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A Redetermination of the Relative Abundances of the Isotopes of Neon, Krypton, Rubidium, Xenon, and Mercury*

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A careful redetermination of isotopic abundance ratios in neon, krypton, rubidium, xenon, and mercury has been made. The mass spectrometer employed was calibrated for mass discriminative effects with a synthetic argon isotope mixture made from essentially pure samples of A^{36} and A^{40}. The present results together with those obtained from an earlier study on carbon, nitrogen, oxygen, argon, and potassium enable one to use the several elements investigated as sub-standards for calibrating mass spectrometers for mass discriminative effects in other instances.

I. INTRODUCTION

IN a previous publication[1] the author reported on a redetermination of isotopic abundance ratios in carbon, nitrogen, oxygen, argon, and potassium. It is believed that this work is more accurate than earlier determinations because the mass spectrometers employed in the study were calibrated for mass discriminative effects with carefully made synthetic isotope mixtures of A^{36} and A^{40}. The investigation has now been extended to include the elements neon, krypton, rubidium, xenon, and mercury. For details on the preparation of the standards and the general procedure the reader is referred to the earlier publication. The instrument used in the present work is that previously designated as MSl. The rare gases used in the present study were all obtained from the Air Reduction Sales Corporation.

II. RESULTS

Neon

Table I gives the results obtained. In making analyses the procedure was to admit the standard and unknown alternately to the instrument. This procedure was repeated three times with an extra run of the standard at the end. Each number given is the average of 10 determinations, scanning of the spectrum being first in one direction and then in the other in order to eliminate the effect of any drift. This general procedure was also followed for the other elements studied. All errors given here and elsewhere in this paper are ***probable errors*** computed in the usual manner.

TABLE I. Comparison of mass spectrometer readings for neon and argon standard A V.

$(A^{36}/A^{40})^{2+}\times 10^5$	$Ne^{21}/Ne^{20}\times 10^5$	$Ne^{22}/Ne^{20}\times 10^5$
1067[a]	286.9	9931
1080	286.1	9944
1067	286.1	9933
1052		
av. 1067±4	286.4±0.18	9936±3.7
corr. 1096±1.5	282.7±0.6	9703±40
Diebeler *et al.*[b]	309 ±20[c]	10180±200[c]
Vaughan *et al.*[d]	300	10810
Bleakney[e]	280[f]	8200[f]
	300[g]	9200[g]
Hibbs[h]	330±10	10800±10

[a] All members in this column corrected for H_2O^+ contribution to the mass 18 peak.
[b] See reference 11.
[c] Maximum deviation.
[d] Vaughan, Williams, and Tate, Phys. Rev. **46**, 327 (1934).
[e] W. Bleakney, Phys. Rev. **43**, 1056 (1933).
[f] For singly charged ions.
[g] For doubly charged ions.
[h] See reference 12.

The abundance ratios found for neon correspond to percentage abundances of 90.92±0.04, 0.257±0.001, and 8.82±0.04 for Ne^{20}, Ne^{21}, and Ne^{22} respectively. With a conversion factor[1] of 1.000278 from the physical to the chemical scale and the assumption that the isotopic weights[2,3] of Ne^{20} and Ne^{22} are 19.9987 and 21.9986 respectively, one computes the atomic weight of neon to be 20.172. This value is to be compared with the International value of 20.183. For convenience of reference the isotopic abundance ratios determined by other recent investigators are given at the bottom of Table I.

In making the present determination the problem was complicated by the fact that sensitive mass spectrometers always have a residual mass 18 peak caused by water vapor. Thus in determining the $(A^{36}/A^{40})^{2+}$ abundance ratio, the 18 peak, and hence the measured ratio, was too high. This effect was eliminated by the following procedure: (a) determination of the 17 as well as of the 18 and 20 peaks while the standard argon mixture was in the mass spectrometer; (b) determination of the ratio of the 18 and 17 peaks while pure A^{40} was admitted to the instrument at the same rate as the argon in (a); (c) from the measurements in (a) and (b) determining the correction to be made for H_2O^+ in the measured 18/20 abundance ratio. Step (b) was taken as an added precaution on the remote chance that the 18/17 abundance ratio for residual water vapor in the machine might depend on the presence of argon in the instrument.

