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THE ATOMIC WEIGHT OF CARBON
The Ratio of Benzoyl Chloride to Silver

by

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The Rice Institute

A Thesis

Presented to the Faculty of The
Rice Institute of Houston, Texas,

In Partial Fulfillment of the

Requirements for the

Degree

of

Doctor of Philosophy

The Rice Institute

1937

37-4722

9/10/37 Chem. Dept.

UMI Number: 3079742

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The atomic weight of carbon has been the subject of a number of careful investigations in the past few years, and as a result of these studies has been changed from its old value, 12.00, to 12.01 in the current report of the Committee on Atomic Weights of the International Union of Chemistry (1). The first evidence that the old value was too low was obtained in 1931, when Patterson, Cawood, and Whytlaw-Gray (2) obtained a preliminary value of 12.010 from gas density measurements on ethylene. Further and more careful determinations made in the Leeds laboratory have confirmed this higher value.

1933 - Woodhead and Whytlaw-Gray (3)	CO	12.011	
1936 - Cawood and Patterson (4)	CO ₂	12.0101	
1936 - Cawood and Patterson (4)	C ₂ H ₄	12.0122	(H=1.0078)

Somewhat higher values for carbon have also been obtained recently from gas density measurements by the Spanish investigators, Moles and Batuecas, as shown below.

1936 - Toral and Moles (5)	CO ₂	12.006	
1934 - Batuecas (6)	C ₃ H ₈	12.005	(H=1.0078)
1934 - Moles and Salazar (7)	CO	12.0065	
1932 - Moles and Salazar (8)	CO	12.006	
1929 - Pire and Moles (9)	CO	12.006	

These results for carbon were not at first supported by mass-spectrographic evidence, but more recent redeterminations of the mass of the C¹² isotope and of the abundance ratio, C¹³:C¹², have yielded values for the chemical atomic weight of carbon which agree with those obtained from gas density work.

For the mass of C¹², the following mass-spectrograph values

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(converted to the chemical scale with the factor 1.00025) are the most recent.

1936 - Aston (10)	12.0005
1937 - Bainbridge (11)	12.0012

For the abundance ratio, the following values are available:

1932 - Jenkins and Ornstein (12)	1:106
1934 - Vaughan, Williams, and Tate (13)	1:92
1935 - Aston (14)	1:138

From these values for the isotopic weight and the abundance ratio, the following values for the chemical atomic weight of carbon may be calculated

$C^{13}:C^{12}$	$C^{12}=12.0005$	$C^{12}=12.0012$
1:106	12.0099	12.0106
1:92	12.0113	12.0120
1:138	12.0078	12.0085

These values are all substantially higher than 12.00, and are in good general agreement with the values obtained from gas density determinations.

The foregoing evidence favoring a value closer to 12.01 than 12.00 is all based on physical, rather than chemical (i.e., stoichiometrical) methods of determination. While these methods are recognized to give valuable information regarding atomic weights, it must be pointed out that they do not actually measure chemical atomic weights. In neither the gas density nor the mass-spectrograph method does a chemical reaction play any part, yet chemical atomic weights are defined by reference to combination or reaction with oxygen. Confirmation of the

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higher value by a chemical method is necessary before the physical evidence can be accepted with certainty. Such supporting evidence has been recently obtained by Baxter and Hale (15), who derived by a purely chemical method the value 12.010 for carbon. It was not until the preliminary report of this work (16) appeared that the change from 12.00 to 12.01 was made by the International Atomic Weight Committee.

In Table I is given a summary of all the chemical determinations of the atomic weight of carbon since 1885. It is of interest to consider these determinations in some detail in order to evaluate them.

The experiments of Hardin on the electrolysis of silver acetate and benzoate were not made with the care characteristic of modern atomic weight work and hence can be given little weight. Neither the salts nor the silver were weighed in the fused state, and it is extremely doubtful whether they were properly dried. In addition, the samples used were all less than a gram in weight, really too small for the most accurate work.

