

Raman Spectrum of the Hydroxyl Ion with High Dispersion

The Raman spectrum of a 10*N* aqueous solution of potassium hydroxide was photographed with a Hilger E1 large quartz spectrograph, using for excitation a hot-cathode helium arc of length 45 cm. The Pyrex tube which contained the solution was surrounded by a filter tube of nickel oxide glass, and the light was focused on it by an elliptical reflector. An exposure time of 100 hours was required.

The spectrum obtained consists of a single broad line having a fairly well defined intensity-maximum which corresponds to a frequency shift of $3603 \pm 4 \text{ cm}^{-1}$. This is in good agreement with the value of $3615 \pm 25 \text{ cm}^{-1}$ recently reported by Woodward.¹ It is somewhat lower than the shift of 3630 cm^{-1} found by Krishnamurti² in crystalline sodium hy-

droxide. The line has a width of about 30 cm^{-1} . That it must be attributed to the hydroxyl ion is beyond doubt.

It was observed that the presence of dissolved sodium or potassium hydroxide greatly influences the structure and the intensity of the water band. We have studied this effect in solutions of various concentrations, using a spectrograph of smaller dispersion. The results will soon be reported in detail.

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May 27, 1931.

¹ L. A. Woodward, *Phys. Zeits.* **32**, 261 (1931).

² P. Krishnamurti, *Indian J. Physics* **5**, 651 (1930).

The Relative Abundance of the Oxygen Isotopes, and the Basis of the Atomic Weight System

Mecke and Childs,¹ as the result of a detailed quantitative investigation of the *A* and *A'* bands of oxygen, find the relative abundance of the oxygen isotopes O^{16} and O^{18} to be 630:1, in sharp contrast to the value 1250:1 found by Babcock² and 1075:1 found by Naudé.³ We have made a careful study of Mecke and Childs' paper, and find several rather doubtful theoretical assumptions. We have accordingly recalculated a portion of their data, using a method that appears to us to be more reliable. Their final result is, however, not essentially changed, and it therefore seems unnecessary to publish the details.

We have also examined Babcock's assumptions, and find two sources of possible error, one due to the fact that the rotational energy levels of the $\text{O}^{16}\text{O}^{18}$ molecule differ from those of the $\text{O}^{16}\text{O}^{16}$ molecule, and the other due to the fact that, in Babcock's work, the mean temperature of the $\text{O}^{16}\text{O}^{18}$ molecule (in the atmosphere) differs from the temperature of the $\text{O}^{16}\text{O}^{16}$ molecule (in the laboratory). Both the energy and the temperature affect the Boltzmann factor, but fortunately the two errors thus introduced by Babcock's neglect of this factor tend to cancel. We find that for the lines used by Babcock,⁴ the maximum resulting error is not more than about ten percent, and so is quite negligible.

Mecke and Childs suggest several possible sources of error in the work of Naudé, but we do not have the information necessary in order to discuss these suggestions. As far as the work of Babcock and of Mecke and Childs is concerned, it would appear that the discrepancy must be due mainly to experimental and not to theoretical errors. It would also appear that the Mecke and Childs result is entitled to much greater weight.

Assuming for the sake of argument that the abundance ratio is really 630 to 1, it follows, as noted by Mecke and Childs, that atomic masses based on $\text{O}^{16}=16$ should be 2.2 parts in 10^4 greater than those based on the chemical system $\text{O}=16$. It is accordingly of importance to test Aston's mass-spectrograph results⁵ on this new basis. Aston,⁶ Birge,⁷ and Naudé³ have previously considered this mat-

¹ R. Mecke and W. H. J. Childs, *Zeits. f. Physik* **68**, 362 (1931).

² H. D. Babcock, *Proc. Nat. Acad. Sci.* **15**, 471 (1929).

³ S. M. Naudé, *Phys. Rev.* **36**, 333 (1930).

⁴ According to a personal communication from Babcock, only the first few lines of the *P* branch were used.

⁵ F. W. Aston, *Proc. Roy. Soc.* **A115**, 487 (1927).

⁶ F. W. Aston, *Nature* **123**, 488 (1929).

ter, but the conclusions depend markedly on the values adopted for the chemical atomic weights. One of us⁷ has already found that the rounded values ordinarily published in atomic-weight tables are not sufficiently accurate for a discussion like this.

Nearly all of Aston's precision measurements are concerned, unfortunately, with elements that are known to consist of a mixture of isotopes. In such cases it is necessary to know the relative abundance of the isotopes of the element in question, as well as of oxygen, in order to compare Aston's result with the chemical atomic weight. For elements like carbon and nitrogen, the two resulting corrections (for oxygen, and for the element in question) tend to cancel, so that Aston's result should agree closely with the chemical atomic weight. Thus in the case of carbon the most probable atomic weight⁷ is 12.0025. Aston's mass C^{12} is 12.0036, which becomes 12.0010 on division by 1.00022 in order to reduce to the chemical scale. Then to obtain an atomic weight of 12.0025, the relative abundance C^{12}/C^{13} should be 650. King and Birge⁸ give 400 for this figure, but their discussion shows that 650 is an equally possible value.

The best atomic weight of nitrogen⁹ is 14.008. Aston finds $N^{14} = 14.008$. To bring the two results into agreement requires a relative abundance $N^{14}/N^{15} = 320$. Naudé found that the abundance $N^{14}/N^{15} = 0.65$ of O^{16}/O^{18} . Using Mecke and Childs' value of O^{16}/O^{18} , one obtains $N^{14}/N^{15} = 409$, a very satisfactory agreement.

