TABLE I. Value of the cross section σ in barns and S_0 in kev-barns at energies shown.

E_p kev (c.m.)	$O^{16}(p,\gamma)F^{17}$ σ barns	S_0 kev-barns	
132–160	See Fig. 4	6.8 ±1.4	UCRL, Livermore
259	(4.9 ±2.7) ×10⁻⁹	4.5 ±2.7	C.I.T.
332	(3.8 ±1.0) ×10⁻⁸	7.6 ±2.0	C.I.T.
580	(2.6 ±0.5) ×10⁻⁷	3.6 ±0.8	C.I.T.
	(3.14±0.34)×10⁻⁷	4.34±0.47	C.I.T.
753	(11.1 ±1.5) ×10⁻⁷	5.83±0.79	U.B.C.

$\epsilon=28\times10^{-21}$ Mev-cm².[4] It is believed that the approximations in expression (4) and uncertainties in the stopping cross section introduce an additional 10% to the error given on the yield.

A systematic error that is difficult to determine is the loss of induced activity due to target erosion during bombardment by the beam. A feeling for the magnitude of this effect on the measured yield was obtained by varying the beam current by a factor of 3 at the same energy. With similar counting statistics no systematic difference was observed. The effect of this error would cause the cross section to be larger than given here.

Table I shows a comparison of the value of S_0 from the measurements at the California Institute of Technology[5] and the University of British Columbia.[6] We believe our value $S_0 = 6.8 \pm 1.4$ kev-barns is in substantial agreement with the values shown here taken at higher bombarding energies.

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[4] Ward Whaling, Kellogg Radiation Laboratory, California Institute of Technology (unpublished).

[5] N. Tanner, California Institute of Technology (private communication).
[6] G. W. Griffiths, University of British Columbia, Vancouver (private communication).

Measurements of Light Masses with the Mass Synchrometer*

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A complete account is presented of all results obtained with the mass synchrometer before November, 1957. Included, besides measurements made before March, 1957, tentative values of most of which have been published with little discussion by the author and/or by others, is an extensive later set of measurements on 40 parent ion doublets. From least squares analyses of 39 of these doublet values and of 11 selected earlier values and from three other earlier values are derived what are believed to be the best values obtainable from all synchrometer data of the mass excesses of the 14 nuclides from which all ions studied are composed. These are H¹, D², He⁴, B¹⁰, B¹¹, C¹², N¹⁴, O¹⁸, Ne²⁰, Ne²², S³², Cl³⁵, Cl³⁷, and A⁴⁰. Best values of all measured doublets are also tabulated. Statistical analyses indicate that, for external consistency of results, the internal errors given should be multiplied by either 2.35 or 3.6 (the larger fraction applying primarily in cases where ions are formed by molecular dissociation). They also indicate that, except in cases where ions are formed with appreciable kinetic energies, the external error of the mean of twenty measurements of a doublet separation made with present techniques is about one part in 4×10^7 of the mass number. The agreement of the best values with the latest comparable values obtained at the University of Minnesota is excellent for the important mass excess C−12 and satisfactory in nearly all other cases. Agreement with comparable values obtained from measurements of nuclear reaction energies is fairly good except for C₃−HCl³⁵ and Cl³⁵−35, the synchrometer values of which appear to be in error.

INTRODUCTION

AFTER conversion of the mass synchrometer in late 1951 from a pulsed beam[1] to an rf[2] device, its modification in 1952 to essentially its present form and development of the peak matching techniques which have so greatly enhanced the precision of doublet measurements, the first reasonably reliable doublet measurements were made in early 1953. These, together with a brief description of the instrument and the measuring equipment and procedure then used, were published in a letter and two abstracts.[3] Since that time a large number of measurements have been made. Results of nearly all but the most recent set of these have also been published by the author and/or by others in reports cited below. However, to date, published

[1] L. G. Smith, Rev. Sci. Instr. 22, 115 (1951); Phys. Rev. 81, 295 (1951).
[2] L. G. Smith, Mass Spectroscopy in Physics Research, National Bureau of Standards Circular No. 522 (U. S. Government Printing Office, Washington, D. C., 1953), p. 117; Phys. Rev. 85, 167 (1952).
[3] L. G. Smith and C. C. Damm, Phys. Rev. 90, 324 (1953); 91, 481 (1953).

TABLE I. Doublet values in μMU. Values in italics are adjusted, others are observed. Best values from all synchrometer measurements are the adjusted values ΔM_5. Errors are internal standard errors of means. For external consistency of all values ΔM_5, errors of those marked with superscript b should be multiplied by 3.6, errors of others by 2.35. Superscripts on errors of synchrometer values give numbers of readings in all cases where these are less than 20. Superscripts in parentheses identify the six values for which readings were obtained on one day only.

M	Doublet	ΔM_1 (gases used)	ΔM_2	ΔM_3	ΔM_4	ΔM_5	ΔM_6
2	H_2-D			1548.98 ± 0.10		1548.573 ± 0.035	1547.7 ± 0.4^d
2	H_2-D			1549.67 ± 0.16			1548.3 ± 1.0^e
28	$(C_2H_4-C_2D_2)/2$					1548.59 ± 0.10	
44	$(C_3H_8-C_3D_4)/4$					1547.58 ± 0.22^a	
4	D_2-He			$25\,612.27\pm0.45^a$			$25\,600\pm2^e$
11	$B^{10}H-B^{11}$			$11\,463.25\pm0.29$		$11\,462.88\pm0.30^b$	$11\,450\pm12^f$
25	$B^{10}B^{11}H_4-(B^{11})_2H_3\}$	$(B_2H_6+C_2H_4)$		$11\,460.92\pm0.72^{(16)\,a}$			
26	$B^{10}B^{11}H_5-(B^{11})_2H_4\}$						
51–62	(45 doublets from B_5H_9)			$11\,462.62\pm0.32$			
12	$B^{11}H-C$			$17\,136.12\pm0.16$		$17\,136.03\pm0.20^b$	$17\,139\pm7^f$
25	$((B^{11})_2H_3-C_2H)/2\}$						
26	$((B^{11})_2H_4-C_2H_2)/2\}$	$(B_2H_6+C_2H_4)$		$17\,134.47\pm0.19^a$			
27	$((B^{11})_2H_5-C_2H_3)/2\}$						
36	$((B^{11})_3H_3-C_3)/3$	$(B_5H_9+C_4H_2)$		$17\,136.35\pm0.31^{(11)}$			
48	$((B^{11})_4H_4-C_4)/4$	$(B_5H_9+C_4H_2)$		$17\,135.53\pm0.21$			
12	D_6-C					$84\,637.55\pm0.35$	
52	$C_3D_8-C_4D_2$				$84\,625.26\pm0.34$	$84\,638.39\pm0.77$	
13	$B^{11}D-CH$			$15\,587.14\pm0.14$		$15\,587.46\pm0.19^b$	
14	$B^{11}DH-CH_2$	$(B_2D_6+CH_4)$		$15\,586.95\pm0.35^{(10)}$			
14	$CD-N$				$11\,030.06\pm0.16$	$11\,031.386\pm0.060$	
20	CD_4-ND_3				$11\,030.07\pm0.20$	$11\,033.04\pm0.42$	
28	$DCN-N_2$					$11\,031.90\pm0.23$	
28	$(C_2D_2-N_2)/2$					$11\,031.59\pm0.15$	
28	C_2D_2-DCN					$11\,031.69\pm0.18$	
14	CH_2-N			$12\,579.67\pm0.12$		$12\,579.959\pm0.065$	$12\,580.0\pm0.3^d$
14	CH_2-N			$12\,578.67\pm0.70^{13\,a}$			$12\,580.3\pm0.4^d$
28	$(C_2H_4-N_2)/2$	$12\,574.65\pm0.80^{14}$		$12\,579.51\pm0.15$		$12\,580.43\pm0.20$	$12\,579.3\pm0.3^d$
44	$(C_2H_4O-N_2O)/2$					$12\,579.88\pm0.27$	
15	$B^{11}D_2-CH_3$			$14\,038.16\pm0.19$		$14\,038.88\pm0.19^{a,b}$	
15	$B^{11}D_2-CH_3$	$(B_2D_6+CH_4)$		$14\,035.14\pm0.45$			
16	$ND-O$				$22\,264.47\pm0.15$	$22\,268.793\pm0.079$	
20	ND_3-D_2O				$22\,264.35\pm0.20$	$22\,268.89\pm0.25$	
28	$DCN-CO$					$22\,268.64\pm0.35$	
16	CD_2-O				$33\,294.53\pm0.17$	$33\,300.179\pm0.082$	
20	CD_4-D_2O				$33\,295.11\pm0.25$	$33\,300.36\pm0.23$	
28	C_2D_2-CO					$33\,299.25\pm0.45$	
44	$(C_3D_4-CO_2)/2$					$33\,299.37\pm0.23$	
16	CH_4-O		$36\,393.59\pm0.89$	$36\,396.01\pm0.20$		$36\,397.33\pm0.11$	$36\,396.1\pm0.5^g$
16	CH_4-O		$36\,390.9\pm1.5^a$				
28	C_2H_4-CO	$36\,387.7\pm1.5^{16}$	$36\,392.9\pm1.0$	$36\,396.36\pm0.36$		$36\,397.50\pm0.35$	$36\,396.0\pm0.5^g$
32	CH_3OH-O_2	$36\,374.8\pm1.6^{13}$	$36\,395.4\pm1.7$	$36\,397.20\pm0.43$			$36\,395.8\pm1.2^g$
44	$C_2H_4O-CO_2$					$36\,395.48\pm0.42$	
44	$(C_3H_8-CO_2)/2$	$36\,387.6\pm1.7^{13}$		$36\,395.12\pm0.48$		$36\,397.50\pm0.256$	$36\,396.6\pm0.8^g$
44	$C_3H_8-C_2H_4O$					$36\,398.13\pm0.47$	
16	CH_4-ND					$14\,128.53\pm0.10$	
28	C_2H_4-DCN					$14\,129.09\pm0.20$	
20	$Ne-A/2$				$11\,247.30\pm0.25$	$11\,251.79\pm0.18$	
20	$Ne-A/2$				$11\,247.20\pm0.33$	$11\,252.43\pm0.37$	
20	$H_2O^{18}-A/2$					$33\,628.79\pm0.14$	
20	$H_2O^{18}-A/2$					$33\,629.16\pm0.24$	
20	$D_2O-A/2$				$41\,931.73\pm0.26$	$41\,940.37\pm0.15$	
20	$D_2O-A/2$				$41\,932.42\pm0.44$	$41\,939.94\pm0.36$	$41\,939.0\pm1.3^d$
20	$ND_3-A/2$				$64\,196.20\pm0.26$	$64\,209.16\pm0.15$	
20	$ND_3-A/2$				$64\,196.14\pm0.60$	$64\,210.53\pm0.48$	
20	$CD_4-A/2$				$75\,226.26\pm0.28$	$75\,240.55\pm0.14$	
20	$CD_4-A/2$				$75\,224.73\pm0.78$	$75\,240.88\pm0.32$	
20	$H_2O^{18}-Ne$					$22\,377.00\pm0.16$	
20	$H_2O^{18}-Ne$					$22\,377.11\pm0.39$	$22\,377.0\pm0.6^b$
20	D_2O-Ne				$30\,684.43\pm0.17$	$30\,688.58\pm0.15$	
20	D_2O-Ne				$30\,684.57\pm0.23$	$30\,688.57\pm0.29$	$30\,687.2\pm0.7^h$
20	ND_3-Ne				$52\,948.90\pm0.19$	$52\,957.38\pm0.15$	
20	ND_3-Ne				$52\,949.25\pm0.31$	$52\,957.08\pm0.27$	
20	CD_4-Ne				$63\,978.96\pm0.20$	$63\,988.76\pm0.15$	
20	CD_4-Ne				$63\,977.93\pm0.38$	$63\,989.35\pm0.27$	
20	$D_2O-H_2O^{18}$					8311.58 ± 0.10	
20	$D_2O-H_2O^{18}$					8311.65 ± 0.14	8310.2 ± 0.4^d
20	$ND_3-H_2O^{18}$					$30\,580.38\pm0.11$	
20	$ND_3-H_2O^{18}$					$30\,581.31\pm0.27$	