The experiments of Dean on the ratio Ag:CN can likewise be given but little weight. The purification processes used were hardly sufficient for atomic weight work, and it is doubtful whether the silver cyanide and cyanate were absolutely dry. Of the two sets of experiments on this ratio, Dean's older determinations are probably the better, due to the fact that the relationship of silver cyanide to silver was determined by intermediate titration with potassium bromide, a procedure capable of considerable accuracy, whereas in the more recent direct determinations, the silver was weighed in the form of a fine powder and must have contained considerable amounts of occluded

Table I

Chemical Determinations of the Atomic Weight of Carbon since 1885

Date	Investigator	Reference	Ratio Obtained	Method	Atomic Wt. of Carbon
1937	Baxter and Hale	(15, 16)	C:O ₂	Combustion of hydrocarbons	12.0104
1934	Baxter and Hale	(17)	Na ₂ CO ₃ :I ₂ O ₅	Titration of Na ₂ CO ₃ with iodic acid	12.004
1924	Dean	(18)	Ag:CN	Reduction of AgCN and AgCNO with H ₂	12.003
1915	Richards and Hoover	(19)	Na ₂ CO ₃ :2Ag	Titration of Na ₂ CO ₃ with HBr standardized against Ag	12.001
1915	Richards and Hoover	(19)	Na ₂ CO ₃ :2AgBr	Titration of Na ₂ CO ₃ with HBr standardized gravimetrically	12.001
1915	Richards and Hoover	(20)	Na ₂ CO ₃ :Na ₂ SO ₄	Conversion of Na ₂ CO ₃ to Na ₂ SO ₄	12.005
1909	Scott	(21)	(C ₂ H ₅) ₄ NBr:Ag	Direct titration	12.018
1900	Dean	(22)	Ag:CN	Titration of AgCN with KBr standardized against Ag	12.013
1896	Hardin	(23)	Ag:C ₂ H ₃ O ₂	Electrolysis of silver acetate	11.999
1896	Hardin	(23)	Ag:C ₇ H ₅ O ₂	Electrolysis of silver benzoate	12.001

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and adsorbed water and air.

The ratio of tetraethylammonium bromide to silver, measured by Scott, is the most satisfactory of all the determinations on theoretical grounds. The salt contains eight atoms of carbon per molecule, and all of the necessary antecedent atomic weights (Ag, Br, N, H) are well established; hence an accurate determination of the atomic weight of carbon should be possible. The direct titration process which can be used for this determination has been well studied and is the classical chemical method of atomic weight investigation. In spite of these advantages, Scott's work cannot be classed with the later work of Richards and Hoover and Baxter and Hale because the bromide salt was not very extensively purified and could not be fused before weighing. In addition, the end-point of the titration was determined by the old method of Gay-Lussac instead of the more accurate nephelometric method.

The remaining determinations to be discussed are the work of the Harvard atomic weight investigators, Richards and Baxter and their students. These determinations were made with careful attention to the details of purification and technique and offer little chance for criticism on these grounds. Of the five determinations, the ratios $\text{Na}_2\text{CO}_3:\text{Na}_2\text{SO}_4$ and $\text{Na}_2\text{CO}_3:\text{I}_2\text{O}_5$ are the least desirable for the determination of the atomic weight of carbon, since the one involves the atomic weight of sulfur and the other that of iodine, both of which are fixed only to two decimals. These determinations were not really intended for fixing the value of carbon, but were made for other reasons.

The ratios $\text{Na}_2\text{CO}_3:2\text{Ag}$ and $\text{Na}_2\text{CO}_3:2\text{AgBr}$ involve a hydrobromic acid

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solution as an intermediate. These ratios are not strictly independent, since the same hydrobromic acid solution was used for both. If this acid contained an active impurity, such as hydrochloric acid, both ratios would be in error and to the same extent. Needless to say, Richards and Hoover made every attempt to guard against such an impurity.

From a theoretical standpoint, sodium carbonate is not a very good substance with which to determine the atomic weight of carbon, since it contains only one atom of carbon and two of sodium per molecule. This fact makes all determinations of the atomic weight of carbon involving sodium carbonate very dependent on the value of sodium. If, for instance, the atomic weight of sodium is in error by 0.001 unit, the resultant value for carbon will be in error by twice this amount.

The ratio of carbon to oxygen determined by Baxter and Hale from the combustion of hydrocarbons is theoretically very desirable, since only the atomic weight of hydrogen is required in the calculations. The hydrocarbons used were so rich in carbon that the resultant atomic weight values are but little affected by the atomic weight of hydrogen. The practical difficulties of this determination are, however, exceedingly abundant. The principal points of difficulty relate to the complete combustion of the material, the complete collection of the water and carbon dioxide evolved, the "blank" corrections which must be applied to each determination, and the reduction of the weight of carbon dioxide to vacuum when it is absorbed by ascarite. In spite of these difficulties, excellent agreement was obtained using three

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different hydrocarbons, chrysene, triphenylbenzene, and anthracene, though another substance, pyrene, gave aberrant results.

Consideration of these chemical determinations of the atomic weight of carbon reveals the striking fact that only one of them, the analysis of tetraethylammonium bromide, was made by the most accurate method developed for atomic weight, namely--the direct titration of halides with silver, and that one many years ago. In view of this fact it seemed desirable to attempt such a determination as a check on the recent work of Baxter and Hale, which, though in agreement with the physical evidence, was obtained by a method which had not previously proven very successful for the purpose (24, 25).

