogen peroxide but none was found.

First Series.

This series consisted of twenty experiments. In the earlier experiments the weight of the hydrogen was determined by the gain in weight of a piece of apparatus containing copper oxide, the water formed by the oxidation of hydrogen being condensed within the same apparatus. The method used will be clear from Fig. 1. About 160 g. of copper oxide were placed in the part of the apparatus represented as lying in the electrical airbath. After sealing the apparatus at the end designed to collect the water, its volume was determined by hydrostatic weighing and a tube of almost the same volume and weight was prepared. The apparatus was then placed in the airbath and heated to 400° while it was connected with a Sprengel air-pump and exhausted. A phosphorus pentoxide tube, sealed to the pump, was interposed between the pump and the apparatus and also a small McLeod gauge¹. The exhaustion was carried to the hundred thousandth of an atmosphere or further and the heating continued for some time.

For connection with the pump and for other similar connections used throughout the work, the end of the apparatus was drawn out to fit a glass socket connected with the pump. The joint was completed by melting a little Khotinsky cement between the parts in contact. Such a joint, if properly made, will hold for an indefinite length of time against atmospheric pressure, without any leakage that can be measured. The

¹ The bulb of the gauge had a capacity of about 16.5 cc. To avoid contaminating the mercury by contact with india rubber, the gauge was sealed below to an upright glass tube about 12 mm. in diameter. In this was a light, loosely fitting glass plunger. By pressing the plunger down the mercury could be easily forced up into the gauge for the measurement.

parts are easily separated by gentle warming and cleaned by warming and wiping with cotton followed by a cloth moistened with alcohol.

After cooling, the apparatus was rinsed with distilled water, wiped with a clean cloth and placed on the balance. The tare and weights were placed on the other pan, the current of dry air started through the balance case and the weighing completed, with the use of the rider, on the following day.

The apparatus was then connected with the source of hydrogen, the copper oxide heated to 300° - 350° and hydrogen passed in for four to six hours. A coil of small tin pipe conveying cold water was placed around the part of the apparatus outside of the airbath to condense the water. By means of the rheostat connected with the electrolytic apparatus it was easy to regulate the supply of hydrogen to correspond with the rate at which it was oxidized by the copper oxide. The operation was always stopped before the copper oxide was all reduced and by heating for a short time after closing the stopcock, the conversion of the last of the hydrogen to water was completed.

After cooling and standing over night, as before, the weight of the

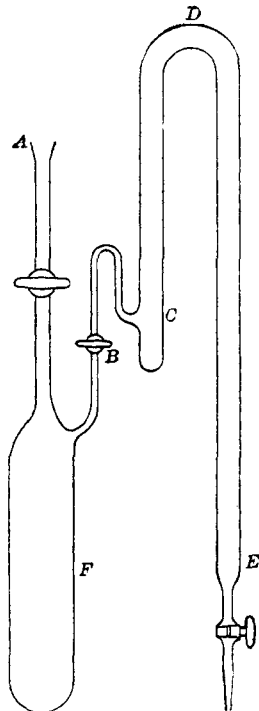


FIG. 2.

hydrogen, which had been introduced, was determined. The apparatus was then connected at A with the apparatus shown in Fig. 2, the other

end, E, of the apparatus being connected with the Sprengel pump. This apparatus was filled with phosphorus pentoxide from C to E. The end at C is designed to collect the phosphoric acid resulting from the deliquescence of the pentoxide, while it is quite necessary that the part C D should be directed up and not down, as otherwise the syrupy phosphoric acid runs down into the unchanged phosphorus pentoxide and seals the tube. The apparatus was, of course, previously exhausted and weighed, using a glass counterpoise of nearly the same volume and weight.