TABLE I.—*Continued*

M	Doublet	ΔM_1 (gases used)	ΔM_2	ΔM_3	ΔM_4	ΔM_5	ΔM_6
20	$CD_4-H_2O^{18}$					*41 611.76* ±*0.11*	
20	$CD_4-H_2O^{18}$					41 612.00 ±0.22	
20	CD_4-H_4O					*30 203.03* ±*0.15*	
44	$C_3D_4-C_2H_4O$					30 203.38 ±0.36	
22	$(CO_2)/2-Ne^{22}$					*3532.51* ±*0.21*	
22	$(CO_2)/2-Ne^{22}$					3531.71 ±0.49	3530.7 ± 0.6[h]
22	$D_2O^{18}-Ne^{22}$					*35 991.13* ±*0.14*	
22	$D_2O^{18}-Ne^{22}$					35 991.20 ±0.14	
22	$D_2O^{18}-(CO_2)/2$					*32 458.62* ±*0.17*	
22	$D_2O^{18}-(CO_2)/2$					32 459.62 ±0.31	
24	$B^{10}B^{11}H_3-C_2$			*45 735.49*±*0.42*[a]		*45 734.95* ±*0.48*[a,b]	
26	$B^{10}B^{11}H_5-C_2H_2$	$(B_2H_6+C_2H_4)$		45 730.99±0.50[19][a]			
28	N_2-CO			*11 236.67*±*0.22*		*11 237.41* ±*0.11*	
28	N_2-CO	11 237.26±0.69		11 236.32±0.28		11 237.81 ±0.22	11 235.5± 0.6[h]
44	N_2O-CO_2		11 237.05±0.65	11 233.60±0.32[a]		11 237.88 ±0.32	
29	$B^{10}B^{11}D_4-C_2H_5$			*39 539.57*±*0.43*		*39 540.65* ±*0.45*[b]	
30	$B^{10}B^{11}D_4H-C_2H_6$			39 541.93±0.66			
30	C_2H_6-NO	48 965.5 ±1.7				*48 977.29* ±*0.13*[c]	
32	O_2-S		*17 764.45*±*0.89*	*17 762.27*±*0.51*		*17 762.04* ±*0.50*[b]	
32	O_2-S		17 764.7 ±1.5	17 762.11±0.55			17 761.2± 0.9[g]
44	CO_2-CS		17 764.3 ±1.1	17 762.6 ±2.1[12]			
32	CH_3OH-S			*54 158.28*±*0.55*		*54 159.37* ±*0.51*[b]	
32	CH_3OH-S			54 163.0 ±2.8[(5)]			
32	$(B^{11})_2D_5-O_2$			*99 319.36*±*0.63*		*99 323.85* ±*0.36*[b]	
32	$(B^{11})_2D_5-O_2$			99 324.80±0.78			
36	C_3-HCl^{35}			23 309.4 ±1.3[a]			
37	C_3H-Cl^{37}			41 951.89±0.98[a]			
40	C_3H_4-A					*68 940.69* ±*0.31*	
40	C_3H_4-A					68 939.45 ±0.38	68 934.6± 1.1[g]
44	N_2O-CS			*28 998.94*±*0.56*		*28 999.45* ±*0.51*[b]	
44	N_2O-CS			28 998.2 ±2.5[(8)]			
44	$C_3D_4-N_2O$					*55 362.95* ±*0.17*	
44	$C_3D_4-N_2O$					55 360.83 ±0.43	
44	$C_3H_8-N_2O$			*61 555.36*±*0.37*		*61 557.24* ±*0.21*	
44	$C_3H_8-N_2O$			61 553.2 ±2.0[(6)]		61 557.42 ±0.67	
48	C_4-SO			*33 031.17*±*1.05*		*33 025.02* ±*0.66*[a,b]	
48	C_4-SO		33 031.8 ±5.8[10]	33 031.1 ±1.5			33 026.9± 1.3[d]
48	$(B^{11})_4H_4-SO$			*101 575.7* ±*1.0*		*101 569.15* ±*0.75*[b]	
48	$(B^{11})_4H_4-SO$			101 566.6 ±2.0[12]			
64	$(B^{11})_5H_9-SO_2$			*155 107.8* ±*1.1*		*155 102.51* ±*0.90*[a,b]	
64	$(B^{11})_5H_9-SO_2$			155 114.6 ±1.8			

[a] Observed values not included in adjustment.
[b] Readjusted value ΔM_3.
[c] Sum of adjusted values ΔM_5 of CH_2-N and CH_4-O.
[d] Quisenberry, Scolman, and Nier, Phys. Rev. 102, 1071 (1956).
[e] Demirkhanov, Gutkin, Dorkohov, and Rudinko. Atomnaya Energ. 2, 21 (1956) [translation: J. Nuclear Energy 3, 251 (1956)].
[f] H. Liebl and H. Ewald, Z. Naturforsch. 11a, 406 (1956).
[g] Quisenberry, Giese, and Benson, Phys. Rev. 107, 1664 (1957).
[h] Scolman, Quisenberry, and Nier, Phys. Rev. 102, 1076 (1956).

results have consisted for the most part of lists of values, often tentative and incomplete, accompanied by little collateral information. It is the purpose of this paper to present a complete account and discussion of all significant measurements made with the mass synchrometer before November, 1957.

The data have been divided into five sets which will be individually discussed in chronological order. Between all but the first two, modifications of either the instrument or measuring techniques were made. All doublet values obtained are listed in Table I in order of increasing mass except that doublets of larger mass whose spacings are equal to or multiples of one of lower mass are listed with the latter. Values of mass excesses derived from the

doublet values are listed in order of increasing mass in Table II. All values, save those identified by superscript b in Table I and superscript c in Table II, are based on entirely independent sets of data. Many values in Tables I and II differ somewhat from corresponding ones previously reported because the former are based on more data or more exhaustive statistical analyses.

In conformity with the usage of others, errors given in the tables and, unless otherwise qualified, elsewhere in this paper are or are derived from standard errors of the means of individual readings. Thus they differ from errors previously reported which were probable errors either of single measurements or of their means. The superscripts on errors in Table I give the numbers of

TABLE II. Mass excesses in μMU. Best values of all synchrometer measurements are those in column 5. Their errors are derived from the internal standard errors of the means which are the observed values in Table I. For external consistency of best values except those marked with superscript c, errors should be multiplied by 2.35. This appears to be a reasonable multiplier for the error of He−4 as well. For other values, marked for reference c, a multiplier of about 3.6 is indicated.

