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# Atomic Masses of the Stable Isotopes, $10 \leq A \leq 30$*†

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The masses of all stable isotopes in the range $10 \leq A \leq 30$ have been measured using the large double-focusing mass spectrometer recently constructed at this laboratory. No serious discrepancies are found between the present results and other mass spectroscopic measurements except at $Ne^{20}$. The masses calculated from nuclear reaction energies are, with the exception of $F^{19}$, lower than the present results.

The agreement between the $Q$-value masses and the present mass spectrometric results is not improved by changing the mass spectrometric secondary standard $C^{12}$ to agree with the $Q$-value result or by making the same percentage change in all mass doublet values. Neither is the agreement improved by a change in either the calibration of the nuclear spectrometers or the mass-energy conversion factor.

Three $Q$-values which are inconsistent with other $Q$-values and also with the mass spectrometric results were eliminated from the nuclear reaction data and the $Q$-value masses recalculated. The new masses are in better agreement with the mass spectrometric results, but are still, with the exception of $F^{19}$, lower than the present mass spectrometric values.

## INTRODUCTION

THERE are two methods which have been used extensively to determine atomic masses, mass spectroscopy and nuclear reaction energies. While the revision of the energies of the natural alpha particles[1] used in calibrating nuclear spectrometers has decreased the discrepancies between the masses determined by these two methods,[2] the results of the two systems are still in disagreement. The $Q$-value masses are in general lower than the mass spectroscopic results. It is of interest to determine whether this discrepancy is a result of experimental errors in the two methods or whether it is of a more subtle nature.

The masses from nuclear reaction energies are determined by finding the sum of the $Q$-values as the requisite nucleons are added to (or taken away from) the $O^{16}$ standard to make the isotope whose mass is desired. Because of the additive nature of the $Q$-values, if agreement between the mass spectroscopic results and the $Q$-value masses is to be found anywhere, it should be in the neighborhood of $O^{16}$.

Mass doublets sufficient to determine the masses of many of the stable isotopes in the range $10 \leq A \leq 30$ have been measured mass-spectroscopically by a number of investigators.[3,4] However, the masses of the isotopes of magnesium have never before been measured. The most comprehensive recent work is that of Kettner[4] which covered the range $12 \leq A \leq 22$.

It is of some importance that the mass spectroscopic results to be compared with the $Q$-value masses come from the same spectrometer in the same period of time so that they are subject to the same systematic errors if any are present. With such a set of mass values one may hope through a comparison with the $Q$-value masses to gain some insight into the systematic errors which may be present in either system.

For these reasons it has seemed fruitful to undertake a complete investigation of the masses of the stable isotopes in the region $10 \leq A \leq 30$. These measurements have been made with the large, double-focusing mass spectrometer recently constructed at the University of Minnesota.[5,6]

## MEASUREMENTS

A set of mass doublets which determine the masses of all stable isotopes in the mass range $10 \leq A \leq 30$ were measured. Table I lists these doublets and their measured values. The errors quoted are the square roots of the sums of squares of the statistical standard error in the set of runs on the doublet, plus a factor to allow for the possible spectrometer calibration error. This method of assigning errors assumes the nonexistence of systematic errors in the spectrometer. An extensive search for systematic errors has yielded negative results.

Each run consists of a total 20 measurements of the mass doublet taken in four different ways to minimize possible systematic errors in the method of measurement.

All the runs on each doublet were not taken at the same time, but were spread out over a period of at least three days. In some cases, several months elapsed between the first and last runs on a doublet with no appreciable change in the measured mass difference. Energy focus is checked before and after each run and the spectrometer adjusted accordingly. All ions, with the exception of those of sodium, aluminum, and magnesium, were obtained from gas samples. Sodium,

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[1] G. H. Briggs, Revs. Modern Phys. **26**, 1 (1954).

[2] A. H. Wapstra, Physica **21**, 367 (1955).

[3] See review article by Duckworth, Hogg, and Pennington, Revs. Modern Phys. **26**, 463 (1954).

[4] M. E. Kettner, this issue [Phys. Rev. **102**, 1065 (1956)].

[5] Scolman, Quisenberry, Collins, Giese, and Nier (to be published).

[6] Quisenberry, Scolman, and Nier, preceding paper [Phys. Rev. **102**, 1071 (1956)].

TABLE I. Mass doublets.[a]

| Doublet | Number of runs | $\Delta M$ (mMU) |
|---|---|---|
| $B^{10}(F^{19})_2-SO$ | 8 | 42.7730±17 |
| $C_4H_4O-B^{11}(F^{19})_3$ | 10 | 21.7052±13 |
| $C^{13}H_4-OH$ | 10 | 31.9253± 7 |
| $CH_2-N^{14}$ | 10 | 12.5803± 4 |
| $CH_4-N^{14}H_2$ | 23 | 12.5804± 5 |
| $C_2H_4-(N^{14})_2$ | 21 | 25.1585± 6 |
| $N^{14}H_2-O$ | 13 | 23.8164± 5 |
| $N^{14}H_3-OH$ | 10 | 23.8159± 6 |
| $(N^{14})_2-CO$ | 21 | 11.2355± 6 |
| $N^{15}H_3-H_2O$ | 10 | 13.0234± 4 |
| $CH_3-N^{15}$ | 10 | 23.3652± 9 |
| $OH-O^{17}$ | 11 | 3.6077± 5 |
| $D_2O-H_2O^{18}$ | 10 | 8.3102± 4 |
| $H_2O-O^{18}$ | 13 | 11.4033±21 |
| $\frac{1}{2}C_4H_4O-OO^{18}$ | 10 | 19.0367± 8 |
| $D_2O-HF^{19}$ | 10 | 16.8944± 5 |
| $HDO-F^{19}$ | 11 | 18.4380±14 |
| $C_5H_9-C(F^{19})_3$ | 10 | 75.2462±20 |
| $D_2O-Ne^{20}$ | 10 | 30.6872± 7 |
| $H_2O^{18}-Ne^{20}$ | 10 | 22.3770± 6 |
| $HDO^{18}-Ne^{21}$ | 10 | 27.2482± 7 |
| $\frac{1}{2}CO_2-Ne^{22}$ | 10 | 3.5307± 6 |
| $\frac{1}{2}COO^{18}-Na^{23}$ | 10 | 7.2592±20 |
| $C_2-Mg^{24}$ | 11 | 14.9621±11 |
| $C_2H-Mg^{25}$ | 10 | 21.9944±10 |
| $C_2H_2-Mg^{26}$ | 10 | 33.0676±10 |
| $C_2H_3-Al^{27}$ | 10 | 41.9548±23 |
| $C_6H_{13}-Si^{28}(F^{19})_3$ | 11 | 129.625 ± 4 |
| $C_6H_{14}-Si^{29}(F^{19})_3$ | 12 | 137.889 ± 7 |
| $C_4H_7O_2-Si^{30}(F^{19})_3$ | 10 | 75.6590±36 |