After exhausting the connecting tubes by means of the pump, the bulb F was placed in a freezing mixture of ice and sulphuric acid, the stopcock B was closed and the stopcock of the copper oxide apparatus opened. By passing hot water through the coil of tin pipe surrounding the part of the apparatus containing the water, the latter was easily distilled into F in the course of two to four hours. By opening B occasionally any permanent gas brought over with the water vapor was allowed to pass on to the pump and transferred by means of the latter to the eudiometer in which the gas was analyzed. When permanent gases were allowed to accumulate in F the passage of the water vapor was checked and condensation occurred in the connecting tubes. This difficulty occurred especially in the last two series, when considerable hydrogen was present, but was rarely experienced in the first three series. After the water had been transferred to F and the bulb containing the copper had been heated to 400° for a short time, the apparatus containing the water was removed and replaced by a tube containing phosphorus pentoxide and the heating of the apparatus continued for some time longer. Only a few milligrams of water were obtained in this manner. The apparatus containing the reduced copper was then cooled and weighed next morning, the loss of weight as compared with the original weight giving the weight of the main portion of the oxygen.

The reduced copper still retains, however, at 400° , either water or hydrogen which cannot be removed by the process described. To obtain this the apparatus was again placed in the electrical airbath, heated to 400° and the copper oxidized as far as possible by means of oxygen from the electrolytic apparatus. The water formed was then removed by connection with a phosphorus pentoxide tube and heating as before. After cooling and weighing, the apparatus was now ready for a second experiment.

In seven determinations of this series the hydrogen was absorbed in palladium and its weight was determined twice, first by the loss in weight of the palladium tube and second by the gain in weight of the copper oxide tube. The palladium tube was given the form shown at A in Fig. 3. The palladium foil was furnished by Heraeus. It was 0.05 mm. in thickness. Three hundred and sixty grams of it were cut into strips

4 cm. wide and these were wound in three rolls which were placed in the tube A. Before use the rolls were placed in a hard glass tube and heated to redness in a current of oxygen. After placing it in A it was heated

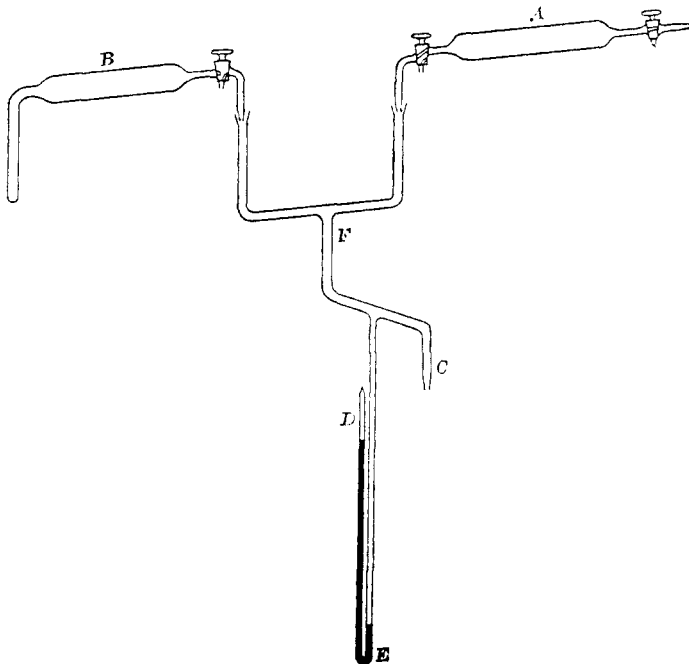


FIG. 3.

for some time in a current of hydrogen till thoroughly dry. It was then cooled and charged with hydrogen and when saturated a current of hydrogen was passed through the tube for a short time. The tube was weighed with a counterpoise and after standing over night, in the same manner as described for the copper oxide tube.

