A Revision of the Atomic Weight of Carbon

By GREGORY P. BAXTER AND ARTHUR H. HALE

For some time it has seemed probable that the International value for the atomic weight of carbon, 12.00, is slightly too low.[1] Most recent determinations of densities and compressibilities of gaseous hydrocarbons and oxides of carbon have yielded values higher than this, and the result of our recent determination of the ratio between iodine pentoxide and sodium carbonate points in the same direction. Furthermore the isotopic weight of C^{12} from mass spectrographic results appears to be greater than 12.00 on the chemical scale[2] and allowance for approximately 1%[2,3] of C^{13} raises the average value for the mixture of isotopes by about 0.01 unit.

We therefore have sought for as direct and simple a method as possible for finding the ratio of carbon to oxygen by gravimetric means. From a theoretical standpoint the combustion of weighed amounts of carbon to carbon dioxide should provide the best means of finding this ratio. But the practical difficulties in preparing really pure carbon are very great, if it is possible to do so at all, while natural carbon is always impure and the composition of the impurities uncertain.

The combustion of organic compounds was used for the purpose many years ago by Dumas and Stas, as well as by Scott in 1909. In these experiments, however, the formula of the substance burned was employed in the calculation, together with the weight of carbon dioxide formed. In general, this method will be more satisfactory the fewer the number of elements contained in the original compound and the higher the percentage of carbon. Dr. James B. Conant pointed out to us that certain aromatic hydrocarbons of high molecular weight, such as chrysene, $C_{18}H_{12}$, contain only a few per cent. of hydrogen and therefore should be ideal for the purpose. Many of these are exceptionally stable and are not difficult to purify. Furthermore, while it is probably possible to obtain some of these free from other similar hydrocarbons, *hydrocarbon* impurity is not necessarily an obstacle since the hydrogen content may

be determined simultaneously with the carbon dioxide by collecting and weighing the water formed during the combustion. No assumption of formula need be made.

We therefore have investigated experimentally the following method. A weighed amount of hydrocarbon was burned in pure oxygen and both the carbon dioxide and the water formed were collected and weighed. From the weight of water the weight of hydrogen was calculated. The difference between the weight of hydrocarbon and the weight of hydrogen yields the weight of carbon in the original material, and from the weights of carbon and carbon dioxide the atomic weight of carbon may be calculated.

The Purification of Hydrocarbons

Pyrene.—It was unfortunate that the first hydrocarbon chosen for examination was pyrene, $C_{16}H_{10}$. It is our belief that we never succeeded in freeing this substance wholly from elements other than carbon and hydrogen. Pyrene was employed, however, in the preliminary stages of developing the analytical technique.

The original material was yellow and besides dirt contained volatile impurities of strong odor. The pyrene was first dissolved in technical toluene and after the solution had been filtered through platinum sponge the hydrocarbon was several times recrystallized from toluene with centrifugal drainage and rinsing of the crystals. All the dirt, most of the color and the odor were thus removed. A preliminary combustion of this material yielded the value for the atomic weight of carbon 12.041. Three more crystallizations from toluene which had been purified with sulfuric acid gave material which yielded 12.032 for carbon.

Another sample was recrystallized six times from redistilled glacial acetic acid and three times from absolute ethyl alcohol. It was then subjected to systematic fractional crystallization first from pure toluene, then from pure benzene, through ten series in all. The final head fraction was odorless but still pale yellow and gave 12.024 for carbon.

The three purest fractions were combined and fractionally distilled in an all-glass (Pyrex) system with an electrically heated fractionating column in high vacuum (mercury vapor pump). The least volatile of the three fractions seemed to be slightly less colored than the others. After crystallization from benzene the most volatile fraction yielded 12.032 for carbon, the least volatile 12.031 and 12.027 (Analysis 41).

The middle fraction was dissolved in pure benzene and passed through four 25 × 2.0-cm. columns of alumina which had been activated at 300°. The product was crystallized, distilled and crystallized once. This treat-

(1) Reports of the Committee on Atomic Weights of the International Union of Chemistry for 1933 and 1934.

(2) Aston, *Proc. Roy. Soc.* (London), **A149**, 400 (1935); *Nature*, **135**, 541 (1935).