The best atomic weight of helium appears to be⁷ 4.0018. Aston obtained 4.00216, or 4.00127 on the chemical scale. The discrepancy is only 1.1 parts in 10^4 , which is within the published limits of error. The most accurate atomic weight of fluorine is due to Moles and Batuecas¹⁰, from the molecular weight of FCH_3 . Using the present best values for C and H, their result is 18.995 ± 0.005 . Aston obtains 19.000, or 18.996 when reduced to the chemical scale. The agreement is entirely satisfactory. In the case of iodine, Aston's result is identical with the best chemical value. The connection with oxygen, in the mass-spectrograph work, is rather indirect, and it is therefore doubtful if this result can be considered to furnish independent evidence on the question. In the case of phosphorus it is the chemical value that is uncertain.

Of the elements that permit an accurate

comparison of the chemical and mass-spectrograph results, there remains only hydrogen. The chemical value⁷ is 1.00777 ± 0.00002 (probable error), as compared with Aston's 1.00778 ± 0.00015 (*limit* of error). Aston's value, reduced to the chemical scale, is 1.00756 and the discrepancy appears to be outside the limits of error. It could be removed by postulating the existence of an isotope of hydrogen of mass 2, with a relative abundance $H^1/H^2 = 4500$. It should be possible, although difficult, to detect such an isotope by means of band spectra.

The above discussion shows that, with the exception of hydrogen, the new Mecke and Childs' abundance ratio gives a satisfactory agreement between the mass-spectrograph and the chemical results. The agreement is in fact somewhat better than that obtained with an assumed abundance ratio of 1250 to 1, or of 1070 to 1. The case of hydrogen, however, distinctly calls for further investigation.

Aston¹¹ has asked for suggestions as to the best basis for chemical atomic weights and atomic masses. We believe that the facts presented in this letter indicate that, from the experimental standpoint, the quantitative relation between the *mean* atomic weight of oxygen, and the mass of the atomic species O^{16} is rather uncertain at the present time, and is likely to remain so for the present. It should also be pointed out that there is as yet no *proof* that the relative abundance of the oxygen isotopes, in different sources, is strictly constant.¹² The possibility that the relative abundance is *not* constant is the most compelling argument for a change in the basis of the atomic-weight system. What that change should be can best be decided by chemists, but we believe that further data are needed before any change is seriously considered. The one point we wish to emphasize here is that there

⁷ R. T. Birge, Phys. Rev. Supplement **1**, 1 (1929). See pp. 19-26 and 69.

⁸ A. S. King and R. T. Birge, Astrophys. J. **72**, 19 (1930).

⁹ G. P. Baxter and C. H. Greene, J. Am. Chem. Soc. **53**, 604 (1931).

¹⁰ E. Moles and T. Batuecas, J. Chim. Phys. **17**, 539 (1919).

¹¹ F. W. Aston, Nature **126**, 953 (1930).

¹² The mass-spectrograph is perhaps the most reliable method for investigating this question.

now exist two systems for the measurement of atomic masses, connected by a relatively *uncertain* factor. For that reason it seems best, for the present, not to convert results obtained on one system into the other system, by

the use of some assumed conversion factor.
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May 27, 1931.

The Masses of O¹⁷

The writers have recently built a new accurate apparatus, in order to obtain, among other values, more exact masses for the nucleus of O¹⁷, since they had concluded that additional data were needed in order to establish definite relations. Urey,¹ however, considers that the data already available demonstrate the existence of three quantum states for this nucleus.

The purpose of this letter is (1) to give, as a minor change, a different set of values for the

ranges of the protons; (2) what is more important, to point out that while we do not disagree with Urey's conclusion above, it seems to us that the few available data should be classified in a slightly different way; (3) and to add a calculation, omitted by Urey, of an inelastic collision between an α -particle and a nitrogen atom as obtained by Harkins and Shadduck.²

The data given in this paper lead to the following calculated values:

TABLE I.

M_0 (nucleus)	M_0 (atom)	$\Delta M_1 \times 10^6$	$\Delta M_2 \times 10^6$
16.99891	17.00328	1	12

Here M_0 represents the rest mass of the oxygen, ΔM_1 is the error of M_0 introduced by a 1 percent error in the energy of the α -particle, and ΔM_2 that due to an error of 10' in the angle ω between the track of the α -particle

and that of the oxygen nucleus. In the calculation, the value 14.00800 (Aston) is taken as the rest mass of the nitrogen atom, as was presumably done also by Urey. The values are collected as follows:

TABLE II. *Mass of O¹⁷.*

Track	M_0 (atom)	Average M_0 (atom)
B4	17.00508	High level 17.00508
B5	17.00330	Middle level 17.00319
H+S 1	17.00328	
B3	17.00300	
B2	17.00148	Low level 17.00148

The values differ somewhat from those of Urey, who omits track H+S 1.

We have excluded from this table the cal-

culated values for the following four tracks as not having a sufficient bearing upon the division into the above three groups.

TABLE III.

Track	M_0 (atom)	Reason for rejection from Table II
H+S 3	17.0050	Agrees well with the value 17.00508 for the B4 track, but one of the pair of photographs of the event was not clear
B7	17.00402	Tracks curved (rejected by Urey)
B6	17.00293	Angle ω too small to give accuracy in M_0
B1	17.00370	Probably as accurate as those listed in Table II, but deviates too far from mean of other three in middle level to offer evidence in favor of the existence of this level

¹ Urey, Phys. Rev. (2) **37**, 923 (1931).

² Harkins and Shadduck, Proc. Nat. Acad. Sci. **12**, 707 (1926).