There are innumerable organic halides which might be used for fixing the value of carbon, though not all of them are very desirable. In general, solid organic compounds offer difficulties in drying, since most of them cannot be fused without danger of decomposition. Liquid compounds, on the other hand, are frequently difficult to purify and offer difficulties in manipulation. In spite of this fact, the liquid compound, benzoyl chloride, appeared to be the most desirable halide for the purpose. It has a simple formula and its properties are well-known. It contains seven atoms of carbon per molecule, and the necessary antecedent atomic weights of chlorine and hydrogen are well established. It is not difficult to prepare, and the parent compound, benzoic acid, is capable of a high degree of purification. Finally, its boiling point (197°) is sufficiently high to suggest that it could be separated from impurities without too much difficulty by vacuum distillation. In consideration of these facts, the measurement

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of the ratio of benzoyl chloride to silver seemed to offer a good opportunity for the determination of the atomic weight of carbon.

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All materials used in this work were carefully purified before use. Throughout the purification work, attention was paid to the exclusion of impurities which might be introduced by the containers and vessels used, and to dust and laboratory fumes.

Water. The water used in the analyses and in the later stages of the purifications was prepared from ordinary distilled water by twice distilling it, first from dilute potassium permanganate made slightly alkaline with sodium hydroxide, then from very dilute sulfuric acid, using condensers of block tin. It was always freshly distilled before use. Tests for chloride impurity were frequently made, but none was ever found.

Nitric Acid. C. P. nitric acid of a high grade of purity was distilled from an all-pyrex vessel and condensed in quartz. The first two-thirds and the last tenth of the distillate were discarded. The central fraction showed no chloride when tested nephelometrically with silver nitrate.

Pyridine. The pyridine used for the hydrolysis of the benzoyl chloride was prepared by distillation of a C. P. grade of exceptional purity. Small head and tail fractions of the distillate were discarded, though none of the fractions, nor even the undistilled material gave any test for chloride on acidification with nitric acid and addition of silver nitrate.

Silver. The preparation of pure silver followed the procedure usually employed in atomic weight work. Impure silver chloride residues were reduced with sugar and sodium hydroxide. The silver formed was well washed, dissolved in nitric acid, and reprecipitated as the

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chloride with hydrochloric acid, again reduced, then fused in an electric furnace on a bed of pure lime, and cooled in a current of methane. After etching with nitric acid, the well-washed buttons were again dissolved, the silver precipitated as the chloride, then once again reduced with sugar and sodium hydroxide from which heavy metals had been removed by electrolysis. After thorough washing, the silver was again dissolved and precipitated from solution by reduction with ammonium formate. The silver obtained was fused and etched. The next step in the process consisted in the electrolytic transport of the silver through a solution of its nitrate. The electrolytic crystals were well-washed, then fused on carefully purified lime in an atmosphere of pure hydrogen. For this purpose the quartz muffle furnace of Johnson (26) was found to be very convenient. After thorough etching, the buttons were dried by heating at about 400° in a high vacuum for an hour or longer. They were stored in a desiccator filled with fused sodium hydroxide. Complete details of the silver purification are given in Archibald's work. (27)

Phosphorus Trichloride. The phosphorus trichloride used in the preparation of benzoyl chloride was obtained by twice distilling the commercial material in an all-pyrex vacuum apparatus. Small head and tail fractions were rejected in the first distillation, and another tail fraction in the second.

Benzoic Acid. This material, from which benzoyl chloride was prepared, was made by the oxidation of Baker's "Analyzed" toluene with potassium permanganate. In order to insure the absence of thiophenes and other sulfur-containing compounds frequently present in toluene,

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the material was first refluxed with mercuric acetate for several hours, then decanted and once distilled.

The oxidation was carried out according to the directions of Ullmann and Uzbachian (28), though certain modifications were found desirable. Portions of toluene weighing 100 g. were placed in a 12-liter flask, equipped with a reflux condenser and air stirrer, containing 7.5 liters of water. The mixture was heated to about 90° by means of a water-bath, then 350 g. of C. P. potassium permanganate was added gradually. The mixture was heated and stirred vigorously for 8 hours or more until the color of the permanganate disappeared. The stirring materially increased the speed of the oxidation and also the yield of benzoic acid obtained.