(3) Jenkins and Orustein, *Proc. Acad. Sci. Amsterdam*, **35**, 1212 (1932).

ment did not remove the color, but three analyses gave C = 12.018, 12.037 and 12.021 (Analyses, 49, 53, 54). Encouraged by this result, we passed a benzene solution of the above first fraction through a 90 × 2-cm. column of activated alumina. The pyrene obtained by evaporating the benzene was alternately distilled with rejection of heads and tails and crystallized. The product of this treatment was almost white but gave C = 12.021 (Analysis 50). Since Clar[4] states that the color of pyrene may be removed by treatment with maleic anhydride, 60 g. of crude pyrene was dissolved in 300 cc. of xylene and refluxed for four hours with 15 g. of maleic anhydride. Treatment with alkali and washing with water followed. This process was twice repeated. The crystals which separated on evaporation were light brown and the color was slightly reduced by three crystallizations from benzene. Five successive slow sublimations in high vacuum, after melting in nitrogen, gradually reduced the color. The product of the fifth sublimation was white, the residue of this sublimation slightly green. After crystallization from benzene two analyses gave 12.021 and 12.020 for carbon (Analyses 51 and 52).

At this point work on pyrene was temporarily discontinued, since the purification and combustion of other hydrocarbons was yielding more interesting and consistent results.

Chrysene.—A small sample of chrysene, $C_{18}H_{12}$, was purified for us by Professor L. F. Fieser by an abbreviation of the processes described below. Using the combustion apparatus before it had been perfected the material gave C = 12.013. Starting with commercial material we prepared a second larger sample. Tetrachloroethane was treated with seven successive portions of concentrated sulfuric acid at 60–70° for a total period of forty hours and then was washed thoroughly with hot water. Distillation followed with rejection of the head fraction which contained most of the residual water. Crude chrysene was dissolved in the purified tetrachloroethane and the solution was digested three times for periods of an hour with small portions of concentrated sulfuric acid at 45°. The color of the chrysene solution was wholly removed by this process. This solution was then washed with water, with sodium carbonate solution, and finally fourteen times with water. No sulfate could be detected after the tenth washing.

To recover the chrysene, the tetrachloroethane together with most of the water was removed by distillation and the chrysene was crystallized from the residual solution and then three times from tetrachloroethane. The product still had a slight grayish tinge. Two crystallizations from purified benzene were followed by two distillations in high vacuum. The product of the first distillation was white but a yellowish film was left in the still. In the second distillation no residue was left. Finally the distilled product was twice crystallized from benzene. The melting point, kindly determined by Dr. E. B. Hershberg, was 254.5–255° (corr.).

Triphenylbenzene.—Two specimens of triphenylbenzene, $C_{24}H_{18}$, were purified in essentially the same way. One had been prepared by Dr. L. W. Blanchard from acetophenone and aniline (I). The other was a commercial

product (II). Three crystallizations from pure benzene yielded a light yellow product. After three distillations in high vacuum the product was faintly yellow. Two more crystallizations from pure benzene yielded a pure white product (Analyses 44 and 48). Part of Sample I was further crystallized seven times from pure benzene without affecting its composition (Analysis 42). The melting point of sample II was 174.3–174.5° (corr.).

Anthracene.—Commercial anthracene, $C_{14}H_{10}$, was crystallized once from acetone and once from benzene. The product was white with blue-violet fluorescence. Then it was twice melted in nitrogen with one-tenth its weight of potassium hydroxide to remove carbazole and distilled at low pressure from the mixture. After melting the material in nitrogen it was again distilled at low pressure and finally was once crystallized from pure benzene; m. p. 216.4–216.7° (corr.).

The Combustion Apparatus

Compressed oxygen, prepared from air by liquefaction, was used throughout the work. It was passed successively over the following substances: potassium hydroxide solution, hot copper oxide, potassium hydroxide solution, solid potassium hydroxide, hot platinum, amalgamated copper gauze, solid potassium hydroxide and phosphorus pentoxide.

Air was passed over hot copper oxide, aqueous silver nitrate, aqueous potassium hydroxide, concentrated sulfuric acid and phosphorus pentoxide.

