

Letters to the Editor.

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The Atomic Weight of Silver.

IN NATURE of Dec. 11, 1926, reference is made to the determination of the atomic weight of silver (*Trans. Chem. Soc.*, 1926, p. 2510) by H. Brereton Baker and H. L. Riley, who, by determining directly the ratio Ag:O in pure silver oxide have obtained the value 107.864 ± 0.0013 . This work, carried out with the greatest ingenuity and with care and exactitude such as has only been reached by Th. W. Richards and his school, is of cardinal importance. As I have the honour to be chairman of the Subcommittee for Atomic Weights of the International Commission on Chemical Elements, I have perhaps the right, as well as the official duty, of offering a few critical remarks. I may be allowed to add that I have studied the literature of atomic weights for fifty years and I was the first to propose, in 1888, the adoption of O = 16 as the standard of atomic weights. A like proposal was made almost simultaneously by Venable in America, and, as is well known, this has become the established practice. As the atomic weights of elements cannot as a rule be determined directly in relation to oxygen, secondary standards are required, and the most modern work published by Richards and his school is being carried out by finding the ratios $x\text{Ag}:\text{RCl}_x$ or $y\text{Ag}:\text{RBr}_y$ to determine the atomic weight of R.

The atomic weight of silver has hitherto been a relative quantity, depending upon the atomic weights of other elements, especially chlorine, potassium, lithium, and nitrogen. As I have shown in critical articles in Abegg's 'Handbook,' it must lie between 107.876 and 107.871, and this view was adopted by the International Commission for Chemical Elements in 1925. In this way the classical value 107.930 of Stas (1865) (declared by Ostwald to be exact to the limit ± 0.004 !) was superseded.

The best determination of the atomic weight of silver published by the Richards school led them to regard the value 107.876 as probably the best, and I agreed with them.

The acceptance of the results given by Baker and Riley would affect the whole series of results of the Richards school, and if we accept 107.864, chlorine would become 35.452-35.450 and nitrogen 13.999, values highly improbable having regard to the whole chemical and physical-chemical work bearing upon these elements.

After a very careful study of the paper of Baker and Riley, I beg permission to point to a possible experimental error which appears to have been overlooked by the authors. They decomposed silver oxide by heat and fused the metallic silver so obtained in an atmosphere of hydrogen. They do not seem to have considered whether silver is not volatile at its melting point, $960^\circ.5$, or a little above this temperature. Now Stas distilled silver with the oxyhydrogen flame, and I found in my work on the atomic weight of tellurium that it may be easily distilled by the flame of air and coal gas. Even on an open support of lime, silver is volatilised by using an ordinary blowpipe, a copious brown deposit (of oxide or possibly colloidal silver) being formed. On heating the metallic silver obtained by the method of Stas in a tube of the hardest Bohemian glass in the vacuum of a Sprengel pump, I found that at a dull red heat a distinct ring of fine particles of metallic silver was deposited on the

cooler part of the tube. Silver, therefore, must have a small but appreciable vapour tension even at 400° - 500° . Prof. H. Krepelka has observed repeatedly that on heating the purest, finely divided ('atomic weight') silver to its melting point in hydrogen, a distinct sublimate of small globules of metallic silver was formed on the cooler parts of the silica tube. From this I conclude that metallic silver is volatilised to a small extent at a temperature near 1000° to which Messrs. Baker and Riley heated it and fused it in hydrogen. Thus they would find their atomic weight too low.

The question arises what would be the magnitude of this source of error. If we assume the real value of the atomic weight to be 107.871 or 107.876, we can recalculate the data. I have done this, and find that if we attribute the difference of Baker and Riley's value from the value 107.871, the loss of silver on fusing would lie between the limits of 0.13 milligram and 0.006 milligram; if we take silver as 107.876, the loss would lie between the limits of 0.20 milligram and 0.06 milligram. If we take the mean atomic weight 107.864 given by Baker and Riley, the losses would be respectively 0.08 milligram and 0.14 milligram.

These quantities are so small that the silver corresponding to them would not be visible in any way in the quartz tube. I confess that I am surprised to find the above values so small, but I offer an explanation and give details in the full paper that will be published elsewhere.

May I say, in conclusion, that many years ago I contemplated a direct determination of the ratio of the atomic weights of silver and oxygen by reduction in hydrogen or in a mixture of hydrogen and nitrogen at the lowest possible temperature, but I could not carry out this most difficult and delicate work alone.

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THANKS to the courtesy of the Editor of NATURE, we are able to reply at once to the very kindly expressed criticism of Prof. Brauner. He considers that there is a possible source of error in our recent determination of the atomic weight of silver owing to the loss of traces of silver, by volatilisation, during its final melting in hydrogen. It is certain that, at the temperature of 900° , silver does give off some vapour, but we are convinced that no silver left the weighed tube. The silica tube was 17 cm. in length, not more than half of which was heated in the furnace. The rest, shielded from the heat of the furnace by asbestos board, together with the ground joint and narrow glass tube, has a length of 20 cm. They were kept cool by fanning during the whole time of the experiment. The current of hydrogen was very slow, about one bubble in 3 seconds.

It is not possible that the silver, which may volatilise at 900° , should escape in the state of vapour. If it escaped at all, it must have been in the form of fine particles of solid metal, and it seems almost inconceivable that no deposit should ever have been observed throughout the eight years during which the experiments have been going on. In the last eighteen determinations the same pair of silica and glass tubes has been used, and microscopic examination fails to reveal any trace of deposit on the part of the silica tube which was cooled, or in the glass tube. A more certain proof, however, is given by the weighings. In each determination the silver was melted several times in the silica tube until its weight was constant to one or two hundredths of a milligram. If there had been any such loss as Prof. Brauner has suggested, such constancy could never have been attained; the weight of the tube would have shown a constant diminution.