[a] C, H, D, and O refer to $C^{12}$, $H^1$, $H^2$, and $O^{16}$, respectively.

magnesium, and aluminum ions were obtained by placing solid samples in a Nichrome boat which was electrically heated to vaporize the samples. The molecules were then ionized by the electron beam. The solids used were sodium chloride and iodide, magnesium metal, and aluminum metal.

The values for the secondary standards $H^1$, $D^2$, $C^{12}$, and $S^{32}$ were those previously measured by using this spectrometer.[6] The values are $H^1=1.0081442\pm2$ amu; $D^2=2.0147406\pm6$; $C^{12}=12.0038167\pm8$; $S^{32}=31.9822401\pm9$.

## THE MASSES

The atomic masses calculated from the doublets in Table I are listed in Table II. The masses of $C^{12}$, $N^{14}$, $N^{15}$, $O^{18}$, $F^{19}$, and $Ne^{20}$ have been measured by means of more than one doublet. Where multiple determinations of the same mass were made, the final value listed, with the exception of $N^{15}$, is the unweighted average. The error listed is the standard error calculated from the deviations of the individual determinations from this average. In the case of $N^{15}$, the result of the $CH_3-N^{15}$ doublet measurement was not used. This was because of the very low intensity of the $N^{15}$ peak.

## COMPARISON WITH MASS SPECTROSCOPIC RESULTS

Table III lists the mass excess $(M-A)$ measured in the present experiments as well as the results of other mass spectroscopic measurements. $C^{12}$ has also recently been measured by Mattauch and Bieri,[7] who obtain a value of $12.0038231\pm33$, and by Smith,[8] who obtains a value $12.0038212\pm38$. The high value, $12.003842\pm4$, previously reported from this laboratory was caused by an error in the $C_4-S^{32}O$ doublet due to the presence of an unresolved satellite.[6] In the present measurements on this doublet, the impurity was readily resolved. Since Ogata and Matsuda[9] utilized the same doublet, their result may be subject to this same error. The other mass spectroscopic values for $C^{12}$, with the exception of Ewald's,[10] are in moderately good agreement with each other. However, they are uniformly higher than the $Q$-value masses, which are in agreement with Ewald's results. Because of Ewald's relatively large error, his results could be said to agree with both the $Q$-value mass and mass spectroscopic results. The disagreement between the $Q$-value mass of carbon and that measured mass spectroscopically is rather typical of the discrepancies mentioned in the introduction. It is, however, especially disturbing because of the use of carbon as a secondary standard in mass spectroscopic measurements.[6]

An examination of the differences between the present results and those of other investigators ($\Delta$=others'

TABLE II. Present mass spectrometric mass values.[a]

| Isotope | Doublet used | Mass obtained (amu) | Final mass (amu) |
|---|---|---|---|
| $B^{10}$ | $B^{10}(F^{19})_2-S^{32}O$ | | 10.016127 ± 4 |
| $B^{11}$ | $C_4H_4O-B^{11}(F^{19})_3$ | | 11.012810 ± 7 |
| $C^{12}$ [b] | $C_4-S^{32}O$ cycle | 12.0038168± 4 | |
| | $\frac{1}{2}C_4H_4O-H_2S^{32}$ cycle | 12.0038164± 6 | |
| | $A^{40}$ cycle | 12.0038147± 8 | |
| | $A^{36}$ cycle | 12.0038197± 6 | |
| | $O^{18}$ cycle | 12.0038161± 7 | 12.0038167± 8 |
| $C^{13}$ | $C^{13}H_4-OH$ | | 13.0074929± 9 |
| $N^{14}$ | $CH_2-N^{14}$ | 14.0075250± 9 | |
| | $(N^{14})_2-CO$ | 14.0075260± 5 | |
| | $N^{14}H_2-O$ | 14.0075279± 6 | 14.0075263± 8 |
| $N^{15}$ | $CH_3-N^{15}$ | 15.0048839±10 | |
| | $N^{15}H_3-H_2O$ | 15.0048793± 4 | 15.0048793± 4 |
| $O^{17}$ | $OH-O^{17}$ | | 17.0045364± 5 |
| $O^{18}$ | $H_2O-O^{18}$ | 18.0048850±21 | |
| | $\frac{1}{2}C_4H_4O-OO^{18}$ | 18.0048850±13 | |
| | $D_2O-H_2O^{18}$ | 18.0048829±13 | 18.0048843± 8 |
| $F^{19}$ | $D_2O-HF^{19}$ | 19.0044428±13 | |
| | $HDO-F^{19}$ | 19.0044468±15 | |
| | $C_5H_9-C(F^{19})_3$ | 19.0044391± 9 | 19.0044429±20 |
| $Ne^{20}$ | $D_2O-Ne^{20}$ | 19.9987942±14 | |
| | $H_2O^{18}-Ne^{20}$ | 19.9987964±15 | 19.9987953±15 |
| $Ne^{21}$ | $HDO^{18}-Ne^{21}$ | | 21.0005209±12 |
| $Ne^{22}$ | $\frac{1}{2}CO_2-Ne^{22}$ | | 21.9983777± 7 |
| $Na^{23}$ | $\frac{1}{2}COO^{18}-Na^{23}$ | | 22.9970913±21 |
| $Mg^{24}$ | $C_2-Mg^{24}$ | | 23.9926713±16 |
| $Mg^{25}$ | $C_2H-Mg^{25}$ | | 24.9937832±15 |
| $Mg^{26}$ | $C_2H_2-Mg^{26}$ | | 25.9908541±14 |
| $Al^{27}$ | $C_2H_3-Al^{27}$ | | 26.9901111±25 |
| $Si^{28}$ | $C_6H_{13}-Si^{28}(F^{19})_3$ | | 27.985821 ± 8 |
| $Si^{29}$ | $C_6H_{14}-Si^{29}(F^{19})_3$ | | 28.985701 ±10 |
| $Si^{30}$ | $C_4H_7O_2-Si^{30}(F^{19})_3$ | | 29.983288 ± 7 |