The arrangement employed for the transfer of the hydrogen to the copper oxide tube is shown in Fig. 3. For greater simplicity the airbaths in which A and B were placed and supported are not shown. The tube C was connected with the Sprengel pump. After exhaustion of the connecting tubes the connection with the pump was cut off by means of a stopcock situated close to the connection with C. The palladium tube was then slowly heated while the copper oxide tube was heated to 350° . The pressure in the system could be easily followed by means of the shortened manometer D E. This contained a small amount of air at D but not enough to carry the mercury beyond the bend at E when the pressure in F fell to zero. The heating of A was so regulated that the pressure was usually a little below that of the atmosphere, the reaction in B

proceeding most rapidly under slightly reduced pressure. The 360 g. of palladium absorbed 2.3 g. of hydrogen and of this 2 g. could be easily expelled at 150°-160°. This amount could be transferred from A to B in three to five hours. The rate of transfer could be followed by the amount of water condensed in B. When enough water had collected, the stopcock of the copper oxide tube was closed and the palladium was allowed to cool till most of the hydrogen in the connecting tubes had been reabsorbed. The stopcock of the palladium tube was then closed and the hydrogen in the connecting tubes pumped out into a eudiometer and measured. This hydrogen varied from 0.02 to 0.14 mg. according to the time allowed for the palladium to cool.

The twenty experiments of the first series gave for the atomic weight of hydrogen as calculated from the weight of the hydrogen and the weight of the oxygen, 1.00819 ± 0.00010 , and from the weight of the hydrogen and water 1.00821 ± 0.00010 . This is a smaller probable error than has been obtained by any previous observer except Keiser and Morley, but it was found at the close of the series that it is subject to a constant error which is, apparently, about three times the "probable error."

It was known at the beginning of the investigation that copper oxide at 400° would retain a small amount of water. It was hoped, however, that this might be made very small and also that by making the end of one experiment the beginning of the next the total amount of water retained would be so nearly constant that it would not affect, appreciably, the result of any experiment in the series after the first. At the close of the last experiment of this series it was thought wise to test this point by transferring the copper oxide to a hard glass tube and heating it in a current of oxygen. To my surprise there was obtained 37.7 mg. of water, although the previous oxidation and heating at 400° had given only 3.3 mg. If we assume this water to have come from the last six experiments of the series, which formed a continuous set in which the end of one experiment was the beginning of the next, the value for the six determinations becomes 1.00782 as calculated from the hydrogen and oxygen or 1.00791 as calculated from the hydrogen and water. It was at once decided to reject the determinations thus far made and which had taken about a year's time and to begin a new series in which this source of error should be eliminated, if possible.

Second Series. Hydrogen from Sulphuric Acid, Weighed Twice.

In this series the hydrogen was weighed in palladium and also after transfer to the copper oxide tube as described above. In order to increase the quantity of hydrogen and reduce the error, after the water had been removed and the copper reoxidized, a second quantity, and in one case a third quantity, of hydrogen was introduced and the water removed. Finally the reduced copper was transferred to a hard glass tube

and oxidized in a current of oxygen and the amount of water formed was determined. The oxygen used was partly from the S. S. White Dental Manufacturing Company and was purified by passing it over red-hot copper oxide and through wash bottles containing a solution of sodium hydroxide and over phosphorous pentoxide. In some of the experiments electrolytic oxygen was used.

Several experiments were made to determine the amount of water taken up by the copper oxide in the transfer to the hard glass tube. In a similar manipulation with dry copper oxide there were obtained 2.63, 1.30, 5.32 and 2.45 mg. of water. This would correspond to an average error of about one part in 10,000. It has not been thought best to apply any correction for this error, partly because of the uncertainty in its amount but chiefly because it is probably balanced by small errors in the opposite direction, due to the retention of water by the copper oxide even after several hours at a red heat in a current of oxygen, and to the retention of a trace of water by the walls or lubricant of the copper oxide apparatus. There is good reason, however, for believing that the error from each of these sources is very small.