After the completion of the oxidation, the bulk of the manganese dioxide formed was removed by suction filtration and the liquid was again placed in the flask and the small excess of toluene distilled off. The solution was then evaporated to about 2 liters, and the remaining dioxide removed by filtration. After heating to near boiling, the solution was made acid with concentrated hydrochloric acid. If the acid is added in the cold, the benzoic acid is immediately precipitated in an exceedingly fluffy form which is difficult to wash. If any of the acid was precipitated in this form, it was redissolved by heating (and addition of water, if necessary), and the solution allowed to cool slowly. On cooling the benzoic acid separated in long needles and finally in plates.

The benzoic acid was collected on a Büchner funnel, using filter paper, and washed with water. It was then dissolved in "Analyzed"

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sodium carbonate, and the solution shaken with ether in a separatory funnel to extract organic impurities not soluble in the carbonate.

The remaining ether was removed by heating, and the benzoic acid again precipitated by the addition of hydrochloric acid in the hot, and collected and washed as before.

To remove the small amount of hydrochloric acid which might be retained by the material, the benzoic acid was once recrystallized from water and collected on a sintered-glass funnel. The crystals were washed twice with water, employing centrifugal draining, and then dried in a vacuum desiccator over phosphorus pentoxide.

The final step in the purification consisted in the sublimation of the benzoic acid. This was done in the apparatus shown in Figure 1. A portion of the dry acid was placed in the retort through the ground joint. The temperature of the oven was raised to about 130° and a gentle current of air sucked through the apparatus, causing the vaporized benzoic acid to be drawn into the glass container below. After a time, however, the neck of the retort became clogged with large crystals of the sublimate. When this occurred the upper stopcock was closed and the apparatus partially evacuated. When the stopcock was again opened, the draft was sufficient to blow the plug out of the neck of the retort, and the sublimation could be resumed as before. After a day's use, the neck of the retort was cleaned by scraping with a glass rod or a stout platinum wire, though occasionally, if the temperature of the oven rose so high that the acid in the neck melted, it was necessary to heat the neck and allow the material to flow back into the retort for resublimation.

Figure 1. Sublimation Apparatus

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Benzoyl Chloride. Benzoyl chloride was prepared by the action of phosphorus trichloride on benzoic acid. The trichloride was employed instead of the more usual pentachloride because the latter substance might, by decomposition into trichloride and chlorine, induce ring chlorination, though this does not ordinarily occur. Moreover, the trichloride is more easily purified than the pentachloride.

The reaction was carried out by placing 317 g. of purified benzoic acid in a 2-liter flask fitted with a reflux condenser connected by means of a ground glass joint. To the acid in the flask was added 175 g. of phosphorus trichloride. The mixture was heated on a steam bath until it became liquid and then for 2.5 hours longer. The resulting material consisted of two layers, the lower being a gummy, water-soluble mixture containing phosphorous acid and a yellow insoluble phosphorus compound of indefinite composition (29). The upper layer consisted principally of benzoyl chloride. This material was decanted into a clean flask.

The remainder of the purification process consisted in the repeated distillation of the benzoyl chloride in an evacuated all-pyrex apparatus. This procedure seemed very suitable for the removal of the principal impurities, HCl , PCl_3 , $\text{C}_6\text{H}_5\text{COOH}$, $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$, H_3PO_3 , and other acids or anhydrides of phosphorus, since all of these substances have boiling points far removed from that of benzoyl chloride.

The distillations were carried out in an apparatus which is shown diagrammatically in Figure 2, and a photograph of one of the set-ups, including the vacuum pump, is shown in Figure 3. This apparatus was constructed of pyrex glass. In order to introduce the benzoyl chloride

Figure 2. Distillation Apparatus

Figure 3. Distillation Apparatus

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into the bulb A for the first distillation, the bulb actually used had an extra side-arm, not shown in the diagram, and the capillary at the top was open. To this side-arm was sealed a long, bent tube containing a capillary constriction near the flask. This arrangement permitted the benzoyl chloride to be introduced into the flask by suction. After this was done, the capillary on the side-arm was sealed. An aspirator was connected to the open tube at the top and suction applied. The liquid was then heated to boiling for a short time to expel most of the air in the flask, and while still boiling the top capillary was sealed. This treatment also served to remove a large part of the more volatile impurities.

The apparatus to the right of the valve e was then evacuated by means of a Cenco Hyvac pump. With the pump still on, the valve was broken with a magnetic hammer. The construction of this type of valve and hammer is described by Richards and Craig (30). To prevent the iron nail inside the hammer from sliding around, it was embedded in paraffin wax. The ring-seal trap f served to prevent fragments of the broken valve-capillary from clogging the constriction g.

