A NOTE ON THE SELECTION OF ATOMIC WEIGHTS

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In applying Cannizzaro's method for finding an approximate value of the atomic weight of an element it is necessary to make an assumption. The assumption commonly made is sufficient but not necessary. The necessary and sufficient condition to be satisfied has been precisely stated. The scope of this restricted assumption has been compared with that of the other and shown to be much narrower.

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There can be no question about the importance of critically examining the assumptions made in formulating a theory. Such a study may reveal the possibility of restricting the scope of some one assumption, thus increasing the probability of its being in agreement with the facts.

What is to be considered here is the method outlined by Cannizzaro for finding an approximate value of the atomic weight of an element. This consists in the analysis of numerous compounds whose molecular weights have been measured. For convenience in discussion some data that may be obtained in this manner have been tabulated.

Compound	*Molecular Weight*	*Per Cent of Carbon*	*Part of Molecular Weight Due to Carbon*
Acetylene	26.0	92.3	24.0
Benzene	78.0	92.3	72.0
Cane sugar	342	42.1	144
Carbon dioxide	44.0	27.3	12.0
Ethyl ether	74.1	64.8	48.0
Mesitylene	120	89.9	108
Methane	16.0	74.9	12.0
Propane	44.1	81.7	36.0
X (hypothetical)	...	..	30.0 (?)

In order to deduce an approximate value for the atomic weight of carbon from the numbers in the last column of the foregoing table it is necessary to make an assumption. An example of how this is frequently worded is to be found in the text of Noyes and Sherrill (*1*) from which the following passage is quoted:

> The multiple of the combining weight adopted as the atomic weight of any element is derived by finding the smallest weight of the element contained in one molecular weight of any of its gaseous compounds. This is the true atomic weight only in case some one of the compounds studied contains in its molecule a single atom of the element; and the adopted atomic weight is therefore strictly only a maximum value, of which the true atomic weight may be a submultiple. The probability that the true atomic weight has been found evidently increases with the number of the gaseous compounds whose molecular weights have been determined.

This is understood to assume that *among the compounds considered there is at least one whose molecule contains a single atom of carbon.* It is the assumption made by Mellor (*2*), Cartledge (*3*) and many others.

Such an assumption is sufficient, and, when all such compounds as have been carefully studied are included in the table, it is certainly justified by the facts. This may explain the failure of many to notice that the assumption, although *sufficient,* is not a *necessary* one.

Now the scope of the assumption needed can be greatly restricted. Each number in the last column is some multiple of the atomic weight, the number of carbon atoms in the molecule determining what that multiple is. Therefore, the greatest common factor of all such numbers must be the atomic weight or some multiple thereof. But this common factor (12) can be recognized even after excluding carbon dioxide and methane from our table. It is clear that the data for two compounds only, such as propane and acetylene, will be sufficient to fix the atomic weight, provided that the number of carbon atoms in the one has no factor in common with the number of carbon atoms in the other.

What follows will supplement the reasoning just given. To show that 12 is a multiple of the true atomic weight it would be sufficient to discover some compound such as the hypothetical X at the end of the table. A value of 12 for the atomic weight of carbon would lead to an absurd conclusion, a molecule containing $2^1/_2$ atoms of that element. That is, the discovery of such a compound would lower the maximum value of the atomic weight from 12 to 6.

Let it be noted here that the results obtained by Cannizzaro's method have been checked in other ways, especially by the atomic number of the element and its position in the periodic table. Hence, the probability that 12 is some multiple of the atomic weight of carbon becomes very small.

From what has been written it is clear that we need not assume the existence of at least one compound whose molecule contains a single atom of carbon. Confidence in the result obtained by this method rests primarily on the fact, that for every compound of carbon whose molecular weight has been accurately measured we would find a multiple of 12 in the last column of the table. Therefore, it is not only *necessary* but also *sufficient* to assume that *among the compounds of carbon considered there are at least two so constituted that the number of carbon atoms in the one is relatively prime* to the number of carbon atoms in the other.*

The assumption just stated is much more restricted than the one commonly made. The table prepared by Professor Reid (*4*) has been examined for the purpose of confirming this. Among the more than two thousand

* Two integers whose greatest common factor is unity are said to be relatively prime.

four hundred compounds of carbon there listed, only 74 have molecules containing a single atom of that element. Yet from the first 44 compounds, no one of which has a molecule containing a single atom of carbon, pairs of compounds which will satisfy the restricted assumption can be selected in 391 different ways.

Literature Cited

(*1*) NOYES AND SHERRILL, "An Advanced Course of Instruction in Chemical Principles," The Macmillan Co., New York City, **1922**, p. 17.

(*2*) MELLOR, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., New York City, **1922–27**, Vol. I, pp. 180ff.

(*3*) CARTLEDGE, "Introductory Theoretical Chemistry," Ginn and Co., New York City, **1929**, p. 92.

(*4*) Van Nostrand's Chemical Annual, Edition of 1918, pp. 250ff.