Seven determinations were made in this series but in one of them the weight of the oxygen was lost. The results were as follows:

	Grams H CuO tube	Grams H Pd tube	Mg. H in T tube	Mg. H from Cu	Cor. H CuO	Cor. H Pd	Average H
1.	3.72469	3.72689	0.15	0.07	3.72462	3.72667	3.72565
2.	3.80383	3.80280	0.17	0.05	3.80378	3.80258	3.80318
3.	3.75898	3.75886	0.18	0.10	3.75888	3.75858	3.75873
4.	2.96309	2.96357	0.05	0.03	2.96306	2.96349	2.96328
5.	2.11437	2.11366	0.08	0.03	2.11434	2.11355	2.11395
6.	3.53126	3.53173	0.19	0.04	3.53122	3.53150	3.53136
7.	3.53963	3.53982	0.19	0.04	3.53959	3.53959	3.53959

	Grams O from loss of CuO	Mg. N	Mg. CO ₂	Mg. water by reoxidation	Grams O corrected	Grams water
1.	29.56469	0.76	0.28	15.26	29.57891	33.30408
2.	30.16645	0.37	2.33	20.25	30.18400	33.98748
3.	29.81141	0.32	0.79	23.28	29.83358	33.59127
4.	23.49099	0.13	0.60	29.61	23.51987	26.48379
5.		0.20	1.16	27.65		18.89214
6.	27.99401	0.38	0.89	36.36	28.02910	31.56024
7.	28.05652	0.24	0.22	40.13	28.09619	31.63554

ATOMIC WEIGHT OF HYDROGEN. SECOND SERIES.

	From H ₂ O	From H ₂ O
1.	1.00765	1.00767
2.	1.00800	1.00799
3.	1.00792	1.00795
4.	1.00792	1.00790
5.		1.00795
6.	1.00791	1.00792
7.	1.00785	1.00786

Mean 1.00787
 ± 0.00003
 Mean of all, 1.00788 ± 0.00002

Third Series. Hydrogen from Sulphuric Acid Weighed after Conversion to Water by Copper Oxide.

In this series hydrogen directly from the electrolytic apparatus was passed into the copper oxide bulb and converted into water. The purpose of the series was more especially to determine whether the purity of the hydrogen had been increased by absorption in the palladium. The results of the series are not as concordant as those of the second but they indicate that the hydrogen directly from the electrolytic apparatus is, if anything, a little lighter and, presumably, a little more pure than after it has been absorbed in palladium. The results were as follows:

WEIGHTS OF HYDROGEN AND OXYGEN, THIRD SERIES.

	Grams H by gain of CuO	H from Cu	Grams H corrected	Grams O by loss of CuO	Mg. N	Mg. CO ₂	Mg. water by reoxidation
1.	2.44282	0.03	2.44279	19.34104	0.16	0.10	56.79
2.	2.18741	0.02	2.18739	17.33722	0.10	0.05	25.98
3.	2.75132	0.03	2.75129	21.80908	0.18	0.05	34.60
4.	4.00068	0.06	4.00062	62.31
5.	4.04061	0.04	4.04057	32.04471	0.17	0.06	32.41

ATOMIC WEIGHT OF HYDROGEN. THIRD SERIES.

	Grams O corrected	Grams water	Atomic Weight from H:O	Atomic Weight from H:H ₂ O
1.	19.39757	21.84042	1.00746	1.00746
2.	17.36305	19.55117	1.00784	1.00780
3.	21.84345	24.59389	1.00764	1.00768
4.	35.75073	1.00803
5.	32.07689	36.11762	1.00772	1.00772
			Mean 1.00767	1.00774
			± 0.00006	± 0.00006
			Mean of all 1.00771 ± 0.00004	

It will be noticed that the amounts of carbon dioxide found are much smaller, owing to the fact that the copper oxide had been freed from it by repeated use. The amount of nitrogen was also smaller, perhaps because of the simpler manipulations involved.

Fourth Series. Hydrogen and Oxygen From Sulphuric Acid Combined by Means of Palladium.