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[1] A. O. Nier, Phys. Rev. **77**, 789 (1950).

[2] K. T. Bainbridge, National Research Council, Preliminary Report No. 1, Nuclear Science Series, 1948.

[3] F. W. Aston, *Mass Spectra and Isotopes* (Longmans, Green and Company, New York, 1942).

Krypton

The procedure in this case was, first of all, to determine the Kr^{82}/Kr^{86} abundance ratio by taking readings alternately on $(Kr^{82}/Kr^{86})^{2+}$ and $(A^{36}/A^{40})^{+}$. The ions in the two cases had so nearly the same m/e value that it was felt that a linear mass discrimination correction factor could be applied safely. The result, $(6654\pm 11)\times 10^{-4}$ for Kr^{82}/Kr^{86}, was then used for making mass discrimination corrections for the remaining krypton isotopes in the spectrum of the singly charged krypton ions. Table II gives the ratios found. The results of earlier investigators are also tabulated for comparison. From the present work the percentage abundances are 0.354±0.002, 2.27±0.01, 11.56±0.02, 11.55±0.02, 56.90±0.1, and 17.37±0.02 for Kr^{78}, Kr^{80}, Kr^{82}, Kr^{83}, Kr^{84}, and Kr^{86} respectively. With a packing fraction[3] of -7.2 and a conversion factor of 1.000278 from the physical to the chemical scale, an atomic weight of 83.805 is computed from these results. The International value is given as 83.7.

Rubidium

Rubidium vapor was distilled into the electron beam from a small furnace mounted in the ion source. Since evaporation took place at a very slow rate from a liquid surface, it was assumed that the vapor leaving the liquid was enriched in light atoms. However, as the light atoms also travel faster to a cold region where they condense, it is assumed that the vapor composition in the electron beam is normal. The rubidium employed was of unknown origin and was the same material used in the author's earlier work.[4]

Two comparisons for rubidium were made. The first was between the previously determined krypton abundance ratio Kr^{86}/Kr^{84} and singly charged rubidium ions. The second comparison was made between doubly charged rubidium ions and argon standard[1] A V. The results are shown in Table III. The weighted average for the Rb^{85}/Rb^{87} abundance ratio from the two determinations is 2.591±3. The error takes account of the fact that the Kr^{86}/Kr^{84} ratio also is based on A V. The new value is to be compared with the following most recent values: Nier,[4] 2.68±0.02; Brewer,[5] 2.59–2.61; Paul,[6] 2.64±0.03. The disagreement between the author's new and old values is perhaps not surprising. A recent determination of zinc and cadmium[7] has shown a similar discrepancy.

Xenon

A preliminary comparison was first made between the standard argon mixture and $(Xe^{128}/Xe^{136})^{3+}$. The value obtained for the latter abundance ratio was then employed for correcting the other isotope abundance radios when the singly charged xenon isotopes were examined. The results found are shown in Table IV. Again, for purposes of comparison the earlier work of Nier[8] and Lounsbury *et al.*[9] are included. The present ratios correspond to percentage abundances of 0.096 ±0.001, 0.090±0.001, 1.919±0.004, 26.44±0.08, 4.08

TABLE II. Comparison of mass spectrometer readings for krypton and argon standard A V.

	$(A^{36}/A^{40})^{+}\times 10^{5}$	$(Kr^{82}/Kr^{86})^{2+}\times 10^{4}$
	1042	6516
	1043	6490
	1034	
	1040	6470
	1035	
Av.	1039±1.2	6492±8.5
Corr.	1096±1.5	6654±11