The earlier combustions were made with a hard glass tube. A removable plug of copper oxide 2.5 cm. long placed ahead of the material to be burned cared for diffusion of hydrocarbon vapors against the oxygen stream. Beyond the boat containing the hydrocarbon was located the main catalyst, 30 cm. long, consisting of alternate layers of copper oxide 5 cm. long and platinized asbestos 0.5 cm. long. The catalyst was heated to dull redness by removable electrically heated sleeves. Since the hydrocarbon was burned slowly by cautious evaporation into the oxygen stream most of the combustion took place at the forward end of the catalyst without any considerable reduction of the copper oxide. The length of the layer of copper oxide was therefore gradually diminished to 7–8 cm. without affecting the results. Furthermore, the introduction of a plug of lead chromate at the forward end of the catalyst was without effect. This apparatus was used in the earlier analyses, in which the ratio C/O_2 was invariably slightly higher than with the improved apparatus used later.

Since with glass the temperature to which the tube could safely be heated was limited and because of short life of the tube, a thick quartz combustion tube was employed in all the later analyses. At the same time the copper oxide was largely replaced by platinum as a catalyst, since the combustion took place slowly in an excess of oxygen. The danger of retention of carbon dioxide and water by the copper oxide was thus diminished as well as that of expulsion of these substances from the hot glass tube. In order to provide for a possible deficiency of oxygen, however, a plug of copper oxide contained in a perforated platinum basket was located at the end of the catalytic layer. In its final form the combustion tube A (see

(4) Clar, Ber., **65**, 1427 (1932).

figure) contained (1) a platinum basket filled with platinized quartz chips (3 cm.), (2) the platinum boat with the hydrocarbon, (3) a roll of platinum gauze (1.5 cm.) at dull redness (650°), (4) a roll of perforated platinum foil (6 cm.) and (5) a perforated platinum basket filled with copper oxide (6 cm.) both at 800°. It was found undesirable to heat the platinum gauze (3) above dull redness because of flashing back of the flame. After passing the gauze, combustion was so far advanced that a higher temperature was safe.

The combustion tubes were connected with the oxygen and air trains by means of carefully ground joints which were sealed with a small quantity of a non-volatile paraffin–rubber grease. Connection with the absorbing train was made by means of a ring sealed capillary tube which prevented contact of the liquid water formed in the combustion with the ground connection (see figure).
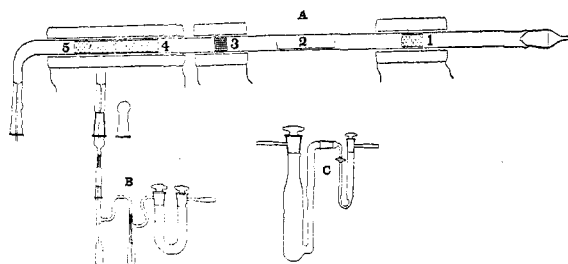

Fig. 1.

It is by no means certain that any of the changes in the combustion tube produced appreciable effects on the results, but the quartz combustion tube in its final form was unquestionably less troublesome and more satisfactory.

The Absorption Apparatus

The original absorption tube for water contained anhydrous magnesium perchlorate followed by phosphorus pentoxide. This had various disadvantages, among them the uncertainty as to the vacuum correction to be applied to the weight of water absorbed. This uncertainty could be removed by condensing the water as liquid. In the final form of the tube, which seemed most satisfactory (B, see figure) the products of combustion, partly in the form of liquid water, were passed through capillaries into cylindrical condensers chilled with ice, then over phosphorus pentoxide. After the combustion was complete, in order to eliminate dissolved carbon dioxide, a part of the water, which was almost entirely in the first bulb, was distilled into the second bulb with the oxygen stream running. Since very little water actually reached the phosphorus pentoxide tube the assumption that it was weighed in the liquid state was legitimate.

The water-absorbing tube was weighed in a constant temperature balance room by direct comparison with a similar glass counterpoise since the volume of air displaced was so large that variations in air density might be of importance if the substitution method was used. The counterpoise was somewhat heavier than the tube plus the water so that weights were removed when the water was

weighed. During the weighing the cap on the entrance side was removed and the inner stopcock on the U-tube was opened, and immediately before the weighing the outer stopcock was temporarily opened, so that the air density was the same inside and outside the system. Even with the cap removed this tube remained constant in weight for hours.