With the best manipulation which it has been possible thus far to secure, the use of copper oxide involves several sources of small constant errors. It is hoped that these errors do not, in the aggregate, exceed one part in 10,000, but it seemed very desirable to find some radically different method which should avoid the use of copper oxide. Such a method consists in absorbing hydrogen in palladium and converting it into water by means of oxygen. This method has already been used by Keiser¹ but his method of manipulation compelled him to use comparatively small amounts of hydrogen and the degree of concordance which he was able to secure was not such that his value for the atomic weight of hydrogen can be used to decide between Morley's value and that found here.

¹ Am. Ch. J., 20, 733.

The problem seemed at first a very simple one but several months were spent in fruitless experiments before a satisfactory method of manipulation was found.

The 360 grams of palladium foil previously used were placed in a somewhat wider tube and were kept from direct contact with the glass by means of small glass beads strung on platinum wires. The stop-cock at one end of the tube was replaced by a tube having a capacity of about 50 cc. At the beginning the palladium tube was heated and charged with hydrogen and partially exhausted several times to remove moisture. It was then heated to 380°-400° and exhausted until the hydrogen showed a residual pressure of 0.50 to 0.70 mm. as measured by the McLeod gauge. At this pressure and temperature 360 g. of palladium retain only 2.3 mg. of hydrogen and the amounts of hydrogen given out for small changes of pressure are as follows :

0.40 to	0.50 mm.	0.11	mg. H
0.50 "	0.60 "	0.10	" "
0.60 "	0.70 "	0.094	" "
0.70 "	0.80 "	0.087	" "
0.80 "	0.90 "	0.080	" "
0.90 "	1.00 "	0.073	" "
3.90 "	4.00 "	0.044	" "
16.90 "	17.00 "	0.020	" "

A change of temperature of 10° for pressures less than 1 mm. corresponds to a change of 0.03 mg. in the amount of hydrogen retained. At the end of an experiment it was easy to bring the apparatus to a condition of temperature and pressure closely approximating that at the beginning and by means of the table a correction of sufficient accuracy could be applied.

After exhausting, and measuring the temperature and pressure as described, the apparatus was allowed to cool, rinsed with distilled water, wiped, placed on the balance and on the following morning it was weighed. It was then charged with hydrogen (about 2.3 grams) and weighed again on the morning of the third day. The apparatus was then connected with the oxygen side of the electrolytic generator. The palladium tube was inclined so that the water formed ran down into the receptacle at the end. The oxygen entered rapidly for a few minutes but the heat generated soon caused the pressure of the hydrogen to increase and check the current. The oxygen then continued to enter slowly, with the stopcock partly closed, for two or three hours. After that the rate at which the oxygen was taken changed quite suddenly, so suddenly that the first time the experiment was tried the electrolyte was drawn over and the electrolytic apparatus was broken. From this time to the end the entrance of the oxygen was regulated by the stop-

cock and was allowed to enter as rapidly as it was thought desirable to run the generator. More than enough oxygen to combine with the hydrogen present was easily introduced. On the fourth day, after weighing, the apparatus was charged again with hydrogen.

On the fifth day the manipulation varied. In some cases oxygen was admitted in excess as on the third day. In other cases, as the end of the oxidation of the hydrogen approached, the apparatus was weighed roughly at intervals and the admission of the oxygen was stopped while 5-10 mg. of hydrogen remained unoxidized. By this method of manipulation a day was saved. On the sixth day, or, when an excess of oxygen was admitted, on the fifth, a small excess of hydrogen was admitted. It was necessary to wait till the following day before weighing.