[a] C, H, D, and O refer to $C^{12}$, $H^1$, $H^2$, and $O^{16}$, respectively.
[b] See reference 6.

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[7] J. Mattauch and R. Bieri, Z. Naturforsch. **9a**, 303 (1954).

[8] L. G. Smith, Third Annual Meeting, Committee E–14, American Society for Testing Materials, 1955 (unpublished).

[9] K. Ogata and H. Matsuda, Phys. Rev. **89**, 27 (1953).

[10] H. Ewald, Z. Naturforsch. **6a**, 293 (1951).

TABLE III. Mass excesses $(M-A)$ in $\mu$MU—comparison with other mass spectroscopic results.

| Isotope | Present results | Kettner[a] (1955) | Δ | Ogata and Matsuda (1953)[b] | Δ | Ewald[c] (1951) | Δ |
|---|---|---|---|---|---|---|---|
| $B^{10}$ | 16 127 ± 4 | | | 16 110±10 | −16 | | |
| $B^{11}$ | 12 810 ± 7 | | | 12 811± 9 | +1 | | |
| $C^{12}$ | 3816.7± 0.8 | 3814 ± 6 | −3 | 3844± 6 | +27 | 3807±11 | −10 |
| $C^{13}$ | 7492.9± 0.9 | 7511 ±11 | +18 | 7505±12 | +12 | 7538±14 | +45 |
| $N^{14}$ | 7526.3± 0.8 | 7545 ± 8 | +19 | 7550± 5 | +24 | 7525±15 | −1 |
| $N^{15}$ | 4879.3± 0.4 | 4875 ± 5 | −4 | 4902± 9 | +23 | 4928±20 | +49 |
| $O^{17}$ | 4536.4± 0.5 | 4542 ± 6 | +6 | | | 4507±15 | −29 |
| $O^{18}$ | 4884.3± 0.8 | 4883 ± 8 | −1 | 4883±20 | −1 | 4875±13 | −1 |
| $F^{19}$ | 4442.9± 2.0 | 4445 ± 8 | +2 | 4444±22 | +1 | 4414±17 | −29 |
| $Ne^{20}$ | −1204.7± 1.5 | −1221 ± 9 | −16 | −1228±13 | −23 | 1229±12 | −24 |
| $Ne^{21}$ | 520.9± 1.2 | 529 ± 8 | +8 | | | 393±23 | −128 |
| $Ne^{22}$ | −1622.3± 0.7 | −1614 ±12 | +8 | −1618±24 | +4 | 1671±19 | −49 |
| $Na^{23}$ | −2908.7± 1.5 | | | | | | |
| $Mg^{24}$ | −7238.7± 1.6 | | | | | | |
| $Mg^{25}$ | −6216.8± 1.5 | | | | | | |
| $Mg^{26}$ | −9145.9± 1.4 | | | | | | |
| $Al^{27}$ | −9899 ± 3 | | | −9891±23 | +8 | | |
| $Si^{28}$ | −14 179 ± 8 | Smith[d] (1955) | | −14 175±16 | +4 | −14 208±32 | −33 |
| $Si^{29}$ | −14 299 ±10 | | | −14 295±21 | +4 | | |
| $Si^{30}$ | −16 712 ± 7 | | | −16 693±31 | +19 | | |
| $S^{32}$ | −17 759.9± 0.9 | −17 761.6± 2.4 | −1.7 | −17 726± 8 | +34 | −17 728±19 | +32 |

[a] See reference 4. [b] See reference 9. [c] See reference 10. [d] See reference 8.

mass−present mass) reveals satisfactory agreement with those of Kettner[4] and of Ogata and Matsuda[9] except at $C^{13}$, $N^{14}$, $N^{15}$, and $Ne^{20}$. Kettner agrees with the present results on $N^{15}$. There is no systematic agreement or disagreement between Ewald's results and the present results nor with the values of the other investigators. An exception is found at $Ne^{20}$, where Ewald's mass value agrees with those of Kettner and of Ogata and Matsuda but disagrees with the present results.

The agreement between the present masses and those of Ogata and Matsuda for aluminum and the isotopes of silicon is not as satisfactory as it appears at first glance. This is because the carbon standard of Ogata and Matsuda is felt to be in error. Changing their mass for $C^{12}$ to the present value results in poorer agreement between their masses and the present results.

Kettner states that he is dissatisfied with his results for $C^{13}$ and $N^{14}$ feeling that they are too high by 15 to 20 $\mu$MU. Reducing his values by this amount would bring them into good agreement with the present results. The results of Ogata and Matsuda for $C^{13}$, $N^{14}$, and $N^{15}$ are determined from doublets involving $C^{12}$ and are thus sensitive to its mass. Reducing their value for $C^{12}$ by 27 $\mu$MU to agree with the present mass would reduce the masses of $C^{13}$, $N^{14}$, and $N^{15}$ each by 27 $\mu$MU, bringing them into better agreement with the present results. This could be considered as additional evidence that their $C^{12}$ mass is too high.