With the vacuum pump still running, the distillation from A to B was effected by heating A in a glycerin bath and cooling B in an ice-bath. Large amounts of HCl and PCl_3 were removed through the pump. The distillation was discontinued when a white solid, probably benzoic acid, began to sublime over at 100° . After further pumping for a brief period, capillary h was sealed and the pump disconnected. Only the first distillation, from A to B, was made with the pump on; in the remainder, the constriction h was sealed before the valve was broken.

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It was now necessary to seal capillary g and disconnect flask A, which contained the residue of the distillation. Preliminary tests of the distillation procedure had shown that it was impossible to seal capillaries with which benzoyl chloride had been in contact merely by heating them with a hot, pointed flame, as is usually done. Whenever this was done, a black char appeared inside the tube at the point of heating, indicating the decomposition of benzoyl chloride retained on the surface of the glass, though no wetness was ever visible.

This difficulty was finally obviated by subjecting all the capillaries to a prolonged baking immediately before sealing them. A special type of electric heater was designed to accomplish this treatment. It consisted of two sections of a large-bore pyrex tube split lengthwise. Around the length of the sections nichrome resistance wire was wound. The two sections of this split-tube heater were placed on the end of a pair of forceps, which permitted them to be held together with the capillary in the center. In series with a suitable resistance, a temperature of about 200° was reached. All the capillaries were heated in this manner for 30 minutes or longer before they were sealed off with a flame. With this procedure, the charring was practically eliminated.

After sealing capillary g, the bulb containing the residue was disconnected. The residue of the first distillation was a rather viscous yellow liquid consisting mainly of phosphorous acid, though considerable benzoyl chloride was also present. The distillate in B was clear and colorless.

The next step consisted in the fractionation of the distilled

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material through the column i. This column was 22 cm. in length. It consisted of a spiral of 2 mm. pyrex rodding wound on a central rod of pyrex. The spiral was ground to fit snugly into its containing tube, which was 10 mm. in diameter. The winding of the spiral and the grinding were done according to the directions of Fahlandt (31).

The distillation was performed by heating B to 70-80° with a glycerin bath while ice water was run through the condenser j. Under these conditions the temperature at the top of the column varied from about 33° to 38°, depending on the temperature of the bath and also on room temperature. By means of the drop-counter, k, the rate of distillation could be determined. It was never allowed to exceed 8-10 drops per minute and was usually less. The reflux ratio was about 2:1. At no time was the liquid brought to boiling.

When the first of the sample bulbs, s, was filled, distillation was discontinued, the capillary of the bulb baked and sealed, and the bulb disconnected. Distillation was then resumed and the next sample collected. The small amount of distillate which collected in the side-arm to which the previous bulb had been connected was removed by gentle heating.

The main fraction of the distillate was collected in a large bulb, C, which was equipped with a capillary valve so that the material could be redistilled.

When the distillation was completed, the apparatus was dismantled and thoroughly cleaned by soaking in sodium hydroxide, sulfuric acid-dichromate "cleaning solution", and water, then dried and reassembled for the next distillation. The remaining distillations were made in a

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manner similar to the one described.

Before each distillation, the apparatus was thoroughly tested for leaks by means of a McLeod gauge which was connected to the pumping system. Before sealing the capillary connection between the vacuum pump and the distillation apparatus, the apparatus was evacuated until the gauge showed that the pressure due to non-condensable gases was about 10^{-5} mm. To achieve this low pressure a dibutyl phthalate diffusion pump connected in series with the Hyvac pump was employed.

The complete distillation diagram is shown in Figure 4. Some points regarding the various distillations may be noted.

In the first fractionation from B to C, a small residue which did not distil at 80° was left in B.

A Widmer fractionating column, (32), was used for the distillation from D to E. Since it was somewhat difficult to operate and did not appear especially advantageous, it was replaced by the simple spiral column in the remaining distillations. During the collection of the first sample of this distillation, the vapor temperature rose to 60° and then fell rapidly, suggesting that HCl was first vaporized, then redissolved in the distillate. This fact is of importance in interpreting the results of the analyses.

In order to obtain sample 14, it was necessary to heat the distillation bulb to $100-110^{\circ}$, the vapor temperature rising to 45° . The reason for this is not clear, though it may have been due to a small amount of air in the apparatus. However, no difficulty was encountered in the subsequent fractionation, and the analysis of sample 14 did not deviate significantly from the other analyses.

Figure 4. Distillation Diagram

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The results obtained from the analysis of the various fractions of the benzoyl chloride seem to indicate that the purification by repeated distillation is a very efficient process. The material seems to have been freed from all its impurities after the third fractionation, for the three further fractionations caused no further change in composition of the various fractions, as determined analytically. That the pure material was so readily obtained is doubtless due to the fact that the impurities present differed so widely in boiling point from benzoyl chloride.