Excess	Δ_2	Δ_3	Δ_4	Δ_5	Others Mass spect.[a]	Q value
H¹−1	8144.19±0.43	8144.695±0.088		8145.395±0.037	8145.1±0.2	8145.2± 1.5[b]
D²−2		14 740.41 ±0.20	14 739.974±0.048	14 742.216±0.044	14 742.5±0.6	14 740.3± 2.8[b]
He⁴−4		3868.55 ±0.60		3872.16 ±0.46[c]		3873.9± 2.6[b]
B¹⁰−10		16 127.21 ±0.46		16 123.87 ±0.31[c]	16 121 ±6	16 118 ± 8[d]
B¹¹−11		12 808.66 ±0.34		12 806.38 ±0.14[c]	12 802 ±8	12 800 ± 8[d]
C¹²−12	3816.8 ±1.5	3817.23 ±0.29	3814.58 ±0.15	3815.75 ±0.11	3815.6±0.4	3811 ± 7[d]
N¹⁴−14	7526.95±0.80	7526.95 ±0.36	7524.50 ±0.16	7526.577±0.085	7525.8±0.3	7519 ± 3[d]
O¹⁸−18				4882.06 ±0.11	4885.4±0.7	4867 ±11[d]
Ne²⁰−20			−1204.48 ±0.20	−1204.15 ±0.17	−1201.8±0.8	−1213 ±16[d]
Ne²²−22				−1624.64 ±0.19	−1622.9±0.6	−1624 ±13[d]
S³²−32	−17 764.45±0.89	−17 762.27 ±0.51		−17 762.04 ±0.50[c]	−17 761.2±0.9	−17 787 ±31[d]
Cl³⁵−35		−20 002.4 ±1.6		−20 007.5 ±1.3[c,e]		−20 036.5± 4.5[f]
Cl³⁷−37		−22 355.5 ±1.3		−22 359.3 ±1.0[c]		−22 369 ±14[g]
A⁴⁰−40			−24 903.56 ±0.55	−24 911.88 ±0.28	−24 907.4±1.8[h]	

[a] See references d, g, h to Table I. (Some of the values have been changed from those given in d and h to account for later results given in g.)
[b] A. H. Wapstra, reference 16.
[c] Readjusted value from observations ΔM_3, Table I.
[d] See reference h of Table I.
[e] This value of Cl³⁵−35 is probably less reliable than the value in the final column.
[f] From weighted mean of Q values for Cl³⁵(p,α)S³² given in reference 15 and synchrometer values of H −1, He −4 and S −32.
[g] From f together with Q values for Cl³⁷(d,α)S³⁵ and S³⁵(β^-)Cl³⁵ given in references 15 and 17 and the synchrometer value of D −2.
[h] Derived from values given in reference g of Table I for C₃H₄−A, C −12 and H −1.

readings of which the values are the means in all cases where these numbers are less than 20. Superscripts in parentheses identify the six values which are the means of readings taken on a single day only.

Throughout this paper H, C, N, O, Ne, S, and A refer to the common (most abundant) isotopes.

APPARATUS AND PROCEDURE

Throughout the first two sets of measurements, rf signals, for which $f/\Delta f$ was measured as sketched in reference 3, were generated by a 150-watt amateur transmitter (Collins, Model 32-V3). A reactance tube for sweeping f and an adjustable capacitor, alternated with a fixed one by a mechanical switch driven by a flip-flop to produce the adjustable Δf, were added to the oscillator circuit. With this equipment, data could not be obtained nearly as readily as with later rf equipment and observations were impossible on very light ions having adequate energy for reasonable intensity and resolution because of the low maximum attainable frequency (32 Mc/sec). However, the fact that they were obtained by the older rf techniques is not alone grounds for judging the reliability of the first two sets of results to be much less than that of later sets.

A complete description of the instrument as it was, except for modifications described below, throughout all work and of the measuring equipment and techniques used to obtain the last three sets of data, as well as an account of many difficulties encountered, has been published.[4] The new rf apparatus, after much debugging, has functioned far more satisfactorily than the older rf equipment. Its chief residual drawback is rather frequent jitter (probably microphonic) of the locked

oscillator which has caused considerable frustration and eye strain but little loss of accuracy in measurements.

All measurements have been made on gaseous samples whose purity has generally been found to be satisfactory. Half-width resolutions attained in the first four sets of measurements were for the most part between 15 000 and 25 000. Values between 10 000 and 15 000 resulted from use of abnormally low rf voltages because of low intensity for H₂−D, D₂−He, B₃¹¹H₃−C₃, and C₄−SO and because of both low intensity and interference by numerous metastable ions[4] for many readings of B₅¹¹H₉−SO₂. Resolutions during the most recent set of measurements ranged from 25 000 to 32 000. Ion energies were between 1000 and 1900 volts in the first two sets of measurements, between 2000 and 3000 volts in the third and fourth sets, and between 3000 and 4000 in the last set. Orders (i.e., ratios of applied to ion cyclotron frequencies) ranged from 140 to 201 in the first two sets and early readings of the third set and from 94 to 145, following incorporation of the more open modulator described in reference 4, throughout the remaining measurements.

The controlled parameter most frequently varied between readings was the order. Often when it was not changed, it was measured, a procedure which also required retuning of all rf circuits as well as readjustment of Δf. Usually, when the order was neither changed nor measured, the resolution was measured. Thereafter, only resetting of Δf (over a wide range) and of the differential gain control were required to restore the match. Occasionally with the new rf equipment, when possible errors due to impure rf wave forms were suspected, the shifted frequency $f-\Delta f$ was alternated with the usual $f+\Delta f$. Other parameters consciously but less frequently

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[4] L. G. Smith and C. C. Damm, Rev. Sci. Instr. 27, 638 (1956).

varied between readings were electron accelerating potential and current and, to a lesser extent, rf voltage and gas pressure. One was generally deterred from varying most of these as well as ion energy over wide ranges by the desire to have optimum intensity and resolution at all times. In many cases, ion currents were so low that variations of these parameters would have resulted in serious losses of precision.

The sensitivity of peak match to ion accelerating voltage in cases of wide doublets, which was observed with the source having an exposed filament used in the first two sets of measurements, was not observed with the enclosed source mentioned in reference 4 and used in all later measurements. Otherwise, except in cases involving ions formed by dissociation with appreciable kinetic energies, conscious variation of parameters seldom produced variations of results immediately noticeable (i.e., larger than the error of resetting without making such changes).

Day-to-day variations of results were noted which sometimes were larger than variations on a single day. Hence in the latest set of results and, for the most part, in the next-to-last set, the procedure was followed of taking only a few measurements (usually about five) on any one day. It should, however, be remarked that analyses of the dispersions of daily means reveal that departures thereof from the means of all results are generally no greater than normal statistical expectancy would predict.

EARLY RESULTS (SETS 1 AND 2)

The measurements reported in references 3 are reproduced with slight modifications in column 3 (ΔM_1) of Table I. These modifications comprise changing the errors as mentioned above and increasing the value of C_2H_6-NO by 3.2 μMU because of inclusion here of 55 measurements originally rejected as less reliable than the 10 of which the value previously published is the mean. Further work indicated that the reliability of these 55 readings is probably not greatly less.

Further measurements made with the old rf techniques until mid-1954 are summarized in column 4 (ΔM_2) of Table I. It is evident that while further work during this period resulted in no change in the value of the relatively close doublet N_2-CO, higher values were obtained for C_2H_4-CO and particularly for CH_3OH-O_2 (which now agrees much better with C_2H_4-CO). Values were also obtained of the doublets O_2-S, CO_2-CS and C_4-SO. Tentative values of all these measurements as well as the published earlier values were published by Duckworth et al.[5] These have been only slightly modified by inclusion of more data in column 4 of Table I except for the errors and the value of C_4-SO. The tentative value of reference 5, namely 33 062.1 μMU, was the mean of 12 measurements where-

in C_4^+ ions were obtained from butadiene (C_4H_6) and in which the intensity of the C_4^+ peak was very low. The value ΔM_2 in Table I is the mean of 10 later measurements wherein C_4^+ ions formed in C_4H_2 gas, though still scarce, were so much more copious as to warrant the complete rejection of the earlier values. The two "adjusted" values of ΔM_2 are simply the weighted means of the two doublets below in each case. (The directly measured value of CH_4-O is rejected because of the very great sensitivity of peak match to instrument parameters.)

By combining the best value of O_2-S with the value of C_4-SO we obtain the value of the mass excess of C shown in column 2 of Table II. By combining this value with those (ΔM_2) of N_2-CO and CH_4-O we obtain the values of the mass excesses of H and N also shown here.

LATER RESULTS (SET 3)

After incorporation of the electronic equipment for generating rf voltages and measuring relative frequency differences on a ratio scaler described in reference 4, further measurements were made both of doublets previously measured and of a considerable number of others. Many of the latter involve ions obtained from samples of B_5H_9, B_2H_6, and B_2D_6. The results of measurements made from late 1954 till mid-1956 are summarized in columns 5 and 3, respectively, of Tables I and II. Tentative values of some of these results were presented at a meeting of Committee E14 of the American Society for Testing Materials in May, 1955, but not published by the author. Along with a later value of C_4-SO they were reproduced by Mattauch et al.[6] and kindly presented by Hintenberger at the conference on mass measurements at Mainz in July, 1956, which the author was unfortunately not able to attend. They were published along with later values of doublets at mass 20 by Hintenberger in the proceedings of that conference.[7]

All values ΔM_3 in Table I are slightly higher than the tentative values reported by others. The value of the very wide doublet D_2-He is 3.3 μMU higher because measurements wherein peaks of different order (and closer spacing) were matched are here replaced with measurements exclusively on peaks of the same order. This change is in line with the estimated correction required for measurements of peaks of different order. Values ΔM_3 of doublets yielding CH_2-N and CH_4-O are generally higher than values ΔM_1 and ΔM_2 of these doublets while values ΔM_3 of doublets yielding N_2-CO are slightly lower. The former result is probably due to improvements in techniques, including better shielding of the source and of electronic components and greater

[5] Duckworth, Hogg, and Pennington, Revs. Modern Phys. 26, 463 (1954).