On the sixth or seventh day, according to the method of manipulation chosen, the water and excess of hydrogen were removed and the apparatus brought back to a condition for the beginning of a new experiment. A receptacle similar to that described on page 1728 was used for the water. On account of the hydrogen which accumulated rapidly in the bulb with the water and stopped the current of water vapor, it was found desirable to give the bulb a capacity of about 100 cc. Any nitrogen present was, of course, carried over with the first portions of the water vapor and hydrogen and this part of the gas was collected and analyzed separately. At the close of the removal of the water, the receptacle for the water was replaced by a phosphorus pentoxide tube which permitted of a free connection between the palladium tube and the pump for the measurement of the residual pressure. It was necessary to heat the palladium tube at least two hours in the electrical airbath to secure constant conditions for the measurement of the residual pressure. This was not understood in the earlier determinations of this series and may be one reason why some of the results are not very satisfactory.

In the results which follow, the amounts of nitrogen and carbon dioxide are given as an indication of the magnitude of the errors which may have been occasioned by traces of these gases or by leakages, but no correction for these gases has been applied.

Theoretically, the weight of the apparatus at the end of an experiment should be the same as at the beginning. Practically, it was almost always heavier because of the retention of a small amount of water. When the hydrogen was allowed to accumulate in the receptacle for water the moisture would condense in the connecting tubes and stopcocks and if allowed to remain for a short time in contact with the lubricant of the stopcock, could not be entirely removed. In some cases minute drops of water could be seen within the bore of the stopcock and these would not evaporate during any reasonable length of time. The gain in weight

of the apparatus during the experiment was, accordingly, assumed to be due to water which had been retained and was added to the weight of water found directly. In cases where condensation was avoided this amount of water was very small or even became negative. (See the following series).

WEIGHTS OF HYDROGEN AND OXYGEN. FOURTH SERIES.							
	Grams H	Mg. cor. for changes of I and P	Mg. H recovered	Grams H corrected	Mg N	Mg CO ₂	Grams O
1.	2.31840	-0.05	39.19	2.27916	0.48	0.02	18.08455
2.	4.13630	-0.06	8.90	4.12734	0.50	...	32.76527
3.	4.18248	-0.24	7.16	4.17556	0.52	0.02	33.13449
4.	4.19599	-0.51	2.02	4.19346	0.15	0.16	33.27384
5.	2.31593	-0.01	8.46	2.30746	18.30863
6.	4.60148	-0.23	4.33	4.59692	0.11	0.08	36.48543
7.	4.63931	+0.14	3.20	4.63625	0.07	0.07	36.79354
8.	4.57292	+0.18	0.36	4.57274	0.02	0.28	36.28666

WEIGHTS OF WATER AND ATOMIC WEIGHT OF HYDROGEN.					
	Grams of Water	Mg. Water retained	Grams Water corrected	Atomic Weight From H:O	Atomic Weight From H:H ₂ O
1.	20.29807	63.21	20.36128	1.00823	1.00830
2.	36.87182	18.61	36.89043	1.00774	1.00780
3.	37.30667	1.20	37.30787	1.00818	1.00821
4.	37.46202	2.51	37.46453	1.00822	1.00831
5.	20.61671	3.14	20.61357	1.00825	1.00839
6.	41.07653	5.09	41.08162	1.00795	1.00797
7.	41.41452	14.53	41.42905	1.00806	1.00808
8.	40.85460	3.74	40.85834	1.00813	1.00817
			Mean.	1.00809	1.00815
				±0.00004	±0.00005
			Mean of all,	1.00812	±0.00003

Fifth Series. Hydrogen and Oxygen From Barium Hydroxide, Combined by Means of Palladium.

The manipulation in this series was essentially the same as in the fourth series. The series has much greater value than the former one, partly as shown by the concordance of the results, partly because the processes of manipulation had been more thoroughly mastered and partly because the electrolyte used gives a greater probability of purity for the hydrogen. In those experiments in which oxygen was introduced last, a small quantity was left in the bore of the three-way stopcock and was usually found in the subsequent analysis of the first portions of gas removed. In one experiment of this series only one-half the quantity of hydrogen was used and too much oxygen was admitted by mistake. This so complicated the manipulation that the experiment was unsatisfactory and it has been omitted from the table. It gave the values 1.00814 and 1.00823.