DETERMINATION OF THE RATIO OF BENZOYL CHLORIDE TO SILVER

DETERMINATION OF THE RATIO OF BENZOYL CHLORIDE TO SILVER

Weighings. Weighings were made on a Troemner balance of high sensitivity. The weights were calibrated by Richards' method (33). The samples of silver were conveniently weighed on tared watch glasses by the method of double weighing, but all other weighings were made by substitution. The air density was determined immediately after each weighing by the method of Baxter (34), and all weights were reduced to the vacuum basis. In calculating the vacuum corrections, the following densities were used: pyrex glass, 2.25; platinum, 21.5; silver, 10.5; weights, 8.36. Weighings were reproducible to 0.02-0.03 mg.

Analytical Procedure. The bulb containing the sample of benzoyl chloride to be analyzed was first washed well and dried. Its exterior volume was determined by weighing it in air and in water of known temperature using a triple-beam balance sensitive to 0.01 g. It was necessary to know this volume in order to calculate the vacuum correction. The bulb was then more thoroughly cleaned with "cleaning solution", followed by several hours soaking and rinsing with water. After wiping the clean bulb with a nearly lintless cloth, it was placed in a desiccator containing fused sodium hydroxide and allowed to stand overnight to dry. Its weight was then accurately determined.

The bulb was placed in a thick-walled flask containing 100 ml. of pyridine and 100 ml. of water, and the flask was closed with a tight-fitting, ground-glass stopper. The bulb was then broken inside the flask by violent shaking, and the benzoyl chloride allowed to react with the aqueous pyridine. After standing eight hours or longer, the flask was opened, and, if necessary, the end of the sealed capillary smashed with a stout glass rod. The solution was then decanted through

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a #42 Whatman filter into a 3-liter glass-stoppered flask. The glass fragments in the thick-walled flask were washed 15 times with 50-ml. portions of water to complete the transfer of the benzoyl chloride. They were then collected on the filter paper. This was best accomplished by first washing them into a 600-ml. beaker and then onto the filter. To remove the last few fragments from the walls of the flask, it was necessary to invert the flask over the beaker and use a wash-bottle with a nozzle bent upward. The glass fragments and filter paper were placed in a previously weighed platinum crucible and the filter paper burned off in an electric furnace. It is an advantage of pyrex glass that its high melting point permits the use of higher temperatures for the removal of the filter paper than does soft glass, thus hastening the work. After cooling 30 min. or longer in a desiccator, the weight of the crucible and glass fragments was obtained. A correction of 0.09 mg. was applied for the ash of the filter paper. The weight of the glass bulb and of the benzoyl chloride sample could then be obtained.

As previously stated, the hydrolysis of the benzoyl chloride samples was carried out in 200 ml. of 50 per cent aqueous pyridine. The chloride samples were completely soluble in this mixture, and within a few minutes after the sample bulb was broken, the solution was perfectly clear. Preliminary hydrolysis experiments using sodium carbonate and sodium hydroxide showed that benzoyl chloride reacted with them far too slowly to be of any use.

After obtaining the weight of the benzoyl chloride, the equivalent weight of silver was calculated, using 12.01 as the atomic weight of

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carbon. A quantity of silver within 2 or 3 milligrams of the calculated amount was then weighed out. The bulk of the silver consisted of fused buttons, though in some instances the last few centigrams were made up with electrolytic crystals which had been dried by heating in a vacuum. The silver, which weighed about 10 g. in each analysis, was placed in a flask fitted with a tower of bulbs and dissolved in 25-30 ml. of 1:1 nitric acid. The flask was heated on an electric hot plate to hasten the solution. After all the silver had dissolved, it was further heated to expel oxides of nitrogen. The solution was then diluted to 500 ml.

Before addition of the silver, the pyridine solution of the benzoyl chloride was acidified with 300 ml. of 1:3 nitric acid. The resultant volume was 1200-1700 ml. The addition of nitric acid did not cause the precipitation of benzoic acid, as might be expected, except in two of the analyses in which a very small amount (which later redissolved) slowly crystallized out.

The precipitation of the chloride was carried out by adding the dissolved silver to the acid solution of the benzoyl chloride in small portions with constant agitation. The last traces of the silver were removed from the flask by 10 washings with water. After the addition of the silver in this manner, the amount was adjusted to the calculated value by the addition of silver nitrate or sodium chloride from carefully prepared solutions of the purified substances. These solutions contained 0.1 mg. of silver or its equivalent of chloride per milliliter. The additions were made from calibrated burettes.