[6] Mattauch, Waldmann, Bieri, and Everling, Z. Naturforsch. 11a, 525 (1956); Annual Review of Nuclear Science (Annual Reviews, Inc., Stanford, 1956), Vol. 6, p. 179.

[7] Nuclear Masses and Their Determination, edited by H. Hintenberger (Pergamon Press, New York, London, Paris, Los Angeles, 1957).

care in avoiding errors due to metastable hydrocarbon ions.

Publication of results was delayed because of increasing evidence of inconsistencies in the data and the discovery, after the results listed by others were obtained, that measured spacings of doublets involving ions formed by dissociation could be altered by many times the error of a single measurement by moving small pieces of iron placed against the outside of the vacuum chamber. (No such change was detected with any doublets involving only parent ions.) Since it had often been found advantageous to "shim" the magnet with such pieces of iron in order to optimize intensity and resolution, much effort was expended in attempts to eliminate this difficulty. The only generally successful remedy found was to diffuse ions at a screen over the slit through which they left the source box as mentioned in reference 4. All readings from which the values ΔM_3 for $CH_3OH - S$, $CO_2 - CS$, and $N_2O - CS$ are derived were obtained with this arrangement. It was also used in obtaining 37 readings of $O_2 - S$, with H_2S, SO_2, or CS_2 as the source of S^+ ions, which were combined with the 25 earlier readings, with H_2S as the source of S^+, from which the earlier tentative value was obtained, to give the observed value ΔM_3 of this doublet. Unfortunately, other values could not be checked with the diffusing screen for lack of adequate intensity. However, the spacing of $N_2 - CO$ when CO^+ ions were formed in CO_2 gas, though quite sensitive to the exact location of a shim, was found to be closest to the usual value when CO^+ ions were formed in CO gas for an adjustment of shims approximately the same as that which had generally been used to give optimum resolution and intensity. Moreover, with no shims, a considerably different value was obtained. Thus we must expect that the values of doublets with dissociation ions in Table I are generally less reliable than those with parent ions only, but that their errors are not all in the same direction or of the same magnitude.[8]

Six of the seven observed values in column 5 of the four spacings, $CH_2 - N$, $CH_4 - O$, $N_2 - CO$, and $C_3H_8 - N_2O$, obtained from measurements on parent ions only, were combined in a weighted least squares calculation to obtain the adjusted values shown of these four spacings. (All are expressible in terms of two spacings.) The value of $N_2O - CO_2$ was rejected as being definitely inconsistent with other values for reasons not well understood.

Subtraction of the adjusted values of $N_2 - CO$ and $CH_4 - O$, respectively, from the observed values of $N_2O - CS$ and $CH_3OH - S$ yielded two additional "observed" values of the spacing $O_2 - S$. The weighted mean

of these and the observed values of $O_2 - S$ and $CO_2 - CS$ is the "adjusted" value ΔM_3 of $O_2 - S$.

Eleven of the remaining fourteen observed values ΔM_3 other than $CH_2 - N$, $D_2 - He$, $C_3 - HCl^{35}$, and $C_3H - Cl^{37}$ have been combined in a second least-squares calculation to obtain the remaining adjusted values shown. By subtracting the adjusted value of $CH_4 - O$ and twice this value, respectively, from the observed values of $(B^{11})_5H_9 - SO_2$ and $(B^{11})_2D_5 - O_2$, "observed" values of $(B^{11})_2H_5 - COS$ and $B_2{}^{11}D_5 - C_2H_8$ were first obtained. These and the other twelve are all expressible in terms of the four differences $H_2 - D$, $B^{10}H - B^{11}$, $B^{11}H - C$, and $C_4 - SO$. In this adjustment it was deemed best to reject the values (marked with superscript a) of $B^{10}H - B^{11}$, $B^{11}H - C$, and $B^{10}B^{11}H_5 - C_2H_2$ obtained from measurements on ions formed in B_2H_6 gas because of deuterium contamination in the sample $(D/H \sim 0.37\%)$ sufficient to cause at least the last two values to be low by an amount roughly estimated to be ~ 3 μMU. Errors of this sort are not expected in other cases (1) because the sample of B_5H_9 used had been fractionated to enrich B^{10} and, like the hydrocarbon samples used, showed very little trace of D content, and (2) because absence of ions of the type $B_2D_6{}^+$ or $BD_3{}^+$ from B_2D_6 assured that $B^{11}DH^+$, $B^{11}D_2{}^+$, $B^{10}B^{11}D_4H^+$, and $(B^{11})_2D_5{}^+$ peaks were free of overlapping peaks of ions containing H_2 in place of a D atom.

From the adjusted values of $O_2 - S$ and $C_4 - SO$ the value of the mass excess of C in column 3 of Table II was derived. Other values in this column were derived from other adjusted values or, in the cases of $D_2 - He$, $C_3 - HCl^{35}$, and $C_3H - Cl^{37}$, from observed values in obvious ways.[9]

It is evident on inspection that many of the observed values ΔM_3 in Table I are inconsistent with the "best" values obtainable from the data. As has been pointed out by DuMond and Cohen et al.[10,11] and by Mattauch et al.,[6] this inconsistency may be measured by the minimized sum of squares, namely, $\chi^2 \equiv \sum_i (D_i - \Delta_i)^2 / \sigma_i{}^2$, where D_i and Δ_i are, respectively, the adjusted and observed values and $\sigma_i{}^2$ the variances of the latter. The expected value of χ^2 is the number of doublets (N) less the number of independent quantities (ν) determined by the adjustment. In the two least squares adjustments made here, these expected values are $6 - 2 = 4$ and $11 - 4 = 7$, while the respective values of χ^2 are 16.0 and

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[8] Values particularly sensitive to motion of the shims were those of $H_2 - D$, $B^{11}D_2 - CH_3$, $CH_4 - O$, $O_2 - S$ (with S^+ from CS_2 or SO_2) $C_3 - HCl^{35}$, $CO_2 - CS$ and $C_4 - SO$. Values of $B^{10}B^{11}D_4H - C_2H_6$ and $(B^{11})_2D_5 - O_2$ were particularly insensitive. The sensitivities of other values were either intermediate or not tested.

[9] For the record, it should be stated that the mass excess values (in μMU) given by the author at the American Society for Testing Materials meeting in 1955 were as follows: $H - 1 = 8143.5 \pm 1.1$; $B^{11} - 11 = 12\ 811.8 \pm 4.6$; $C - 12 = 3821.2 \pm 3.8$; and $S - 32 = -17\ 761.6 \pm 2.4$. These are, of course, based on doublet values published in references 6 and 7 and errors are based on probable errors of a single reading. The mass excess of C was obtained from the derived value $C_4 - SO = ((B^{11})_5H_9 - SO_2) - \frac{5}{2}[(B^{11})_2H_5 - C_2H_3] - (C_2H_4 - CO) = 33\ 046.3 \pm 15.0$ μMU.
[10] J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. 25, 691 (1953).
[11] Cohen, DuMond, Layton, and Rollett, Revs. Modern Phys. 27, 363 (1955).

TABLE III. Values of mass excesses, $(D-\Delta)^2/\sigma^2$, χ^2, etc. for various least squares adjustments of observed values ΔM_3. In readjustments II, the doublets $B^{11}D_2-CH_3$, C_4-SO, and $(B^{11})_5H_9-SO_2$ have been excluded. Values χ^2 are the sums of all terms $(D-\Delta)^2/\sigma^2$ except those in parentheses. Values $(\chi^2)'$ are the sums for all doublets common to the original adjustment and to readjustments I. $N=$number of doublets, $\nu=$number of independent quantities determined in an adjustment.

Quantity	Original adjustment	Readjustments			
		I Corrected for α	I Uncorrected for α	II Corrected for α	II Uncorrected for α
Mass excesses					
$B^{10}-10$	16 127.21±0.46	16 124.79±0.30	16 123.82±0.30	16 124.79±0.31	16 123.87±0.31
$B^{11}-11$	12 808.66±0.34	12 806.98±0.13	12 806.30±0.13	12 806.98±0.14	12 806.38±0.14
$S-32$	−17 762.27±0.51	−17 764.12±0.46	−17 763.39±0.46	−17 762.69±0.50	−17 762.04±0.50
Values of $(D-\Delta)^2/\sigma^2$					
H_2-D	19.20	...	...	...	...
$B^{10}H-B^{11}$	3.90	0.42	0.87	0.46	0.68
$\frac{1}{3}[(B^{11})_3H_3-C_3]$	0.52	0.79	1.71	0.79	1.06
$\frac{1}{4}[(B^{11})_4H_4-C_4]$	8.37	7.00	4.09	7.00	6.00
$B^{11}DH-CH_2$	0.31	3.00	1.47	3.00	2.14
$B^{11}D_2-CH_3$	44.5	73.5	64.9	(73.6)	(68.1)
$B^{10}B^{11}D_4H-C_2H_6$	13.00	2.59	4.73	2.55	3.80
O_2-S	...	6.80	5.42	0	0.02
CH_3OH-S	...	1.37	0.65	2.80	1.65
$(B^{11})_2D_5-O_2$	38.2	14.77	2.10	14.57	1.50
CO_2-CS	...	0.21	0.15	0.05	0.07
N_2O-CS	...	0.89	1.06	0.14	0.24
C_4-SO	0	11.77	10.20	(18.80)	(16.40)
$B^{11}H_4-SO$	20.5	3.48	3.14	1.32	1.62
$(B^{11})_5H_9-SO_2$	14.3	46.55	40.0	(58.4)	(46.9)
χ^2, etc.					
χ^2	162.8	173.5	140.5	32.7	18.8
$[\chi^2/(N-\nu)]^{\frac{1}{2}}$	4.82	3.97	3.58	2.02	1.53
$(\chi^2)'$	143.6	164.3	133.2	...	...