All investigators have determined $S^{32}$ by measuring the $O_2-S^{32}$ doublet. Therefore, this mass is not dependent upon the value of any other secondary standard. The excellent agreement with the very precise mass synchrometric determination of Smith[8] supports the present results. Further evidence for the correctness of the present value is the fact that our measurements on the $SO_2-Zn^{64}$, and $O_2-\frac{1}{2}Zn^{64}$ doublets yield the same value for the mass of $Zn^{64}$.[6]

Smith[8] has also measured the mass of $B^{11}$ and obtains 11.0128118±46 amu in excellent agreement with the present result.

Unfortunately, there is no supporting evidence for the present mass of $Ne^{20}$ which differs from the values reported by all other investigators. However, good agreement was obtained between the values calculated from the $H_2O^{18}-Ne^{20}$ and the $D_2O-Ne^{20}$ doublets. All three mass peaks had high intensity and the deviations between individual runs were very small, in no case far enough away from the average to give a result approaching the value of the other investigators. An extensive search was made for a possible contaminate on any of the mass peaks, with negative results. Also, the triplet cycle formed by the three peaks at mass 20 had zero closure error.[6] It seems improbable that further measurements would yield a value as low as those reported by the other investigators.

## COMPARISON WITH Q-VALUE RESULTS

Table IV lists the present values as well as the results of the Q-value calculations of Li[11,12] and Wapstra[2] and the statistical analysis of Drummond[13] using data from both mass spectroscopy and nuclear reactions.

The present results are in better agreement with Drummond's[13] values than with either set of Q-value masses. This might be expected since Drummond's calculation included both mass doublet values and nuclear reaction energies and would thus be shifted toward the mass spectroscopic results as compared to

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[11] Li, Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).
[12] C. W. Li, Phys. Rev. **88**, 1038 (1952).
[13] J. E. Drummond, Phys. Rev. **97**, 1004 (1955).

TABLE IV. Mass excesses $(M-A)$ in μMU comparison with $Q$-value results.

| Isotope | Present results | Li[a] (1951, 1952) | Δ | Wapstra[b] (1955) | Δ | Drummond[c] (1955) | Δ |
|---|---|---|---|---|---|---|---|
| $B^{10}$ | 16 127 ± 4 | 16 114±28 | −13 | 16 119± 6 | −8 | 16 113 ± 4 | −14 |
| $B^{11}$ | 12 810 ± 7 | 12 789±23 | −21 | 12 795± 6 | −15 | 12 799 ± 4 | −11 |
| $C^{12}$ | 3816.7± 0.8 | 3804±17 | −13 | 3803± 5 | −14 | 3827.5± 2.4 | +10 |
| $C^{13}$ | 7492.9± 0.9 | 7473±14 | −20 | 7478± 5 | −15 | 7493.5± 2.8 | +1 |
| $N^{14}$ | 7526.3± 0.8 | 7515±11 | −11 | 7520± 3 | −6 | 7527.0± 2.2 | +1 |
| $N^{15}$ | 4879.3± 0.4 | 4863±12 | −16 | 4862± 5 | −17 | 4883 ± 5 | +6 |
| $O^{17}$ | 4536.4± 0.5 | 4533± 7 | −3 | 4534± 5 | −2 | 4529 ± 5 | −7 |
| $O^{18}$ | 4884.3± 0.8 | | | 4855± 8 | −29 | 4874 ± 9 | −10 |
| $F^{19}$ | 4442.9± 2.0 | 4456±15 | +13 | 4448± 7 | +5 | 4443 ± 6 | 0 |
| $Ne^{20}$ | −1204.7± 1.5 | −1223±20 | −18 | −1231± 9 | −26 | −1227 ± 5 | −22 |
| $Ne^{21}$ | 520.9± 1.2 | 504±22 | −17 | 499±10 | −22 | 495 ± 6 | −26 |
| $Ne^{22}$ | −1622.3± 0.7 | −1642±25 | −20 | −1646±12 | −24 | −1649 ±10 | −27 |
| $Na^{23}$ | −2908.7± 2.1 | −2945±25 | −36 | −2947±11 | −38 | −2946 ± 7 | −37 |
| $Mg^{24}$ | −7328.7± 1.6 | −7371±26 | −42 | −7360±15 | −31 | −7356 ± 9 | −27 |
| $Mg^{25}$ | −6215.8± 1.5 | −6255±27 | −38 | −6248±15 | −31 | −6259 ±10 | −42 |
| $Mg^{26}$ | −9145.9± 1.4 | −9198±29 | −52 | −9202±23 | −56 | −9186 ±13 | −40 |
| $Al^{27}$ | −9899 ± 3 | −9928±30 | −29 | −9919±16 | −20 | −9903 ± 9 | −4 |
| $Si^{28}$ | −14 179 ± 8 | −14 233±32 | −54 | −14 225±19 | −46 | −14 195 ± 9 | −16 |
| $Si^{29}$ | −14 299 ±10 | −14 350±35 | −51 | −14 340±20 | −41 | −14 313 ± 9 | −14 |
| $Si^{30}$ | −16 712 ± 7 | −16 763±37 | −51 | −16 748±19 | −36 | −16 729 ±11 | −17 |
| $S^{32}$ | −17 759.9± 0.9 | −17 816±42 | −56 | −17 804±26 | −44 | −17 770 ± 7 | −10 |

[a] See references 11 and 12.
[b] See reference 2.
[c] See reference 13. Drummond's values are the result of a statistical analysis using both reaction energies and mass spectroscopic doublet measurements.

the pure $Q$-value calculations. However, since Drummond used input data now believed to be in error, a comparison with his results may not be profitable.

The two sets of the $Q$-value masses are the results of least squares adjustment of the nuclear reaction $Q$-values. A calculation of $Q$-value masses in this region was published in May, 1955, by Wapstra.[2] At this time, a greater number of more accurate $Q$-value measurements were available than at the time of Li's[11,12] computation. For this reason the errors quoted are smaller than Li's. In addition, Wapstra has made allowances for recent changes in the natural alpha-particle energies used in calibrating nuclear spectrometers.[1] It is mainly due to this recalibration that Wapstra's masses differ from those of Li, especially in the region $A > 20$. The remainder of this paper will be confined to a comparison of the present results with those of Wapstra.