The solutions were vigorously shaken several times over a period

DETERMINATION OF END-POINT

of three days to coagulate the silver chloride, then allowed to stand at least two days longer before making any nephelometric tests. The final volume was between 2250 and 2750 ml., depending on the amount of wash water which had been used.

Determination of the End-point. The end-point of the analyses was determined nephelometrically using a nephelometer of the Richards type. The nephelometric test suspensions were prepared by the use of the "uniform" precipitation device described by Scott and Hurley (35). After the first tests on the analytical solutions had shown whether an excess of silver or chloride was present, suitable additions of silver nitrate or sodium chloride were made, using the very dilute standard solutions already mentioned. By further tests and additions, if necessary, the analyses were brought to the end-point of equal opalescence. When three or more consecutive tests showing equal-opalescence were obtained, the analyses were judged to be at the end-point. The nephelometric tests on the solutions were made over a period of 3 weeks or longer except in the case of the last two analyses, which were observed for only two weeks. After each test the solutions were vigorously shaken and allowed to stand 36 hours or longer before another test was made.

Because of the rather large amount of pyridine used to dissolve the benzoyl chloride, the analytical solutions contained considerable amounts of so-called "extra compounds." The final concentrations of these substances were approximately as follows: pyridinium nitrate, 0.5 M; benzoic acid, 0.04 M; nitric acid, 0.2 M. That these substances might exert an effect on the silver chloride precipitate such that the

DETERMINATION OF END-POINT

end-point of equal-opalescence would not be valid was a possibility which could not be ignored, although Johnson (36) found no significant effects in tests of a large number of "extra compounds" present in various atomic weight determinations. In order to make a test of this point, two very pure silver chloride precipitates which were at hand were washed 11 times with water, followed by 4 washings with 0.16 M nitric acid. The washings were made over a period of two weeks. Nephelometric tests were made on the fourth nitric acid washing of the two precipitates. Two tests on each solution gave identical ratios, 1.00, indicating equivalence of silver and chloride. The nitric acid was then replaced with a solution containing pyridinium nitrate and nitric acid in approximately the same concentration as in the analytical solutions. After shaking and standing for a week to allow the solution to become saturated with silver chloride, duplicate tests on the two solutions gave values of 1.00 and 1.02 for the opalescence ratio. That no significant change in the ratio occurred indicates that the "extra compounds" present in the analytical solutions are without effect on the end-point. The fact that the test solutions did not contain benzoic acid seems unlikely to vitiate the test, since the concentration of this substance in the analytical solutions was relatively so small that it could hardly have had any significant effect on the end-point.

Results of the Analyses. The results obtained from the analysis of ten samples of the benzoyl chloride are given in Table II. These analyses formed a consecutive series and no accidents or mishaps occurred. All the weights given in the table are corrected to the

Results of Analyses of Benzoyl Chloride

$\Delta G = 107.880, H = 1.0078, CI = 35.457$

[illegible]

ANALYTICAL RESULTS

vacuum basis. In column 5 is given the weight of silver added (or subtracted as chloride) after the nephelometric measurements were begun. These figures do not include the small additions previously made to bring the weight of the silver to the calculated value. The latter are included in the weights given in column 4. The total amount of silver or chloride added from the dilute standard solutions did not exceed 3.5 mg. except in the first analysis, in which a total of 5.50 mg. of silver was added.

The first analysis must be excluded from the calculations not only because the result obtained differs so widely from those of the nine other analyses, but also because there is a strong presumption that fraction 4 contained a small amount of HCl. This presumption is based on the behavior of the Widmer column during the collection of the previous fraction, already mentioned in the description of the purification.

The ratio obtained from analysis 3 is somewhat higher than the others. If, in addition to analysis 1, this analysis is also excluded, the atomic weight of carbon becomes 12.0102. Since no explanation for the high results of this analysis is known, it seems preferable to retain it in the calculations.

The current International values for the atomic weights of hydrogen, chlorine, and silver were used in the calculations. The atomic weight of carbon calculated from the ratio of benzoyl chloride to silver is not, however, very dependent on these antecedent atomic weights. If, as is not unlikely, the atomic weight of hydrogen is somewhat higher than the present accepted value, the value for carbon

ANALYTICAL RESULTS

would be lowered slightly. Using Aston's latest value for hydrogen (10), which is 1.0081 on the chemical scale, the mean value for carbon becomes 12.0102. This value is also obtained if 107.879 is used for silver. That these changes have so little effect on the value for carbon is, of course, due to the fact that benzoyl chloride contains 7 atoms of carbon per molecule.