163. These numbers make it clear that the internal errors given in Table I are too small, presumably because significant variables were not sufficiently randomized in taking the data. Specifically these numbers indicate that, for external consistency of the results, the errors of the six observed and four adjusted values of the first adjustment should be multiplied by a factor of about $(16/4)^{\frac{1}{2}}=2.0$ while those of the eleven observed and adjusted values of the second adjustment should be multiplied by about $(163/7)^{\frac{1}{2}}=4.8$. To avoid confusion and to conform with the practice of others, none of the errors in Tables I and II has been multiplied by such factors; i.e., all are internal errors. Individual values of $(D-\Delta)^2/\sigma^2$ for the eleven doublets of the second adjustment are listed in column 2 of Table III.

MODIFICATIONS OF THE INSTRUMENT

In an attempt to reduce errors, particularly of measurements on ions formed by dissociation, the instrument was virtually rebuilt during the spring of 1956 and modified as follows.

The circumferential baffles and the deflecting plates in front of the source slit (S_1) visible in Fig. 2 of reference 4 were removed. The detector housing was mounted on a nearby radial tube extending outside the vacuum chamber through a Sylphon bellows into the amplifier box. A fine axial wire through the tube connects the detector plate with the amplifier input. Adjustment for zero splitting of the two components of a peak is now done by motion of the detector and its housing along a nearly radial line. Hence possible errors due to failure to shift deflecting voltage between scannings of the two peaks of a doublet are avoided.

The source has also been redesigned and removed about three inches from S_1. Gas is admitted directly to the Nichrome ionization chamber and can escape only through the slits through which electrons enter and leave and the 0.1-in. diameter hole whence ions are drawn (not pushed as before). After traversing similar holes in two accelerating electrodes and passing between deflecting plates which allow radial positioning, the ion beam is focused on S_1 by a lens comprising two holes $\frac{3}{16}$ in. in diameter in two radial plates about $\frac{3}{16}$ in. apart. Between the lens and S_1 it passes between a pair of plates which provide for its axial centering on S_1. As with previous source arrangements, the (adjustable) potentials for focusing and positioning the beam on S_1 are obtained from a bleeder across the high voltage supply so that all are maintained inversely proportional to mass as the two peaks of a doublet are scanned.

The source and the accelerating, deflecting, and focusing electrodes have been enclosed in a housing whose ends, along with the attached base plate for slits S_1, S_5, and S_6, are soldered to the chamber wall. The (enlarged) housing, which extends about 3.5 in. on either side of the base plate, and the plate are provided with wide flanges to which new gold-plated copper cover plates (without excess holes) may be made sufficiently

tight with close-spaced screws to insure that the main flow of gas into the rest of the chamber occurs through S_1. The housing, the base plate, and the inner wall of the brass chamber were gold plated. Provision was made for exhausting the source housing past a cold trap through a second oil diffusion pump. The length of S_1 has been reduced to $\frac{1}{8}$ in.

These changes resulted in considerable reduction of the axial extent of the ion beam and of background pressure in the main chamber without appreciable loss of intensity. Unfortunately they did not eliminate the possibility of errors due to differences in orbit distributions of the two components of a doublet which was still detectable by distortion of the magnetic field, even with the effective length of the modulator slits reduced (by the adjustable baffles described in reference 4) to 0.1 in. However, they did obviate the necessity of placing iron "shims" against the vacuum chamber to optimize resolution. Loss of intensity due to large divergence of the beam as it leaves the source is indicated by blackening on the first lens plate over an area nearly an inch in diameter.

RESULTS (SET 4)

The failure to eliminate errors in cases of dissociation ions focused attention on the validity of the statement made in reference 4 that no mass excesses can be obtained without measurements on doublets involving such ions. That this statement is incorrect was pointed out to the author during the summer of 1956 by Richard Feynman, who suggested that one way of obtaining mass excesses from doublets with only parent ions would be to combine measurements of $C_2H_4 - CO = CH_4 - O$ with those of a doublet involving two hydrocarbons, one of which could be formed from the other by replacing a C atom with twelve H atoms. The simplest such doublet is $C_9H_{20} - C_{10}H_8 = H_{12} - C$ at mass 128. Because of difficulties with unresolved peaks containing C^{13} and the relatively poor accuracy of a measurement at such a high mass number, it appeared better to the author to measure instead a doublet comprising two types of deuterocarbon ions of which one could be formed from the other by replacement of a C atom with six D atoms. The simplest such doublet is $C_3D_8 - C_4D_2$ at mass 52. This could be combined with measurements of $CD_4 - D_2O = CD_2 - O$ to yield values of the mass excesses of C and D. Accordingly, samples of C_3D_8 and C_4D_2 were kindly prepared by S. Thompson and D. Christman of the Brookhaven Chemistry Department and purified by the latter by gas chromotography.

A series of measurements of $C_3D_8 - C_4D_2$ was made, in the process of which care was taken to avoid possible error due to ions of mass 52 containing $C^{13}H$ in place of CD. Peaks of these ions are located 2.92 mMU or one part in 17 800 below each of the main peaks and thus were not resolvable with the resolution then available. From measurements of the mass 51 peak in each sample, the H/D ratio of each was obtained. Hence was deter-

mined the ratio of intensity of each $C^{13}H$ peak to the corresponding main (CD) peak at mass 52. Fortunately the latter ratio was somewhat lower in the freshly prepared C_4D_2 sample and could be increased to near equality with that in the C_3D_8 sample simply by having the C_4D_2 in contact with the glass walls of the gas-handling system at room temperature for a day or two because of exchange of D atoms in C_4D_2 with H atoms in light water adsorbed on the glass. (Such exchange does not occur with the saturated deuterocarbon C_3D_8.) The H/D ratio measured for the C_3D_8 sample indicated that $C^{13}C_2D_7H^+/C_3D_8{}^+ = 0.9\%$. Measurements of doublet spacing were made with the ratio $C^{13}C_3DH^+/C_4D_2{}^+$ between 0.7% and 1.1%. Over this range no systematic variation of the spacing was observed. Absence of error due to the presence of higher hydrocarbons giving unresolved $C_4DH_2{}^+$ ions in the C_4D_2 sample was assured, *after purification*, by the absence of any traces of $C_4D_2H^+$ ions at mass 53.

The result of these measurements is shown in column 6 (ΔM_4) of Table I as are measurements on the ten possible doublets at mass 20 involving the five ions A^{++}, Ne^+, D_2O^+, $ND_3{}^+$, and $CD_4{}^+$. Also shown here are adjusted values obtained by weighted least-squares adjustment of the ten measured spacings at mass 20. Combining the value of $C_3D_8 - C_4D_2 = D_6 - C$ with the adjusted value of $CD_4 - D_2O = CD_2 - O$ gives values of the mass excesses of D and C. With this value for $D - 2$ and the best values of the other three doublets involving D_2O, values of the excesses of N, Ne and A were obtained. These five excess values are given in column 4 of Table II. They were presented at the Washington meeting of the American Physical Society in 1957,[12] while the adjusted values of the ten doublets at mass 20 have been published in reference 7 and by Duckworth[13] who also gives the measured value of $C_3D_8 - C_4D_2$. Errors previously published were probable errors of the means. Aside from being converted to standard errors of the means, they and a few excess values have been very slightly modified here by a recheck of the least squares calculation.

The value of χ^2 determined from the values for the ten doublets at mass 20 is 20.88. Since the ten doublets are all expressible in terms of four independent ones, the expected value of χ^2 is $10 - 4 = 6$. Thus, to obtain external consistency of the ten adjusted values, errors in column 6 of Table I and column 4 of Table II should be multiplied by $(20.88/6)^{\frac{1}{2}} = 1.87$.

RESULTS (SET 5)

Following the obtaining of the results just discussed, the ever-present concern that errors might be caused by surface charges on walls was heightened by the unusual and ominous observation that, immediately after rf voltage was reduced to give maximum current to the

[12] L. G. Smith, Bull. Am. Phys. Soc. Ser. II, **2**, 223 (1957).
[13] H. E. Duckworth, Revs. Modern Phys. **29**, 767 (1957).

detector and returned to its working value, intensity was only about 20% of its original value, to which it returned gradually in about 30 seconds. Coupled with the fact that resolution was somewhat below its theoretical value, this observation led to repetition of some of the measurements at various energies differing by a factor of two. Definite systematic dependence of measurements on energy were not found but resolving power and intensity were both considerably lower at 1200 volts than at the customary value of 2500 volts. Thus the instrument was taken apart and cleaned with detergent and a gold-plated baffle was installed to prevent ions from striking the long wall of the source housing after one complete revolution. (The orbit of accepted ions after one turn lies about $\frac{3}{16}$ in. from this wall.)