In Fig. 1, the differences between the $Q$-value masses of Wapstra and the present values are plotted against mass number for all stable isotopes in the range $10 \leq A \leq 30$ and also for $S^{32}$. Agreement within the errors is found only at $B^{10}$, $O^{17}$, and $F^{19}$, all other $Q$-value masses being lower than the present results.

Two methods have been used in an unsuccessful attempt to adjust the present mass spectrometric results to bring them into better agreement with the masses calculated from nuclear reactions.

In the first attempt, the present value of the secondary standard $C^{12}$ was lowered by 14 μMU to agree with the $Q$-value mass. The consequences of this change were then examined. This adjustment brings the magnesium, aluminum, and silicon masses into somewhat better agreement with the $Q$-value results. It makes the disagreement worse at $O^{18}$, $Ne^{21}$, and the boron isotopes. A serious objection to this change is found in the disagreement it causes between the individual determinations on $O^{18}$, $F^{19}$, and $Ne^{20}$. Moreover, it has the effect of destroying the excellent agreement between the results from our instrument and the $Q$-value masses for $H^1$ and $D^2$ and does nothing to reconcile the large disagreement at $S^{32}$.[6]

In the second attempt, all mass doublet values were changed by the same percentage. The change made, +1.7 parts per thousand, was chosen so that the adjusted value for the $O_2-S^{32}$ doublet yielded a result for $S^{32}$ in agreement with the $Q$-value mass. A correction of this sort would be necessitated by an error in the calibration of the instrument. A calibration error, but not of this magnitude, is possible since the calibration of the resistance bleeder in terms of which the mass dispersion is measured is rather difficult.[5] This adjustment of the doublets results in somewhat better agree-

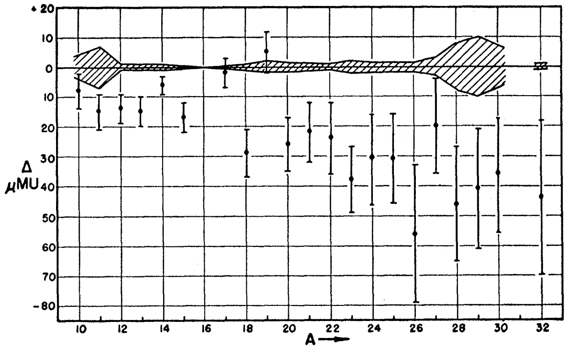

FIG. 1. Differences between the present mass spectrometric masses and Wapstra's $Q$-value masses (Δ = Wapstra's mass − present mass spectrometric mass) *versus* mass number. The errors shown on the points are those associated with Wapstra's values. The shaded area represents the errors in the present mass spectrometric results.

TABLE V. Nuclear cycles with large closure error.

| Reaction cycle | $\Sigma$ ($\mu$MU)[a] |
|---|---|
| (1) $F^{19}(d,\alpha)O^{17}-F^{19}(p,\alpha)O^{16}-O^{16}(d,p)O^{17}$ | $20\pm15$ |
| (2) $Ne^{21}(d,p)Ne^{22}-F^{19}(\alpha,p)Ne^{22}-Ne^{21}(d,\alpha)F^{19}$ | $33\pm19$ |
| (3) $O^{17}(d,\alpha)N^{15}-O^{17}(d,p)O^{18}-O^{18}(p,\alpha)N^{15}$ | $20\pm19$ |

[a] Hereafter all masses and mass excesses will be in $\mu$MU unless otherwise stated.

ment in the region $20\leq A\leq 27$, but increases the discrepancies everywhere else, especially for the isotopes of boron and silicon. For $O^{18}$, $F^{19}$, and $Ne^{20}$ the change also disturbs the good agreement between the several values obtained using different doublets. In addition, it destroys the agreement between the nuclear and mass spectrometric results for hydrogen and deuterium. The most serious objection, however, is found in its effect on the present excellent agreement between the hydrogen mass and the "hydrogen mass unit" determined from the $C_4H_8O_2-C_4H_7O_2$ mass difference.[6] The measurement of this hydrogen mass unit using so wide a doublet is a sensitive test of the mass spectrometer.

## EXAMINATION OF THE Q-VALUES

As a check on the consistency of his data, Wapstra has used the method of closed cycles. In his tables 3.2, 3.3, 3.4 and 3.5, he has listed reaction cycles which give the sum zero, D, $D(d,p)He^3$, $He^4-2D$, respectively. The closure of all cycles in Tables 3.3, 3.4, and 3.5 is satisfactory, although the values for the cycles which give the sum $He^4-2D$ (Wapstra's Table 3.5) seem to decrease for cycles involving isotopes of higher mass number. However, in the reaction cycles giving the sum zero (Wapstra's Table 3.2), three cases are found where the cycle closure error is outside the experimental error. These are listed in our Table V.

It is to be noted that the cycles listed involve mass differences for which the $Q$-value and mass spectrometric results differ. Also, the $O^{17}(d,p)O^{18}$, $Ne^{21}(d,p)Ne^{22}$, and $F^{19}(\alpha,p)Ne^{22}$ reactions which appear in these cycles became available too late to be included in Wapstra's calculation, although he indicates that future computations should include them. Wapstra states that the $F^{19}(\alpha,p)Ne^{22}$ reaction is inconsistent with the other $Q$-values.

We shall now use the mass spectrometric results in an attempt to discover which of the $Q$-values involved in these cycles may be in error. To facilitate the comparison between the two systems, the $Q$-values taken from Wapstra's Table 3.1 are converted to mass excess differences. For example, from the $O^{16}(d,p)O^{17}$ reaction with a $Q$ of 1918 kev one calculates the mass excess difference, $O^{17}-O^{16}-1$, as equal to 4535 $\mu$MU. In making the conversions from $Q$-values to mass differences, Wapstra's values for the mass of the neutron, $H^1$, $D^2$, and $He^4$ and for the conversion factor from mass to energy have been used. Errors are not included in the following discussion since its purpose is to uncover incorrect $Q$-values and the errors associated with the reaction energy measurements are of no help in this search.