A buoyancy correction was applied not only for the air displaced by the liquid water but also for that displaced by the water vapor necessary to saturate the interior of the absorption tube (total interior volume exclusive of the U-tube containing the phosphorus pentoxide = 15 ml.). Through oversight the initial weight of the absorption tube was obtained when it was filled with ordinary air. The assumption was therefore made that this air was 50% saturated in the initial weighing. The correction was calculated from the barometric reading and air density at the time of weighing. In most experiments this correction amounted to +0.25 mg.

A negative correction was applied for air dissolved in the water, which amounted to −0.022 mg. per ml. of water weighed.

Except in the first few experiments the carbon dioxide was absorbed in ascarite (asbestos impregnated with fused sodium hydroxide). Since this material is also a good drying agent, prevention of the escape of water from the absorption tube was simplified and, since it is a solid, equalization of air pressure in all parts of the interior during weighing does not present the difficulties met when a solution of caustic is employed as absorbing agent. The absorption tube (C in figure) consisted of two parts connected with a well-ground joint. The larger part was filled with ascarite, the smaller with resublimed phosphorus pentoxide. Refilling with ascarite after each analysis was necessary, but the phosphorus pentoxide remained almost unchanged. In order to avoid swelling and choking the ascarite particles were graded in size, the coarser material being placed at the inlet end.

This tube was weighed by direct comparison with a similar counterpoise in the fashion already described for the water tube.

The correction for air displaced by absorbed carbon dioxide was computed as follows. For whatever carbon dioxide is absorbed as sodium bicarbonate the problem is simple. One mole of carbon dioxide combines with one mole of so-

dium hydroxide (mol. vol. = 18.8)[5] giving one mole of sodium bicarbonate (mol. vol. = 38.2). The increase in volume is therefore 19.4 ml. per mole of carbon dioxide, or 0.44 ml. per gram of carbon dioxide. Any water of hydration of the sodium hydroxide is carried on to be absorbed later in a similar form by the unused sodium hydroxide or the sodium carbonate.

If the carbon dioxide is absorbed as sodium carbonate, for one mole of carbon dioxide two moles of sodium hydroxide (2 mol. vol. = 37.6) yield one of sodium carbonate (mol. vol. = 41.9) and one mole of water which presumably either remains as water of hydration of sodium carbonate or is carried along in the gas current and absorbed by the sodium hydroxide as water of hydration. The volume of a mole of water in sodium carbonate heptahydrate is 16.0 ml., in the hexahydrate 15.4 and in sodium hydroxide monohydrate 15.3. If the average of these three values, 15.6, is used the increase in volume due to the absorption of one mole of carbon dioxide is 19.3 ml., or 0.44 ml. per gram.[6]

For computing the vacuum corrections of the hydrocarbons the densities were required. That of pyrene was found by fusing a 3-g. sample in nitrogen in a platinum boat, which had been weighed in air and under water, and determining the weight of the sample. The boat and contents were then immersed in water and after removal of air at low pressure the weight under water at known temperature was found. Three determinations at 22.7° gave 1.271, 1.271, 1.272; average 1.271.

The density of chrysene was found by the method of floating equilibrium, using lumps of fused material in calcium chloride solution. Air was removed as completely as possible by evacuation. Three determinations at 20° gave 1.274, 1.274, 1.273; average 1.274.

The density of triphenylbenzene was found exactly as in the case of pyrene. Three determinations at 30.3° gave the values 1.200, 1.199, 1.199; average 1.199.

The density of anthracene was determined as in the case of chrysene. One determination at 17° gave 1.251; two at 20° gave 1.250, 1.252. The value 1.251 is used in the calculations.

The density of sodium hydroxide monohydrate

(5) "I. C. T." values are used for densities.
(6) Rossini [*Bur. Standards J. Research*, **6**, 39 (1931)] by similar reasoning finds 0.45 ml. per gram.

was determined by the method of floating equilibrium in a mixture of dibromoethylene and benzene. Four determinations at 25° gave 1.699, 1.698, 1.705, 1.703; average 1.701.

Method of Combustion

To prepare the hydrocarbons for weighing about 3 g. was placed in a weighed platinum boat and brought barely to the melting point in a current of nitrogen by means of an aluminum block furnace. After cooling in nitrogen and standing in a desiccator for some time the material was weighed and the air density observed. None of the hydrocarbons were appreciably volatile at room temperature. A fused 7-g. sample of pyrene in one hundred and eighty-four hours lost only 0.33 mg., while similar experiments with the other three showed negligible changes in weight.