After reassembly of the instrument, the ominous observation could not be repeated and resolution was up to or slightly above its theoretical value. An extensive series of measurements was then made on 40 doublets containing only parent ions. These were: the 15 possible differences at mass 20 between the five previously used ion species plus H_2O^{18+}; the three doublets at mass 22 involving Ne^{22+}, $(CO_2)^{++}$, and D_2O^{18+}; the 10 possible ones at mass 28 containing CO^+, N_2^+, DCN^+, $C_2D_2^+$, and $C_2H_4^+$; the 10 at mass 44 involving CO_2^+, N_2O^+, $C_2H_4O^+$, $C_3D_4^+$, and $C_3H_8^+$; and the doublets $C_3D_8 - C_4D_2$ and $C_3H_4 - A$ at masses 52 and 40, respectively. The measured values of the 40 doublets are given under ΔM_5 in Table I. Also shown here are adjusted values (those not marked with superscript b) obtained from a weighted least squares calculation which yielded directly the values shown (not marked with superscript c) in column 5 of Table II of the mass excesses of the eight nuclides in terms of which all 40 doublets are expressible. This calculation was performed on the Brookhaven punched-card machines with the kind help of Peter Mumford of the Applied Mathematics Department. In it the observed value of $C_3H_8 - C_3D_4$ was omitted because of evidence of error caused by overlapping of the $C_3D_4^+$ peak and the weak $C^{13}C_2H_7^+$ peak from C_3H_8. For the observation of $C_3D_8 - C_4D_2$, a fresh sample of C_4D_2 was kindly prepared and purified by Christman and precautions as before were taken to avoid error due to peaks containing $C^{13}H$ in place of CD. Similar precautions to avoid errors from such ions or from ions containing H_2 instead of D were also taken in all other cases.

The value of χ^2 obtained from the values of the 39 doublets used in the adjustment is 171.5, while its expected value is $39 - 8 = 31$. Thus again we conclude that significant parameters have been inadequately randomized and that errors of values not marked with superscript b in column 7 of Table I and not marked with superscript c in column 5 of Table II should be multiplied by $(171.5/31)^{\frac{1}{2}} = 2.35$ in order that the values be externally consistent.

It should be noted that the latest set of data includes three different parent ion cycles from which mass excesses may be determined. Besides the cycle (I) previously employed for getting the masses of D and C, these are as follows: (II) $D - 2 = \frac{1}{4}(CD_4 - \frac{1}{2}A) - \frac{1}{8}(C_3H_4 - A) + \frac{1}{8}(CH_4 - O)$; and (III) $D - 2 = \frac{1}{4}\{D_2O^{18} - \frac{1}{2}(CO_2)\} + \frac{1}{4}(D_2O - H_2O^{18}) + \frac{1}{8}(CH_4 - O)$. Because the more elegant least-squares computation uses all the data, excesses obtained from these cycles are probably not the best values. However, it may be of interest to note that with the measured doublet values (including weighted means of those yielding $CH_4 - O$ and $CD_2 - O$) the three cycles give the following values:

from cycle I, $D - 2 = 14\ 742.273 \pm 0.098$,

$$C - 12 = 3815.25 \pm 0.22;$$

from cycle II, $D - 2 = 14\ 742.445 \pm 0.096$;
from cycle III, $D - 2 = 14\ 742.474 \pm 0.087$.

These values are all externally consistent with the "best" values in column 5, Table II.

COMPARISONS OF SYNCHROMETER RESULTS

It will be noted that the values ΔM_5 in Table I are consistently higher than corresponding values ΔM_4. The discrepancies in adjusted values are plotted vs doublet spacing (ΔM) in Fig. 1 where the half-length of each vertical line represents 2.35 times the standard error of the difference. Clearly the discrepancies are correlated with ΔM and the best simple relation is direct proportionality. The solid line is the regression line fitted to the eleven points. The only apparent explanation of this correlation is the assumption that the earlier data are in error because of the presence, while they were being taken, of a small electric field predominantly in the inward radial direction. The presence of such a field (E) over the entire orbit (of radius r) would raise the cyclotron frequency (ω) of an ion of charge e, mass m, and energy V by the fractional amount $\delta\omega/\omega = Ee/mr\omega^2 = Er/2V$. Since the spacing is computed from the relation $\Delta M = M(\Delta\omega/\omega)$ and since $\Delta\omega$ is not changed
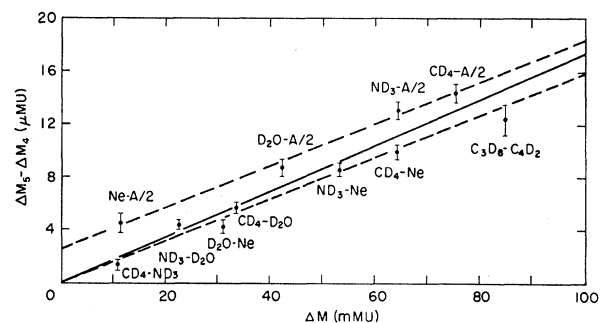

FIG. 1. Differences between adjusted values ΔM_5 and ΔM_4 vs doublet spacing ΔM. The solid line is the regression line through the origin for all points. The lower dashed line is a similar one for points representing doublets not involving A^{++} ions. The parallel dashed regression line is for the four doublets that do involve A^{++} ions. Errors are external standard errors of the differences (i.e., internal errors $\times 2.35$).

while ω is raised, we see that the fractional error caused in the computed value of ΔM is $\delta(\Delta M)/\Delta M = -Er/2V$. In the earlier experiments V was about 2500 volts for all doublets so that we should expect an electric field to cause the same fractional error in spacing at mass 52 as at mass 20. It is interesting that, with the slope of the regression line and the value $r = 12.7$ cm, this relation gives $E \sim 0.07$ volt/cm. Since accepted ions pass close to a wall (i.e. the source housing) whereon surface charges (presumably deposited by the fanned out beam after one turn) could cause an electric field only over about one tenth of its orbit, this field would be expected to be ~ 0.7 volt/cm. If this interpretation is correct, the baffle that prevents ions from striking the long wall of the source housing would appear to have greatly reduced the probability of occurrence of an insidious source of error.

It is further evident from Fig. 1 that all the points for the four doublets containing A^{++} ions lie considerably above the solid regression line while all but one other lie below it. The lower dashed line is the regression line for the seven latter points, while the upper one is a parallel regression line for the former four which lies 2.58 μMU higher. We see that these two dashed lines represent all data well within statistical uncertainty, while the solid one does not. However, what physical reason can be adduced to explain why, in the earlier experiments, the A^{++} peak was displaced by 2.58 μMU more below its expected position than the peaks of singly charged ions is not as yet clear. It is true that doubly charged ions have twice the energy and therefore half the fractional thermal energy spread of singly charged ions. In fact, it was noted that the A^{++} peak was a slightly narrower function of both accelerating voltage and frequency. However, it is not obvious how this could lead to a greater relative shift of the A^{++} peak by an electric field since in all other respects A^{++} ions should behave exactly as singly charged ions of mass $A/2$.

The adjusted values ΔM_3 obtained from measurements on parent ions only of the four spacings, $CH_2 - N$, $CH_4 - O$, $N_2 - CO$, and $C_3H_8 - N_2O$ are all slightly lower than the adjusted values ΔM_5 of these spacings. The discrepancies are plotted vs doublet separation (ΔM) in
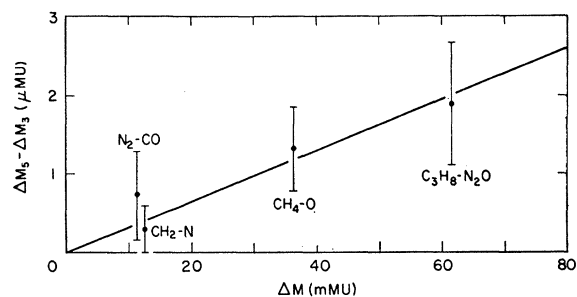

FIG. 2. Differences between adjusted values ΔM_5 and the four adjusted values ΔM_3 obtained from parent ion doublets only. The regression line through the origin is shown. Errors are external standard errors of the differences (i.e., internal errors $\times 2.35$).

Fig. 2. Here also the half-length of each vertical line is 2.35 times the standard error of the difference. Again a linear regression line through the origin represents the discrepancies better than any horizontal line, particularly the axis, $\Delta M_5 - \Delta M_3 = 0$. This fact appears to indicate that a small inward radial electric field may have caused the earlier results to be slightly low. However, it should be pointed out that the earlier measured value of $C_3H_8 - N_2O$, which is the mean of only six readings obtained on but one day, had very little effect on the four earlier adjusted values. Thus the evidence of systematic error due to electric fields in the earlier results is primarily the fact that the discrepancy for $CH_4 - O$ is larger by less than 1 μMU than the mean of the discrepancies for $N_2 - CO$ and $CH_2 - N$. When it is recalled that the results in column 5 (ΔM_3) were obtained under a greater variety of conditions than those in column 7 (ΔM_5) and over a longer period, during which the instrument was cleaned several times and the wall of the source housing was shorter, this evidence does not seem strong enough to justify multiplication of all earlier doublet values by $(1+\alpha)$ where α is the slope of the regression line of Fig. 2, namely $\alpha = 3.25 \times 10^{-5}$. The most important evidence provided by Fig. 2 is that this value of α is only about one-fifth of that of the lines in Fig. 1 so that at least no such serious systematic errors are indicated in the values ΔM_3 as in the values ΔM_4.