TABLE VI. Analysis of Cycle 1.

| Mass difference | From $Q$-values | Present results | Kettner[a] |
|---|---|---|---|
| $F^{19}-O^{17}-2$ | $-70$ | $-93$ | $-97$ |
| $F^{19}-O^{16}-3$ | 4445 | 4443 | 4445 |
| $O^{17}-O^{16}-1$ | 4535 | 4536 | 4542 |
| Closure error | 20 | ... | ... |

[a] See reference 4.

The analysis of Cycle 1 which is shown in Table VI is very clear. It indicates that on the basis of the present mass spectrometric results, the $F^{19}-O^{17}-2$ mass excess difference calculated from the $F^{19}(d,\alpha)O^{17}$ reaction is in error by approximately 20 $\mu$MU units. This conclusion is also supported by Kettner's[4] results.

Table VII shows Cycle 2. On the basis of this cycle, Wapstra rejected the $F^{19}(\alpha,p)Ne^{22}$ $Q$-value as being inconsistent with the other reaction energies. From the present mass spectrometric results one would state instead that the $Ne^{21}-F^{19}-2$ mass difference, and hence the $Ne^{21}(d,\alpha)F^{19}$ $Q$-value, are in error by about 30 $\mu$MU. The conjecture is also supported by Kettner's results. Further evidence will be mentioned later.

TABLE VII. Analysis of Cycle 2.

| Mass difference | From $Q$-values | Present results | Kettner[a] |
|---|---|---|---|
| $Ne^{22}-Ne^{21}-1$ | $-2147$ | $-2143$ | $-2143$ |
| $Ne^{22}-F^{19}-3$ | $-6070$ | $-6065$ | $-6059$ |
| $Ne^{21}-F^{19}-2$ | $-3956$ | $-3922$ | $-3914$ |
| Closure error | 33 | ... | ... |

[a] See reference 4.

Table VIII shows Cycle 3. The $Q$-value for the $O^{17}(d,p)O^{18}$ reaction is too recent to be included in Wapstra's calculation. We are in moderately good agreement with the mass difference calculated from this reaction, but the mass spectrometric measurements indicate that the $O^{18}-N^{15}-3$ difference is in error by 15 to 20 $\mu$MU. The conclusion is not as clearly drawn from the present results as from Kettner's data.

Additional evidence supporting the conclusions reached in the analysis of Cycles 2 and 3 can be obtained by considering two longer cycles which should also have cycle sums equal to zero. The first of these is shown in Table IX.

Cycle 2′ also contains the $Ne^{21}-F^{19}-2$ mass excess difference. If this value is reduced by 30 as suggested by the results of the analysis of Cycle 2, the closure error is reduced from 43 to 13 $\mu$MU. This cycle also indicates a possible error in one of the $Q$-values yielding the $Ne^{20}-O^{18}-2$ mass difference. A second long cycle, 3′, is shown in Table X. Again the agreement is fairly good for all mass differences except the $O^{18}-N^{15}-3$ value. If this mass difference is reduced 15 μMU as was suggested by the analysis of Cycle 3, the closure error is reduced to 3.

It is possible to construct other cycles which contain the reactions whose $Q$-values are suspect. In all cases, essentially the same result is obtained; the closure errors are reduced if the $Q$-values in question are changed by the amounts and in the directions indicated in the discussion above.

We have then, by using the mass spectrometric results to examine the nuclear reactions involved in nuclear cycles with large closure errors, found three $Q$-values which seem to be in error. They are the $O^{18}(p,\alpha)N^{15}$, $F^{19}(d,\alpha)O^{17}$, and $Ne^{21}(d,\alpha)F^{19}$ reactions. In addition, we have found that the three reactions $O^{17}(d,p)O^{18}$, $F^{19}(\alpha,p)Ne^{22}$, and $Ne^{21}(d,p)Ne^{22}$ not included in Wapstra's adjustment are entirely consistent with the mass spectrometric results.

It is perhaps significant that in each of the three suspect reactions, the particles whose energy was measured were alphas.

TABLE VIII. Analysis of Cycle 3.

| Mass difference | From $Q$-values | Present results | Kettner[a] |
|---|---|---|---|
| $O^{17}-N^{15}-2$ | −330 | −343 | −333 |
| $O^{18}-O^{17}-1$ | 340 | 348 | 341 |
| $O^{18}-N^{15}-3$ | −10 | 5 | 8 |
| Closure error | 20 | ··· | ··· |

[a] See reference 4.

## RECALCULATION OF THE MASSES FROM NUCLEAR REACTION ENERGIES

We now use the results of the preceding examination of the nuclear reaction energies to discard some $Q$-values and proceed to recalculate the masses from nuclear reaction energies. We wish to emphasize that we have not adjusted any nuclear reaction energy to agree with the present mass spectrometric results, but have merely used these results as a guide in discovering which reactions are probably in error in cycles where the $Q$-values disagree with each other. We have used Wapstra's $Q$-values except for the removal of the $O^{18}(p,\alpha)N^{15}$, $F^{19}(d,\alpha)O^{17}$, and $Ne^{21}(d,\alpha)F^{19}$ reactions which we have found to be inconsistent. In addition, the $O^{17}(d,p)O^{18}$, $F^{19}(\alpha,p)Ne^{22}$, and the $Ne^{21}(d,p)Ne^{22}$ reactions, which were included in Wapstra's list but not in his least squares adjustment, were used.

We will include only the range $12 \leq A \leq 23$ since examination of the reactions shows, that to a first approximation, all isotopes with mass number higher than that of $Na^{23}$ are determined by the mass of this isotope because all reaction chains connecting the higher isotopes with $O^{16}$ pass through this nucleus. In a similar way all isotopes lower than $C^{13}$, with the exception of $C^{12}$, are determined by the $C^{13}$ mass. This is not strictly true since, in the least squares adjustment, use is made of cycles whose sums are not zero and these may include reactions both above and below $Na^{23}$ (or $C^{13}$). In our calculation we will use only nuclear cycles whose sums are zero.

