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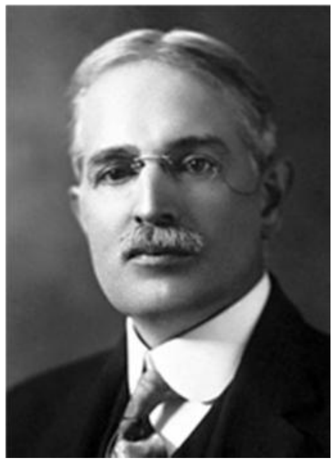
Nobel Prize in Chemistry 1914



Theodore William Richards

The Nobel Prize in Chemistry 1914 was awarded to Theodore W. Richards *"in recognition of his accurate determinations of the atomic weight of a large number of chemical elements"*.

RESEARCH INFORMATION:

The Royal Swedish Academy of Sciences resolved in 1915 to award the Nobel Prize in Chemistry for the year 1914 to Theodore William Richards, Professor at Harvard University, Cambridge, Mass., U.S.A., in recognition of his exact determinations of the atomic weights of a large number of the chemical elements.

Of the work accomplished by Professor Richards in determining the atomic weights of so many elements it has been maintained - and with perfect truth - that it represents a gigantic task. Ever since the year 1887, when Richards, who was then not quite twenty years of age, assisted Josiah P. Cooke in the redetermination of the ratio between hydrogen and oxygen in water, his labours have gone on uninterruptedly right up to the date of the awarding to him of the Nobel Prize, covering consequently a period of more than a quarter of a century.

The result of this labour has been that no less than thirty atomic weights have been redetermined with a degree of accuracy undoubtedly never before attained, and by the employment moreover of methods that, by comparison with those in earlier use, mark a very appreciable advance.

Twenty-one of the atomic weights referred to have been determined by Richards himself or under his immediate guidance, while the determination of the others has been carried out in accordance with his methods by pupils trained under him.

It should be pointed out that the determinations in question embrace all those elements (viz. oxygen, silver, chlorine, bromine, iodine, potassium, sodium, nitrogen and sulphur), whose atomic weights are customarily termed fundamental, on account of their forming the basis for the determination and calculation of the atomic weights of all the other elements.

From a purely quantitative point of view alone, the work involved in these determinations is very considerable indeed. Apart from Berzelius, the great pioneer in the department of atomic-weight determination, there is assuredly no one investigator who has contributed anything like so much as Richards, either in bulk or scope, towards the development of experimental stoichiometry. That becomes very obvious if we compare the case of Stas, whose reputation as the most distinguished authority in this field of inquiry since the decease of Berzelius was based upon his determinations - exceedingly rigorous for that time of day - of 12 atomic weights, including it is true in their number all the fundamental elements. It is well known that throughout the last three decades of the nineteenth century Stas's atomic-weight determinations had the repute of being of well-nigh unassailable precision; nor did Richard himself apparently, to begin with, consider it requisite to subject them to a thorough-going re-testing process, being disposed rather to accept them as authoritative as long as he could. At all events the elements that he set about determining in the period immediately succeeding the accomplishment, in conjunction with Cooke, of his first scientific investigation, were all of them those that were not included in the series of investigations carried out by Stas, viz. copper, barium,

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strontium, zinc, magnesium, nickel, cobalt, iron, uranium, calcium, and caesium. For by far the majority of these elements he was able to show that earlier determinations were subject to considerable sources of error, which the methods adopted and practised by himself enabled him to avoid or render nugatory. That was especially the case with one element of exceedingly great importance for quantitative analysis, viz. barium, and that is the more remarkable as its atomic weight had previously been determined by such eminent investigators as Dumas and Marignac.

In the process of determining the atomic weight of strontium by the aid of its chloride, Richards had, it is true, as early as 1894, fancied that he had obtained values and proportions diverging considerably from those arrived at by Stas, but it was not until the year 1904, that, equipped with the additional experience of another ten years' assiduous application to his task, he felt himself justified in seriously and publicly calling in question the correctness of a number of Stas's determinations.

With an acumen and wariness that left no room for uncertainty, he proceeded at that juncture to demonstrate that Stas's atomic weight for sodium was too high, while conversely that for chlorine was too low although these values had been up to that time universally accepted as correct. The statements thus made by Richards were received at the time with a certain amount of surprise, but they have been superabundantly confirmed by tests applied by succeeding investigators.

There then followed a redetermination of almost all of the other atomic weights arrived at by Stas (with the exception of carbon), and these too, in the majority of cases, were found to require exchanging for more exact values. Of those readjustments there was one that gave rise to quite a sensation in the scientific world, viz. when Richards demonstrated that Stas's atomic weight for silver, 107.938, which up to that time had been assumed to be correct to the third decimal, ought really to be reduced as far as to 107.876, subject to a possible variation of +- 0.004.