WEIGHTS OF HYDROGEN AND OXYGEN. FIFTH SERIES.

	Grams H	Mg. cor. for changes of t° and P	Mg. H recovered	Grams H corrected	Mg. N	Mg. CO ₂	Mg O	Grams O
1.	4.61443	-0.07	2.56	4.61180	0.11	0.17	...	36.60909
2.	4.62877	00.0	5.19	4.62358	0.08	0.03	0.13	36.69575
3.	4.60386	-0.02	5.31	4.59853	0.22	0.00	1.31	36.50484
4.	4.56300	+0.04	4.72	4.55832	0.06	0.00	0.29	36.17887
5.	4.21188	-0.04	7.85	4.20399	0.11	0.00	0.11	33.37000

WEIGHTS OF WATER AND ATOMIC WEIGHT OF HYDROGEN.

	Grams Water	Water retained	Grams water corrected	Atomic Weight	
				From H:O	From H:H ₂ O
1.	41.21934	1.71	41.22105	1.00779	1.00779
2.	41.30740	9.07	41.31647	1.00798	1.00806
3.	41.09872	3.40	41.10212	1.00776	1.00780
4.	40.74186	-2.82	40.73904	1.00795	1.00790
5.	37.56732	6.04	37.57336	1.00782	1.00786
			Mean,	1.00786	1.00788
				±0.00003	±0.00003
			Mean of all.	1.00787	±0.00002

The mean of the four series, giving them equal weight, is 1.00787 from the hydrogen and oxygen and 1.00791 from the hydrogen and water. The second and fifth series have, however, much greater weight than the third and fourth, and when we consider, further, that there was probably a trifling loss of water, especially in the third series, the value 1.00787 seems to be the most probable result which can be calculated from the work.¹

It has seemed of interest to recalculate Morley's results on the oxygen basis for comparison with the result here given.

ATOMIC WEIGHT OF HYDROGEN, MORLEY'S RESULTS.

1.	1.00765	1.00778
2.	1.00751	1.00766
3.	1.00768	1.00774
4.	1.00755
5.	1.00773	1.00750
6.	1.00773	1.00778
7.	1.00777	1.00786
8.	1.00764	1.00761
9.	1.00759	1.00752
10.	1.00752	1.00737
11.	1.00746	1.00734
12.	1.00744	1.00771
	Mean, 1.00761	1.00763
	±0.00002	±0.00003
	Mean of all, 1.00762	±0.00002

¹ The mean of the results of the 23 determinations in which the hydrogen and oxygen were weighed is 1.00791 and the mean of the 25 determinations in which the hydrogen and water were weighed is 1.00794. The mean of all, considered as a single series of 48 determinations, is 1.00793 ± 0.00002.

The difference between this result and that given above is greater than can be accounted for on the basis of accidental errors. While the average of the results of the best determinations by either observers approaches more nearly to the result of this investigation than to Morley's value, it does not seem justifiable to calculate a mean on such a basis. For reasons which will be given in a later paper the most probable value which we can get at the present time seems to be the average between Morley's value and that here given. That average is 1.00775. Morley's value and my own each differ from this by one part in 8,000.

Change in Weight of the Hydrogen When Converted Into Water.

As was stated in the introduction, one purpose of this investigation was to secure, if possible, some evidence of a change of weight which might occur in a reaction in which a large amount of energy is dissipated. In twenty-five experiments the same hydrogen was weighed, first, as absorbed in palladium and, second, after conversion into water by means of the copper oxide. The results were as follows:

Gain of CuO	Loss of Pd	Diff. Mg.	Gain of CuO	Loss of Pd	Diff. Mg.
1.04216	1.04295	+0.79	0.95151	0.95207	+0.56
1.46493	1.46642	+1.49	1.98130	1.98053	-0.77
0.96114	0.96231	+1.17	1.82248	1.82205	-0.43
1.51279	1.51296	+0.17	2.04840	2.04816	-0.24
1.17961	1.17973	+0.12	1.71048	1.71042	-0.06
1.22273	1.22268	-0.05	1.96621	1.96648	+0.22
1.13563	1.13541	-0.22	0.99685	0.99707	+0.22
1.30184	1.30150	-0.34	2.11434	2.11335	-0.79
1.22851	1.22699	-1.52	2.20439	2.20472	+0.33
0.99563	0.99600	+0.37	1.32683	1.32678	-0.05
1.24243	1.24270	+0.27	2.07207	2.07281	+0.74
1.24639	1.24754	+1.15	1.46752	1.46678	-0.74
1.52682	1.52706	+0.24			
			36.72299	36.72562	+2.63

An examination of these results shows that in fourteen experiments the hydrogen as weighed in the palladium appeared heavier, while in eleven experiments the hydrogen after conversion into water appeared heavier. The average difference between the two weights of a given quantity of hydrogen was 0.52 mg. or one part in 3,000 while the average amount by which the hydrogen as weighed in the palladium appeared heavier was 0.11 mg. or one part in 14,000. It is clear that these results do not justify any conclusion either way with regard to a change in weight of the hydrogen during the reaction other than that if any change of weight occurs it must be very small. It seems scarcely possible that a change of so much as one part in 10,000 of the weight of the hydrogen takes place. It is, possibly, of interest to note that so far as the results furnish any indication whatever, they point toward a trifling loss of

weight, a result which would agree with Landolt's elaborate study of the question.¹ It is hoped that this problem may be taken up again by a method capable of giving more accurate results.

BUREAU OF STANDARDS.
Washington, August, 1907.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY No. 147].

THE STEREOCHEMISTRY OF INDIGO. PRELIMINARY COMMUNICATION.

BY K. GEORGE FALK AND J. M. NELSON.

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Organic compounds which contain a double bond are capable in general, of existing in two geometrical-isomeric forms. The following lists include a number of these compounds of which one or both of the isomers are colored.

Double bond between two carbon atoms (>C=C<). (When the spacial relations were not given with this group of compounds, the lower melting form was assigned the *cis* structure).

Substance	<i>Cis</i> Form		<i>Trans</i> Form	
	M.P.	Color	M.P.	Color
Dibenzoyl ethylene ²	111°	intense yellow	134°	colorless
Diethoxynaphthostilbene ³	185-186°	yellow	...	"
Benzaldesoxybenzoin ⁴	88-89°	yellow	101-102°	"
Diphenyldinitroethylene ⁵	105-106°	yellow	186°	deeper yellow
Piperonylacrylic acid methyl ester ⁶	107°	yellow	111°	almost white
α -Benzal- γ -diphenylitaconic acid ⁷	...	yellow	...	colorless
" " anhydride ⁷	218°	red	267°	"
Dibenzalsuccinic acid ⁷	218°	yellow	254°	"
" " anhydride ⁷	263°	yellow	...	"
Oxidation product of β -benzoylpropionic acid ⁷	sublimes	red	sublimes	yellow

The general conclusion to be drawn from the accompanying tables is that if a compound exists in two geometrical isomeric forms and one of these isomers is colored, the other isomer will either be colorless or possess a different color from the first. For the special classes of compounds considered, the following relations may be deduced:—

For compounds containing a double bond between two carbon atoms the *cis* forms are more deeply colored.

For oximes, the *anti* forms have higher melting points, are more deeply colored and less soluble.

For hydrazones the *anti* (α) forms have lower melting points, are more deeply colored, and more soluble.

For diazosulphonates, the *syn* forms are more deeply colored.

¹ Z. physik. Chem., 55, 589.

² Ber., 33, 3795; 35, 168. ³ J. pr. Chem., 47, 72. ⁴ Ber., 34, 3897.

⁵ Ibid., 34, 619. ⁶ Ibid., 24, 618. ⁷ Werner "Stereochemie", p. 214.