In order possibly to obtain further evidence of errors in the results ΔM_3 in Table I and to determine presumably better excess values than those in column 3 of Table II, it is of interest to combine the latest excess values of H, D, C, and N with the values ΔM_3 of all doublets containing B and S in a least squares adjustment. (With these excess values assumed known, all doublets are expressible in terms of the mass excesses of B^{10}, B^{11} and S.) Such a "readjustment" has been made involving 14 such earlier doublets, namely the ten, aside from $H_2 - D$, used in the previous second adjustment and the four from which the mean value ΔM_3 of $O_2 - S$ was determined. (Again doublets involving ions from B_2H_6 have been rejected.) The readjustment has been made both with and without correction of all measured values by the factor α. Values obtained by these readjustments (I) of the $\nu = 3$ mass excesses and of $(D - \Delta)^2/\sigma^2$ for the $N = 14$ doublets as well as of χ^2 and $[\chi^2/(N-\nu)]^{\frac{1}{2}}$ are shown in columns 3 and 4 of Table III. For comparison, similar values for the original adjustment of $N = 11$ doublets are shown in column 2 of this table. Also shown are values of the sum $(\chi^2)'$ of terms for the ten doublets common to all three adjustments. It is apparent that the fit for these ten is better with the uncorrected values and worse with the corrected ones than the fit of the original adjustment. It is also apparent that the uncorrected readjustment I requires particularly large corrections for the three doublets, $B^{11}D_2 - CH_3$, $C_4 - SO$, and $(B^{11})_5H_9 - SO_2$, while such

corrections are required for seven of the eleven doublets in the original adjustment. Hence readjustments (II) corrected and uncorrected for α have been made of the $N = 11$ doublet values other than these three. Results of these readjustments are given in columns 5 and 6 of Table III. We see that, principally because of the wide doublet $(B^{11})_2D_5 - O_2$ (whose value is believed to be fairly reliable), the fit is materially better for the uncorrected values. We note also that the main effect of excluding the three doublet values is a lowering of the adjusted value of $O_2 - S$ resulting in a better fit of the eleven doublet values while not greatly increasing the corrections required in the three excluded ones.

In view of all these considerations, the values obtained by the uncorrected readjustment II have been adopted as the best values yielded by all synchrometer results. The best values of the three mass excesses in column 6 of Table III are reproduced marked for reference c in column 5 of Table II, while the best doublet values obtained therewith are shown marked for reference b in column 7 of Table I. Because of the exclusion of the three experimental doublet values, it would appear best to adopt the value 3.6 as the factor by which the errors of all these values and corresponding observed values should be multiplied since this multiplier is required for external consistency of all results if the three doublet values are not excluded. "Best" values of the mass excesses of He, Cl^{35}, and Cl^{37}, obtained by combining the latest values of the mass excesses of H, D, and C with the doublet values ΔM_3 of $D_2 - He$, $C_3 - HCl^{35}$, and $C_3H - Cl^{37}$, are also shown with arrows in column 5 of Table II. A multiplier of about 2.35 is indicated for the errors of $D_2 - He$ and $He - 4$ and of at least 3.6 for the errors of $C_3 - HCl^{35}$, $C_3H - Cl^{37}$, $Cl^{35} - 35$, and $Cl^{37} - 37$.

That the values of $B^{11}D_2 - CH_3$ and $C_4 - SO$ should be less reliable than others is not surprising in view of the particular sensitivity of each to distortion of the magnetic field and the low intensity of C_4^+ peaks. It *is* surprising that the measured value of the parent ion doublet $(B^{11})_5H_9 - SO_2$ should be low by about 12 μMU. Possibly this may be accounted for by low intensity of $B_5H_9^+$ peaks and large backgrounds caused by metastable ions. Remeasurement of this doublet would appear in order. It may be noted that this doublet has the largest spacing and largest mass number of any doublet measured and that the discrepancy of 12 μMU is one part in 1.3×10^4 of the former and in 5.3×10^6 of the latter. It is primarily this discrepancy, plus the low value of $(B^{11})_2H_5 - C_2H_3$, which accounts for the high value of $C - 12$ given by the author at the meeting of the American Society for Testing Materials.[9] It may also be noted that the observed value of each of the three doublets involving ions from B_2H_6 is, as expected, lower by a few μMU than the value obtained *via* either the original adjustment or the readjustment.

Comparison of the adjusted value ΔM_5 of $H_2 - D$ in

Table I with the value 1549.27 ± 0.18 μMU obtained subsequently[14] following another cleaning with narrowed slits and higher resolution from measurements on $C_2H_4 - C_2D_2$ alone reveals a discrepancy 1.6 times the external error of the difference. A wholly satisfactory explanation of this discrepancy is not apparent. It does not appear that all doublet values ΔM_5 in Table I are systematically in error, since a recheck of three others at mass 28 gave substantially unaltered results. Though the decision is debatable, it was deemed best to utilize a set of results all obtained under the same experimental conditions, and hence perhaps more self-consistent, for determining the mass difference $T - He^3$. Past experience would indicate at least that this procedure would be more apt to avoid errors in such a small mass difference caused by electric fields should such fields have been different in measurements of the observed values ΔM_5 and in later measurements. If the value ΔM_5 of $H_2 - D$ were used instead of the value 1549.27 μMU, the values obtained for the mass difference $T - He^3$ and the neutrino rest mass would be higher, respectively, by 0.70 μMU and 0.65 kev than those given in reference 14. A completely satisfactory determination of these quantities within the errors given (which should probably be multiplied by about 2.4) will apparently not be available until further work is done. It may be noted that the value of $D_2 - He$ in reference 14 agrees within internal error with the value ΔM_3 in Table I.
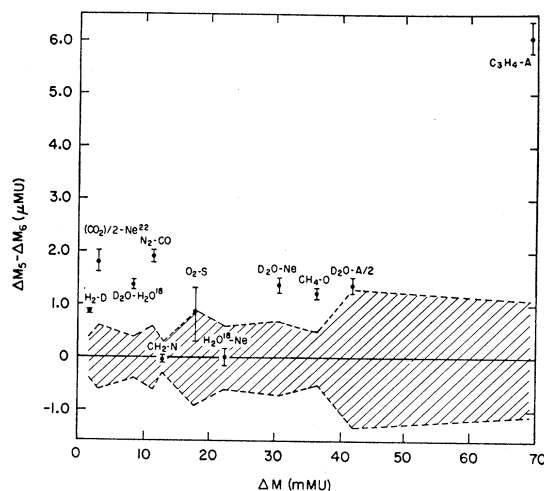

FIG. 3. Differences between best synchrometer doublet values and latest values of the Minnesota group *vs* doublet spacing (ΔM). Errors of the latter are indicated by the shaded area and, as for the synchrometer values, are internal standard errors. No point is shown for $C_4 - SO$ because the adjusted synchrometer value depends entirely on other doublet values and differs appreciably from the measured value.

[14] L. Friedman and L. G. Smith, Phys. Rev. 109, 2214 (1958). In this Letter, very minor errors occur in the values of $H - 1$, $T - 3$, $He^3 - 3$, and $T - He^3$. These values should be, respectively (in μMU), $8145.395^- \pm 0.037$, $17\,007.04 \pm 0.38$, $16\,987.00 \pm 0.22$, and 20.04 ± 0.21.
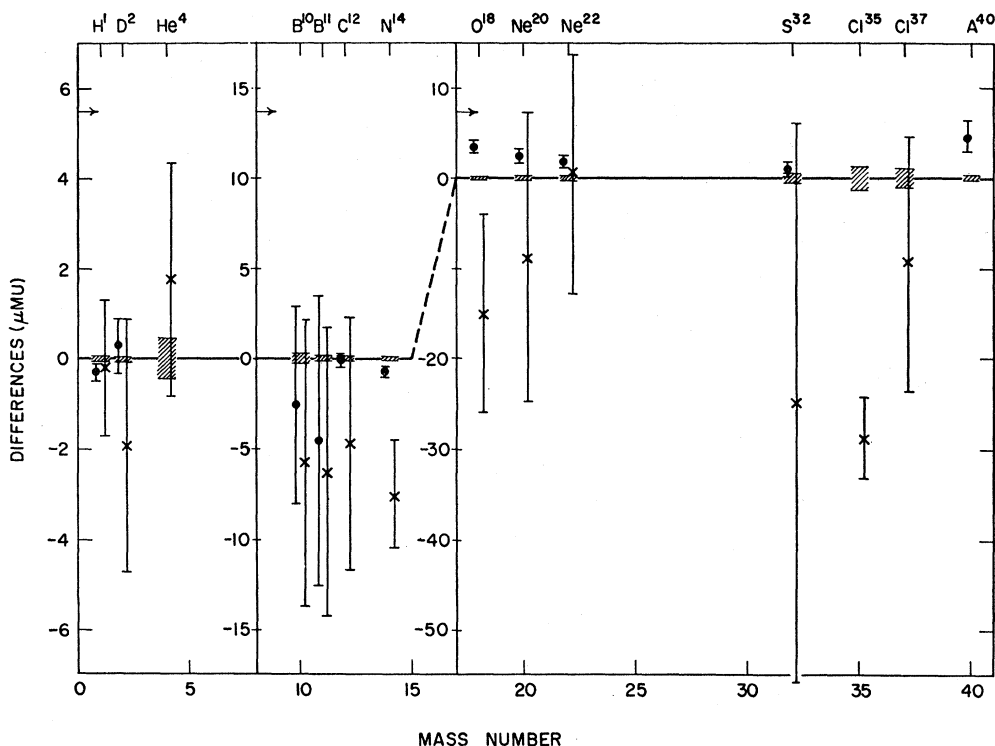
FIG. 4. Differences vs mass number between mass excess values determined by the Minnesota group (points) and from nuclear reaction Q values (crosses) and those determined with the mass synchrometer. Errors of the synchrometer values are indicated by the shaded areas. Like those of the Minnesota values, they are derived from internal standard errors.