TABLE IX. Analysis of Cycle 2′.

| Mass difference | From $Q$-values | Present results |
|---|---|---|
| $F^{19}-O^{16}-3$ | 4445 | 4443 |
| $Ne^{21}-F^{19}-2$ | −3956 | −3925 |
| $Ne^{21}-Ne^{20}-1$ | 1730 | 1726 |
| $Ne^{20}-F^{18}-2$<br>$F^{18}-O^{18}$ | $\left.\begin{matrix}-7868\\1795\end{matrix}\right\}-6073$ | −6089 |
| $O^{18}-O^{17}-1$ | 340 | 348 |
| $O^{17}-O^{16}-1$ | 4535 | 4536 |
| Closure error | 43 | ··· |

The 17 unknowns (masses) are overdetermined by the 24 equations (mass excess differences). For this reason, it is necessary to adjust the set of equations in some fashion so that any reaction path taken to an isotope yields the same result for its mass. We first considered cycles, which should have sums equal to zero, involving only three mass differences. The individual mass differences in the cycle were then adjusted so that the cycle sum became zero. Each mass difference was adjusted by an amount inversely proportional to the square of its error. When the same mass difference appeared in more than one cycle, the cycles were adjusted simultaneously so that each gave the same adjusted value for this mass excess difference. This procedure was then repeated for cycles constructed from four mass differences without readjusting the mass excess differences previously adjusted using cycles containing only three mass differences. This was continued using larger and larger cycles until all mass differences had been included in at least one cycle. There was no case in which the unadjusted closure error of a cycle was greater than the square root of the sum of the squares of the individual errors. In all cases the amount of adjustment of the individual mass differences did not exceed the quoted error and in most cases was less than half this error. The errors on the adjusted mass difference values, $D^*$, were calculated by using the formula employed by Li[11];

$$(P_1^*)^2=P_1^2\left[1-\frac{P_1^2}{\sum_i P_i^2}\right],$$

TABLE X. Analysis of Cycle 3′.

| Mass difference | From $Q$-values | Present results |
|---|---|---|
| $O^{16}-N^{14}-2$ | −7520 | −7526 |
| $O^{17}-O^{16}-1$ | 4535 | 4536 |
| $O^{18}-O^{17}-1$ | 340 | 348 |
| $O^{18}-N^{15}-3$ | −10 | 5 |
| $N^{15}-N^{14}-1$ | −2647 | −2645 |
| Closure error | 12 | ··· |

TABLE XI. Mass excesses ($M-A$) in $\mu$MU.

| | Recalculated from $Q$-values | $S$ (recalculated $Q$-value mass—Wapstra's mass) | Present mass spectrometric result | $\Delta$ |
|---|---|---|---|---|
| $B^{10}$ | 16 118± 8 | − 1 | 16 127 ± 4 | − 9 |
| $B^{11}$ | 12 800± 8 | 5 | 12 810 ± 7 | −10 |
| $C^{12}$ | 3811± 7 | 8 | 3816.7± 0.8 | − 6 |
| $C^{13}$ | 7483± 6 | 5 | 7492.9± 0.9 | −10 |
| $N^{14}$ | 7519± 3 | − 1 | 7526.3± 0.8 | − 7 |
| $N^{15}$ | 4868± 6 | 6 | 4879.3± 0.4 | −11 |
| $O^{16}$ | 0000 | 0 | 0000 | 0 |
| $O^{17}$ | 4533± 4 | 1 | 4536.4± 0.5 | − 3 |
| $O^{18}$ | 4867±11 | 12 | 4884.3± 0.8 | −17 |
| $F^{19}$ | 4450± 8 | 2 | 4443 ± 2 | + 7 |
| $Ne^{20}$ | − 1213±16 | 18 | − 1204.7± 1.5 | − 8 |
| $Ne^{21}$ | 518±16 | 19 | 520.9± 1.2 | − 3 |
| $Ne^{22}$ | − 1624±13 | 22 | − 1622.3± 0.7 | − 2 |
| $Na^{23}$ | − 2930±16 | 17 | − 2908.7± 1.5 | −21 |
| $Mg^{24}$ | − 7343±20 | 17 | − 7328.7± 1.6 | −15 |
| $Mg^{25}$ | − 6231±20 | 17 | − 6216.8± 1.5 | −14 |
| $Mg^{26}$ | − 9185±28 | 17 | − 9145.9± 1.4 | −39 |
| $Al^{27}$ | − 9902±21 | 17 | − 9899 ± 3 | − 3 |
| $Si^{28}$ | −14 208±24 | 17 | −14 179 ± 8 | −29 |
| $Si^{29}$ | −14 323±25 | 17 | −14 299 ±10 | −24 |
| $Si^{30}$ | −16 731±24 | 17 | −16 712 ± 7 | −19 |
| $P^{31}$ | −16 422±29 | 17 | | |
| $S^{32}$ | −17 787±31 | 17 | −17 759.9± 0.9 | −27 |

where $P_1^*$ is the error in the adjusted value of $D_1 \pm P_1$, $P_i$ refers to the error in the mass difference $D_i$ for one of the reactions in the cycle, and the sum in the denominator is taken over all the mass differences in the cycle.

The adjusted mass excess differences were then used to determine the atomic masses of the stable isotopes from $B^{10}$ to $S^{32}$. The mass excesses, along with the present mass spectrometric results, are listed in Table XI. The values for $A>23$ and for $B^{11}$ have been calculated by adding the differences between the recomputed $Q$-value result and Wapstra's value for $Na^{23}$ and for $C^{13}$, respectively, to Wapstra's values.

The errors are the square roots of the sums of the squares of the adjusted mass differences used in obtaining each mass, with the exception of the masses of $A>23$ and $B^{10}$ and $B^{11}$, where the increase in the present errors over Wapstra's results for $Na^{23}$ and $C^{13}$, respectively, have been added to the errors quoted by Wapstra.