The final value for the atomic weight of carbon which is calculated from these analyses, 12.0104, is in exact agreement with the mean calculated from all of the combustion analyses of Baxter and Hale (15), excepting those which they themselves rejected. This concordance in chemical determinations, combined with the good agreement with the physical values, suggests that the value 12.010 may be safely adopted for the atomic weight of carbon.

Discussion of Results. The results of the present investigation indicate, by their agreement with those of Baxter and Hale (15) and with the physical evidence, that the atomic weight of carbon is very close to 12.010. In view of this fact, it is of interest to consider again some of the older chemical determinations in order to discover what implications this may have.

Of the determinations of the atomic weight of carbon summarized in Table I, only those of Baxter and Hale on the ratio $\text{Na}_2\text{CO}_3:\text{I}_2\text{O}_5$ and of Richards and Hoover on the ratios $\text{Na}_2\text{CO}_3:2\text{Ag}$, $\text{Na}_2\text{CO}_3:2\text{AgBr}$, and $\text{Na}_2\text{CO}_3:\text{Na}_2\text{SO}_4$ were sufficiently accurately determined to be of much importance, but these ratios were measured with great care. It will be noted that in all of these four determinations, the carbon involved is in the form of sodium carbonate. It has been previously

DISCUSSION OF RESULTS

pointed out in the Introduction to this thesis that sodium carbonate is not a very good substance to use for the determination of the atomic weight of carbon, since it contains so little of this element. In order to calculate the value of carbon from sodium carbonate, it is necessary to subtract the weight of two atoms of sodium. This makes the resultant value for carbon carry twice the error to which the atomic weight of sodium may be subject.

This argument may be reversed in considering the atomic weight of sodium. Because sodium carbonate contains two atoms of sodium to one of carbon, the value obtained for sodium after subtraction of the single atom of carbon contains only half the error to which the atomic weight of carbon is subject. This reversed argument does not, however, apply in the case of the ratio $\text{Na}_2\text{CO}_3:\text{Na}_2\text{SO}_4$, which is arithmetically unsuitable for the calculation of the atomic weight of sodium, since it would require the use of values for carbon and sulfur known to four decimals in order to obtain sodium to three. If, however, there is no experimental error inherent in the determination of the other three ratios, they should provide the best determinations of the atomic weight of sodium yet performed, provided the atomic weight of carbon is available for the calculation. With this last provision now apparently capable of fulfillment, it is of interest to make these calculations.

Employing the value 12.010 for carbon and the current International values for silver, bromine, and iodine, the following values for the atomic weight of sodium are obtained.

DISCUSSION OF RESULTS

$\text{Na}_2\text{CO}_3:2\text{Ag}$	22.993
$\text{Na}_2\text{CO}_3:2\text{AgBr}$	22.993
$\text{Na}_2\text{CO}_3:\text{I}_2\text{O}_5$	22.994

These values are in good agreement, but are somewhat lower than the present accepted value for sodium, 22.997. They are, however, in agreement with the value 22.994 obtained by Johnson (37) in 1933 from a determination of the ratio $\text{NaCl}:\text{Ag}$.

Unfortunately, no determination of the atomic weight of sodium by the mass-spectrograph method has been made, therefore it is impossible to seek verification of these low values from this source. A physical value, 22.9972, has, however, been recently obtained by Pollard and Brasefield (38) from a study of the nuclear reaction $\text{Ne}^{20} + \text{He}^4 \rightarrow \text{Na}^{23} + \text{H}^1$. When converted to the chemical scale with the factor 1.00025, the figure 22.9915 is obtained for sodium. While this value is probably not as accurate as the number of figures given would indicate, it is near enough to those obtained from the carbonate ratios and to Johnson's value to be looked upon as confirming a lower value for sodium. Although any final judgment at this time is probably premature, this concordance suggests that the present International value for the atomic weight of sodium is 0.003-0.004 units too high.

SUMMARY

SUMMARY

A careful determination of the ratio of benzoyl chloride to silver has been made and the results of nine very concordant analyses give as the mean value of the ratio the figure 1.303009 ± 0.0000085 , from which the atomic weight of carbon is found to be 12.0104 ± 0.00009 .

The concordance of this result with the value obtained by Baxter and Hale from the combustion of hydrocarbons, and also with recent mass-spectrograph values suggests that the value 12.010 be adopted for the atomic weight of carbon.

Using the value 12.010 for the atomic weight of carbon, the atomic weight of sodium has been calculated from mass ratios involving sodium carbonate. These calculations give a value close to 22.993 for sodium, indicating that the present accepted atomic weight for sodium, 22.997, is too high.

The author wishes to express his appreciation to Dr. Arthur F. Scott for his interest and assistance in this work.

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