Most of Richards's atomic-weight determinations are so exact, that any variation there may be is measured in thousandths, i.e. is of the same degree of magnitude as the apparent volumes of the electrons. Their correctness has been controlled in several ways, both by Richards's own counter-experiments and by the work of other investigators, and in almost every case the agreement has been found to be entirely satisfactory. The scientific world has moreover accorded them an ever-growing need of recognition, which from 1909 onwards may be said to have borne an official stamp, for in that year the atomic weights established by Richards and his school were accepted to the fullest extent by the international commission, which had been charged with the tasks of critically reviewing the recent advances made in stoichiometry and of drawing up year by year an atomic-weight table for general use based upon the results of that review. Not only have Richards's atomic weights been directly embodied in this table; they have also been adopted as a basis for the recalculation of some atomic weights of an earlier date.

What has essentially contributed to enhance the confidence felt in the reliability of the results Richards has come to, is the fact that he has not rested content with demonstrating the incorrectness of the earlier determinations, but has over and above that been at pains, wherever feasible, to detect in detail the actual causes of the mistakes and to point out expedients for obviating them for the future. Stas in his time developed to a high degree of perfection the mechanico-physical manipulations that form a feature of the technical process of atomic-weight determination. He succeeded, thanks partly to that and partly to his making use of very large quantities (several hundred grams) of material, in reducing the errors in calculation practically speaking to nil. Richards demonstrated, however, that the chemical operations that have to be resorted to in an atomic-weight determination give rise, as a rule, to more numerous and less easily controllable sources of error than do the purely mechanical processes and the readings of weights recorded, and made it clear that the value of the latter, however important they are in themselves, incurred the risk of becoming illusory because of uncertainties in the readings.

By operating with very large quantities in weight, Stas unconsciously laid himself open to one of the most serious of the sources of error referred to, that of carrying out his precipitating reactions in much too concentrated solutions, the consequence of which was that the undissociated salts present in the solution were condensed on the phases separated off in solid form, thereby impurifying them in a much higher degree than the experimenters, with the knowledge they possessed at that time, had reason to expect. That would seem to have been specially the case with the haloid salts of silver, which Stas employed to a large extent. Realizing that the errors in question are diminished in the same proportion as the number of free ions present in the solution is increased, Richards has succeeded in exempting himself from this error by employing smaller quantities (from 5 to 20 grams) of the substance being experimented with, and by working in very dilute and consequently highly dissociated solutions.

Among the other sources of error that have been pointed out by Richards as exercising a much greater influence than investigators have been inclined to attribute to them, we may mention the following in particular: (1) the presence of hygroscopic moisture in almost all the substances employed for atomic-weight determinations; (2) a remarkable degree of solubility in apparently insoluble compounds, especially precipitates, and the attribute possessed by precipitates of remaining suspended in a fluid in exceedingly finely diffused form; (3) the inclusion and occlusion of solvents in crystals, so termed fixed solutions; (4) the occlusion of gases in metal oxides and other solid bodies; (5) impurities resulting from the vessels employed in the various operations.

In order to remove as far as possible the source of error (1) above, Richards has constructed special apparatus, on the one hand for the expulsion of every trace of moisture from substances, and on the other for the exact weighing of those substances in an absolutely dry atmosphere, free from every risk of the absorption of water (bottling apparatus). With a view to being able to detect and determine even the minutest; trace of any precipitate suspended in a fluid, Richards, by adopting and adapting an earlier idea, has constructed his well-known nephelometer, which, by the use of reflected light, allows of a reliable quantitative assessment being made of "opalizing" quantities of substance so small that they could be determined gravimetrically only with the utmost difficulty, if indeed at all. The fact deserves mention that the said instrument, in addition to its serviceability for atomic-weight determination, has been made use of in several different departments of chemical and physical analysis. With a view to rendering the recrystallization process more effective, Richards has combined it to a large extent with centrifugation. By this adoption of an ancillary means long tried and found useful in chemical practice, he has not only secured a very appreciable saving of time and labour, but has also succeeded in approaching considerably nearer than ever before to the desired ideal of chemically pure substances. With the aid of the phaserule Richards has carried out a detailed investigation of the factors that determine the retention or disappearance of the occluded gases in metal oxides, and by so doing has materially added to the requisites precedent for a complete mastery of these phenomena. Finally, by exchanging in numerous cases vessels and apparatus of glass (and to some extent also of platinum) for others made of quartz, he has protected himself from the most serious effects of the disadvantageous circumstances referred to under (5) above.

Moreover, in almost every one of Richards' treatises there are to be found descriptions of methods and manipulations that mark noteworthy improvements as compared with those practised before his day, and prove likewise that, in the course of his able and consistently pursued appropriation of the aids and resources, both theoretical and technical, that modern times have evolved, he has been capable of entirely transforming the methodics of atomic-weight determination to suit his purposes, in a way that cannot fail to be of utility to other investigators too in this particular field of labour. The work he has thus accomplished as a reformer of chemical methods and practices is by no means the least significant phase of his achievement. Thanks to it his labours as a whole assume far wider proportions than the exact determinations worked out by him personally and by his pupils would imply, and they will undoubtedly exercise a profound effect on future stoichiometric investigation.

For more details please visit:

http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1914/present.html