COMPARISONS WITH THE RESULTS OF OTHERS

At present it appears that the only other mass spectrometric results of precision comparable with the synchrometer results are those obtained by the group under Professor Nier's direction at the University of Minnesota. The author is convinced that a prime reason for this fact is the use exclusively to date in the synchrometer and the Minnesota instruments of electrical recording such that the two ion groups of a doublet follow identical paths. He believes that a second principal reason is the adaptation to a conventional instrument, sparked by T. L. Collins, of the rapid oscillographic display and peak-matching techniques after they had been shown[3] capable of yielding such astonishingly high precision without requiring comparable long-term stability of magnetic field, accelerating voltage, etc. For these two reasons, both groups have been able to measure reliably the positions of peaks to much smaller fractions of their widths than has otherwise been possible.

Comparison of the two most recent sets of synchrometer results with the latest results published by the Minnesota group and reproduced in Tables I and II provides further evidence for rejecting the earlier of the two sets as being unreliable. A plot (Fig. 3) of the differences between the best synchrometer values and the latest ones published by the Minnesota group of eleven doublets vs their spacing (ΔM) reveals no such proportionality correlation as do Figs. 1 and 2. It shows further that the synchrometer values are in general

slightly higher but that, except for C_3H_4-A, all discrepancies are less than $2\ \mu MU$. In view of the (internal) errors shown, the discrepancies would appear to be statistically significant. However, the above statistical studies and those by Wapstra[15] of the Minnesota results indicate that errors of both sets of doublets should be multiplied by a factor between 2 and 3 for external consistency. Hence the agreement for ten of the eleven doublets measured by both groups *does* appear to be within statistical uncertainty. Though less good than the fortuitously nearly perfect agreement pointed out by Mattauch et al.,[6] of earlier tentative results for six doublets measured by both groups, the agreement indicated in Fig. 3 is far better than between any two other sets of mass spectrometric doublet values from different laboratories.

Because values of mass excesses obtained by the two groups are generally based on different doublet combinations, it is of interest to compare these values as well. For this purpose, the differences of values shown in Table II are plotted vs mass number in Fig. 4. The Minnesota values given in references d and h of Table I have been revised by the author to conform with later values of H − 1, C − 12, and S − 32 given in reference g of Table I. Their errors are determined as in references d and h of Table I except that internal errors are used where these are greater than rms departures of values from their unweighted means. Probably the most significant result of the comparison of values measured by

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[15] A. H. Wapstra, Physica **21**, 367 and 385 (1955).

the two groups is the excellent agreement of the Minnesota value of $C-12$ obtained from the single parent-ion doublet $\frac{1}{2}(C_4H_4O)-H_2O_2$ with the latest synchrometer value obtained from combination of many parent-ion doublets. In every case, save that of O^{18}, the discrepancy in mass excess value is within 2.5 times the standard (internal) error of the difference.

The fact that errors of the best mass synchrometer results are all less than errors of the Minnesota results is doubtless due partly to the greater number of doublets on which the former are based. It appears to be due in part also to the necessity of allowing for uncertainties in resistance calibrations which has no counterpart in measurements based on relative frequencies and obtained by counting cycles.

In column 6 of Table II are given what appear to be the best values of mass excesses yielded by measurements of nuclear reaction Q values. Values for mass numbers $A<10$ are taken from Wapstra's adjustment[15] while those for $10\leqslant A\leqslant 32$ are the revised values of reference h of Table I. The values for $Cl^{35}-35$ and $Cl^{37}-37$ were obtained by combining the best synchrometer values of $H-1$, $D-2$, $He-4$, and $S-32$ with the weighted mean of the three latest Q values[16] for the reaction $Cl^{35}(p,\alpha)S^{32}$ and with the Q values[16,17] for $Cl^{37}(d,\alpha)S^{35}$ and $S^{35}(\beta^-)Cl^{35}$. The differences between the reaction and synchrometer values of mass excesses are also plotted in Fig. 4. The agreement is appreciably poorer than between the two sets of mass spectrometric results but is within the larger errors of the reaction values for all nuclides except N, O^{18}, and Cl^{35}. The discrepancy of 29 μMU for $Cl^{35}-35$ cannot reasonably be attributed to the Q-value measurements of $Cl^{37}(p,\alpha)S^{35}$ or to the synchrometer values of $H-1$, $He-4$, or $S-32$ and therefore indicates an unusually large error of the synchrometer value of C_3-HCl^{35} due presumably to large initial kinetic energy of C_3^+ ions formed in C_4H_2 gas. It would appear therefore that the reaction value of $Cl^{35}-35$ in Table II is considerably more reliable than the synchrometer value.

SUMMARY AND CONCLUSION

All significant measurements made with the mass synchrometer before November, 1957 and listed in Table I have yielded results on 65 doublets (the bracketed doublets and the 45 from B_5H_9 yielding $B^{10}H-B^{11}$ being each considered as one doublet). These are expressible in terms of 46 distinct mass differences. A survey of the results has led to the adoption of the 42 adjusted values and the derived value of C_2H_6-NO listed under ΔM_5 in Table I and the observed values ΔM_3 of D_2-He, C_3-HCl^{35}, and C_3H-Cl^{37} as the best values of the 46 differences obtainable from all the data. The corresponding best mass excess values from which

all 46 differences are exactly derivable are the 14 values listed in column 5 of Table II. In adopting these as best values, we have rejected all results ΔM_4 and the corresponding mass excesses in column 4 of Table II as being very probably in error, presumably because of electric fields due to surface charges. We have also ignored all results obtained before June, 1954, 15 of 29 observations ΔM_3, and the value ΔM_5 of $C_3H_8-C_3D_4$. Seven of these were excluded for special reasons, while in other cases it is believed that later measurements provide more reliable values. Thus the latter value and those of the three doublets obtained with B_2H_6 gas were rejected because of suspected errors due to unresolved satellite peaks, while the values ΔM_3 of $B^{11}D_2-CH_3$, C_4-SO, and $(B^{11})_5H_9-SO_2$ were excluded chiefly because adjustments indicated them to be particularly in error. The five other doublets studied besides these seven for which no measured values were used in determining the best values are H_2-D, CH_2-N, CH_4-O, C_2H_6-NO, and CH_3OH-O_2. Thus the best values are based on the latest measurements of 53 doublets, of which 50 are interrelated.

Two least-squares adjustments of these 50 values, one involving the 39 ΔM_5 and the other the 11 ΔM_3, have indicated ratios of external to internal errors of 2.35 and 3.60, respectively. That these ratios are greater than unity presumably means that all variables affecting measured values have not been sufficiently randomized in the taking of the data. The only reasonable way at hand to compensate for this defect of measuring techniques is to multiply by 2.35 the errors of values not marked with superscript b in column 7 of Table I and not marked with superscript c in column 5 of Table II and by 3.6 the errors of the adjusted values ΔM_5 that are so marked, the corresponding observed values ΔM_3, and the values marked with superscript c of the mass excesses of B^{10}, B^{11}, and S. It also seems reasonable that the errors of D_2-He and $He-4$ be multiplied by 2.35 and that those of $Cl^{37}-C_3H$ and $Cl^{37}-37$ be multiplied by at least 3.6. The values of C_3-HCl^{35} and $Cl^{35}-35$ appear to be definitely unreliable.

It appears that, except in the case of C_3-HCl^{35}, the particular source of error observed in cases of doublets involving dissociation ions has not seriously affected the best values adopted, and that in general reasonable allowance for this source of error is provided by the larger multiplier (3.6).

The best values are in good agreement with the recent results of the Minnesota group and in fairly good agreement with values obtained from nuclear disintegration energies.

In conclusion, it should perhaps be mentioned that, while variations with time of results obtained with the mass synchrometer have occurred, they have been, for the most part, less than those of results obtained with more conventional instruments during the same period. It also seems fair to say that the precision of results has

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[16] D. M. van Patter and W. Whaling, Revs. Modern Phys. **29**, 757 (1957).
[17] L. J. Lidofsky, Revs. Modern Phys. **29**, 773 (1957).

compared quite favorably with that of the most precise results obtained elsewhere. In this connection, it is of interest to note that the rms value of the ratio of adjustment required to mass number for all 39 doublets of the most recent adjustment is 2.24×10^{-8}, while that for the 14 doublets of the readjustment I of values ΔM_3 is 6.52×10^{-8}. For all 53 doublets, the rms value is 3.32×10^{-8} and, for the 52 excluding only $B^{11}D_2 - CH_3$, it is 2.45×10^{-8}. It therefore seems fair to say that, except in cases of ions with large initial kinetic energies, the mean of about twenty measurements of a doublet made with the mass synchrometer in its present form can be expected to have an external precision of about one part in 40 million. This figure agrees with the observation[3] that the (internal) *probable* error of a single reading is about 10^{-3} of the half-width of a peak for a resolution of 30 000.

Finally, it would seem well to point out that this instrument and associated techniques are much newer and less well known than others. In fact, to date, the synchrometer as a precision measuring device suffers from many defects such as inadequacies of vacuum technique, ion optics in the source, detector sensitivity, electronic gear and general precision workmanship which are common to the developmental or prototype stage from which it has yet to emerge. Should most of these defects be remedied, as seems quite possible in a new, enlarged device, precision more than ten times greater than that so far attained would appear a distinct possibility. Attainment of such precision is certainly not precluded by uncertainties in the dispersion relation, i.e., in frequency measurements.