With the catalysts 4 and 5 at 800° the combustion tube was swept out with oxygen for one-half hour. The boat with the hydrocarbon was then introduced, the absorption train was attached and the other sections of catalyst, 1 and 3, were heated to 650°. Next the section of the tube containing the hydrocarbon was gradually heated until the first portion of the catalyst following began to glow and this condition was maintained until the hydrocarbon was completely volatilized. In the earlier experiments this heating was effected by a piece of angle iron and wide flame below, together with a row of small flames above. Later this method, which required considerable attention, was discarded for that of electrical heating with a coil of nichrome wire wound around the tube. By this method the control of the volatilization was far better and easier and required little attention. During the whole of the combustion a small excess of oxygen was maintained. In all the later experiments where platinum was used as catalyst presumably the copper oxide took no major part in the reaction.

In all cases some charring occurred during the volatilization of the hydrocarbon. The residual carbon was burned by raising the temperature of the boat to redness. No residue then remained.

Some of the water formed in the combustion condensed in the end of the tube. Most of this flowed through the exit capillary into the water absorption tube. The remainder was evaporated into the current of oxygen and later air used to sweep out the tube. The sweeping with oxygen was continued for an hour after combustion was

TABLE I

ATOMIC WEIGHT OF CARBON

Pyrene

Analysis	Sample, g.	H_2O, g.	H, g.	C. g.	CO_2, g.	O, g.	Ratio C : O_2	At. wt. of C
41	2.99013	1.33408	0.14926	2.84087	10.39935	7.55848	0.375852	12.027(3)
49	3.01048	1.34368	.15033	2.86015	10.47557	7.61542	.375574	12.018(4)
50	2.98963	1.33393	.14924	2.84039	10.40172	7.56133	.375647	12.020(7)
51	2.98645	1.33646	.14952	2.83693	10.38895	7.55202	.375652	12.020(9)
52	2.95223	1.31720	.14737	2.80486	10.27197	7.46711	.375629	12.020(1)
53	3.00584	1.33905	.14981	2.85603	10.44893	7.59290	.376145	12.036(6)
54	2.99016	1.33489	.14935	2.84081	10.40328	7.56247	.375646	12.020(7)
						Average	.375735	12.023(5)

Chrysene

39	2.78044	1.31209	0.14680	2.63364	9.65247	7.01883	0.375225	12.007(2)
40	2.69258	1.27609	.14277	2.54981	9.34368	6.79387	.375310	12.009(9)
45	2.97782	1.41063	.15782	2.82000	10.33447	7.51447	.375276	12.008(8)
47	2.99649	1.41913	.15877	2.83772	10.39870	7.56098	.375311	12.010(0)
						Average	.375281	12.009(0)

Triphenylbenzene

42	3.00012	1.59012	0.17790	2.82222	10.34136	7.51914	0.375338	12.010(8)
44	2.99773	1.58730	.17759	2.82014	10.33463	7.51449	.375294	12.009(4)
48	2.99639	1.58592	.17743	2.81896	10.33026	7.51130	.375296	12.009(5)
						Average	.375309	12.009(9)

Anthracene

55	2.99484	1.51453	0.16945	2.82539	10.35398	7.52859	0.375288	12.009(2)
56	2.04930	1.03682	.11600	1.93330	7.08554	5.15224	.375235	12.007(5)
						Average	.375262	12.008(4)
					Average excluding pyrene results			12.009(1)

complete, with the tube hot. After cooling in oxygen this gas was displaced by dry air, and the absorption tubes were weighed by comparison with their counterpoises. The density of the air was observed at the time of each weighing.

In the table weights have been corrected for the buoyant effect of the air. All experiments with the improved form of combustion apparatus are included, except those abandoned when incomplete because of some accident.

In spite of the fact that pyrene consistently has yielded higher results for the atomic weight of carbon than the other hydrocarbons, without affording any known reason for the difference, the agreement of the results obtained with the other three is an indication that the lower value for carbon, 12.009, is more nearly correct. Presumably also this is a maximum value. Further purification of these hydrocarbons and the investigation of new ones is desirable before any final conclusion can be drawn, and this work is now under way.