We suspect that Wapstra's result for $B^{10}$ is in error since it is inconsistent with the $Q$-value mass differences for $B^{11}-B^{10}-1$, $C^{13}-B^{10}-3$, and also with the result of the Wisconsin group[14] for the energy of the $B^{10}(\alpha,p)C^{12}$ reaction. All of these indicate that the mass excess of $B^{10}$ should be 16 118±8 $\mu$MU instead of the value 16 124±8 calculated from Wapstra's results.

The differences between the recomputed $Q$-value masses and the mass spectrometric results are shown graphically in Fig. 2. As can be seen, the agreement of the mass spectrometric results with the recomputed $Q$-value masses is much better than with the results of Wapstra's calculation (see Fig. 1). This is especially true for $A>20$. Agreement within the errors is obtained for 14 out of the 20 masses in question. However, with the exception of $F^{19}$, all the masses determined from nuclear reaction energies are lower than the present mass spectrometric results.

The disagreement of $O^{18}$ is particularly disturbing since it is connected to $O^{16}$ by a simple reaction chain and has been determined mass spectrometrically using several independent doublets. The mass spectrometric value for this mass is supported by the results of microwave spectroscopy[15] which measures the mass difference ratio $(O^{17}-O^{16})/(O^{18}-O^{16})$. The value for this ratio from microwave spectroscopy, 0.5010420±80, is in better agreement with the present mass spectroscopic result, 0.5010446±9, than with the $Q$-value result, 0.5010507±20.

Examination of Fig. 2 shows that the $O^{16}(d,\alpha)N^{14}$ reaction is important since it largely determines the mass of $N^{14}$ and $N^{15}$ and through them all the masses of lower $A$. It can be seen that if the masses of $N^{14}$ and $N^{15}$ and all lower masses were raised 7 $\mu$MU to bring $N^{14}$ into agreement with the present mass spectrometric results, excellent agreement would be obtained between the two sets of masses for the range $10 \leq A \leq 16$. While the $O^{16}(d,\alpha)N^{14}$ reaction energy has been measured several times with good agreement between the various measurements,[16] a reexamination of this reaction or an equivalent set would be valuable.

It does not seem that a change in either the calibration energies of nuclear spectrometers or in the mass-energy conversion factor would improve the agreement between the mass spectrometric and the $Q$-value masses. Such a change has the effect of raising (or lowering) all $Q$-value masses above $O^{16}$ by an amount approximately proportional to their separation from $O^{16}$ while lowering (or raising) all masses below $O^{16}$. Since all $Q$-value masses are lower than the mass spec-

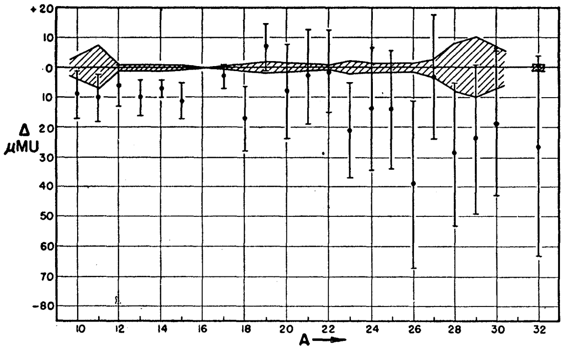

FIG. 2. Differences between the present mass spectrometric masses and the recalculated $Q$-value masses ($\Delta$ = recalculated $Q$-value mass − present mass spectrometric mass) *versus* mass number. The errors shown on the points are those associated with the recalculated $Q$-value masses. The shaded area represents the errors in the present mass spectrometric results.

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[14] R. A. Douglas (private communication, 1955).

[15] Geschwind, Gunther-Mohr, and Townes, Revs. Modern Phys. **26**, 444 (1954).

[16] See review article by D. M. Van Patter and Ward Whaling, Revs. Modern Phys. **26**, 402 (1954).

trometric results, such a change would improve the agreement on one side of $O^{16}$ and make it worse on the other. The improvement brought about in the region $A > 16$ by such a change can be equally well obtained by increasing the $Q$-value mass of $Na^{23}$ and all masses of higher $A$ by about 26 $\mu$MU in the same manner as described for $N^{14}$.

A possible objection to our recalculation of masses from nuclear reaction energies lies in the fact that it will apparently destroy the good agreement between the $Q$-value and the mass spectrometric results for $H^1$ and $D^2$.[6] This objection can be answered in two ways; first, since all isotopes below $A = 10$ are reached by reaction paths which pass through $B^{10}$ and Wapstra's mass of $B^{10}$ is apparently in error, it is possible that his quoted results for $H^1$ and $D^2$ are also in error. If this is the case, it means that the masses for $H^1$ and $D^2$ will change very little from Wapstra's values since the recalculated $Q$-value mass of $B^{10}$ is almost the same as Wapstra's quoted value. Second, an error in one or more $Q$-values involving isotopes of $A < 10$ could lead to values for $H^1$ and $D^2$ in agreement with the mass spectrometric results even though the masses of the heavier isotopes were in disagreement. In any case, the mass difference between $H^1$ and $D^2$ will not be changed by the present calculation since it is largely determined from nuclear cycles whose sum is this mass difference.

We conclude that there is no simple or obvious way to reconcile the differences between the mass spectrometric results and the $Q$-value masses. We feel that there is no discrepancy of a fundamental nature between the two sets of mass values and that further careful measurements, both of mass spectroscopic doublets and nuclear reaction energies, may reconcile the differences.

An attempt should be made to improve the accuracy of the mass spectrometric results for $F^{19}$, not only for its own sake, but also to decrease the errors associated with the masses of the isotopes of boron and silicon which were obtained from doublets involving fluorides. While we believe that any of the present mass spectrometric results may be subject to alterations slightly outside the quoted errors which are, after all, primarily statistical, we feel that the masses of aluminum, sodium, and magnesium are particularly subject to such changes because their ions were obtained from solid samples. It has been our experience that doublet measurements involving ions obtained from solids evaporated in a furnace are not in general as reliable as those involving only gases. On the other hand, because of the good agreement between multiple determinations, we have a great deal of confidence in the present mass spectrometric results for $C^{12}$, $N^{14}$, $O^{18}$, and $Ne^{20}$.

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