Various uncertainties are involved in the calculation of the results, but these are small in magnitude. Aston[7] has recently found the mass of H^1

(7) Aston. *Nature.* **135**, 541 (1935).

($O^{16} = 16.0000$) to be 1.0081. When this is corrected to the chemical scale and allowance is made for 1/5000 of H^2 the atomic weight of hydrogen becomes 1.0081. If this value for hydrogen is used instead of the conventional value 1.0078 the atomic weight of carbon calculated from our data is lowered by 0.0002 unit only. Variations in the isotopic composition of coal tar hydrogen and in that of compressed oxygen have been reported but these are too small to affect our final result appreciably. However, we have preserved the water resulting from the combustions with the expectation of comparing it with samples of known isotopic composition.

It is interesting to compare the results with those to be expected on the basis of the formulas of the hydrocarbons burned. In the following table the atomic weights 1.0078 and 12.009 have been employed for hydrogen and carbon, respectively.

In view of the low total percentage of carbon and hydrogen obtained from pyrene one might conclude either that the purified pyrene still contained elements other than carbon and hydrogen or that the combustion of this substance was incomplete. The high temperature of the catalyst

at the exit end of the combustion tube makes the latter possibility less likely.

TABLE II

Pyrene, $C_{16}H_{10}$

Analysis	% Carbon	% Hydrogen	Total
41	94.903	4.992	99.895
49	94.953	4.994	99.947
50	94.941	4.992	99.933
51	94.925	5.007	99.932
52	94.944	4.992	99.936
53	94.857	4.984	99.841
54	94.938	4.995	99.933
Average	94.923	4.994	99.917
Average omitting 41 and 53	94.940	4.996	99.936
Calculated	95.016	4.984	

Chrysene, $C_{18}H_{12}$

	% Carbon	% Hydrogen	Total
39	94.731	5.280	100.010
40	94.692	5.302	99.994
45	94.701	5.300	100.001
47	94.696	5.299	99.996
Average	94.705	5.295	100.000
Calculated	94.702	5.298	

Triphenylbenzene, $C_{24}H_{18}$

	% Carbon	% Hydrogen	Total
42	94.060	5.930	99.990
44	94.074	5.924	99.998
48	94.076	5.921	99.997
Average	94.070	5.925	99.995
Calculated	94.079	5.921	

Anthracene, $C_{14}H_{10}$

	% Carbon	% Hydrogen	Total
55	94.341	5.658	99.999
56	94.348	5.660	100.008
Average	94.345	5.659	100.003
Calculated	94.345	5.655	

With the other hydrocarbons the variations in the percentages of the individual elements would be more disconcerting if it were not that the totals are in no case far from 100 per cent. It may well be that these variations are in part at least due to residual hydrocarbon solvent in the material weighed. In every case the heavy hydrocarbon was crystallized from benzene before the final fusion in preparation for weighing. This fusion was never prolonged and traces of solvent might well have escaped evaporation. In general the effect would be to raise the percentage of hydrogen and lower that of carbon, but the atomic weight of carbon would not be affected. Similarly if the heavy hydrocarbons still contained *hydrocarbon* impurities of any sort, the atomic weight of carbon would not be affected although the percentages of carbon and hydrogen would not correspond exactly to the formula assumed.

Aston's[2] most recent value for C^{12}, 12.0048 (O^{16} = 16.0000), using the conversion factor 1.00025, when corrected to the chemical scale, becomes 12.0018. If the atomic weight of carbon is 12.009 the abundance ratio of C^{13} is 1 to 138. This is in accord with Aston's estimate of the abundance ratio, 1 to 140, but smaller than that found by Jenkins and Ornstein,[3] 1 to 106, and by Vaughan, Williams and Tait,[8] 1 to 92. With Aston's abundance ratio and packing fraction, $+4.0 \times 10^{-4}$, and the conversion factor 1.00025, the atomic weight of carbon on the chemical scale becomes 12.009, a value identical with ours.

As stated before, we view these results as preliminary. On the other hand, they seem to afford support to other evidence accumulated during the past few years through measurements of gas densities and with the mass spectrograph, that the atomic weight of carbon is not far from 12.010.

CAMBRIDGE, MASS.   RECEIVED DECEMBER 7, 1935

(8) Vaughan, Williams and Tait, *Phys. Rev.*, 46, 327 (1934).