	$(Kr^{78}/Kr^{86})\times 10^{5}$	$(Kr^{80}/Kr^{86})\times 10^{4}$	$(Kr^{82}/Kr^{86})\times 10^{4}$	$(Kr^{83}/Kr^{86})\times 10^{4}$	$(Kr^{84}/Kr^{86})\times 10^{3}$
	2115	1341	6741	6736	3314
	2103	1332	6726	6731	3297
	2086	1326	6795	6716	3288
Av.	2101±5.7	1333±2.9	6754±14	6728±4	3300±5
Corr.	2039±12	1308±6	6654±11	6653±13	3276±6
Dibeler *et al.*[a]	2088	1305	6710	6636	3314
Lounsbury *et al.*[b]	1962	1278	6598	6586	3271
Nier[c]	1985	1297	6597	6597	3268
Nier (recalculated)[d]	2060	1353	6759	6716	3307

[a] See reference 11.
[b] See reference 9.
[c] See reference 8.
[d] See discussion at end of present paper.

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[4] A. O. Nier, Phys. Rev. **50**, 1041 (1936).

[5] A. K. Brewer, J. Am. Chem. Soc. **60**, 691 (1938).

[6] W. Paul, Zeits. f. Physik **124**, 244 (1947).

[7] W. T. Leland and A. O. Nier, Phys. Rev. **73**, 1206 (1948).

[8] A. O. Nier, Phys. Rev. **52**, 933 (1937).

[9] Lounsbury, Epstein, and Thode, Phys. Rev. **72**, 517 (1947).

TABLE III. Comparison of mass spectrometer readings for doubly charged rubidium and argon standard A V, rubidium and krypton.

	$(A^{36}/A^{40})^+$ $\times 10^5$	$(Rb^{85}/Rb^{87})^{2+}$ $\times 10^3$	$(Kr^{86}/Kr^{84})^+$ $\times 10^4$	$(Rb^{85}/Rb^{87})^+$ $\times 10^3$
	1070	2582	3075	2568
	1076	2580	3071	2588
	1068	2567	3072	2583
	1071			2576
Av.	1071±1.2	2576±3.2	3072±0.9	2579±3
Corr.	1096±1.5	2589±4	3053±6.5	2595±6

±0.01, 21.18±0.05, 26.89±0.07, 10.44±0.02, and 8.87±0.01 for Xe^{124}, Xe^{126}, Xe^{127}, Xe^{128}, Xe^{129}, Xe^{130}, Xe^{131}, Xe^{132}, Xe^{134}, and Xe^{136}, respectively. The mean mass number is 131.390 which when combined with a packing fraction[3] of −4.1 and a conversion factor of 1.000278 from the physical to the chemical scale yield an atomic weight of 131.300. The present International value is given as 131.3.

Mercury

In this case a sample of laboratory mercury was employed. Since this Laboratory has its own mercury purifying apparatus the sample chosen could be considered as a kind of average of the various samples of mercury employed in the laboratory in recent years. Approximately one cc of mercury was placed in a glass appendagê attached to the main vacuum system of the mass spectrometer. The temperature of the appendage was adjusted to give the size peak desired and was in the neighborhood of −15°C. Table V gives the results obtained. The instrument was calibrated for mass discrimination by employing both the Kr^{80}/Kr^{86} and Xe^{128}/Xe^{136} abundance ratios previously determined. Since the doubly charged ions of mercury were employed, their m/e values were greater than those of the calibrating gas in the one case and less in the other. No significant differences in the two sets of results were observed. Because of the small size of the Hg^{196} peak no attempt was made to establish a new value for the relative abundance of the Hg^{196} isotope and the author's earlier Hg^{196}/Hg^{198} ratio, 0.0146, should be assumed to determine the Hg^{196} relative abundance.

The new values for the relative abundances lead to a mean mass number of 200.627 which when combined with a packing fraction[3] of 1.7 and the conversion factor 1.000278 from the physical to the chemical scale yield an atomic weight 200.605. The International value is 200.61.

III. DISCUSSION

The errors given in the present study are all probable errors based on the assumption that systematic errors have been reduced to negligible proportions. Thus one might expect that there would be a very good chance that the quantities measured here should agree with the true values within, let us say, three times the probable errors given. Thus it is hard to reconcile the present results on neon with any of the other determinations given in Table I. In all cases the neon was obtained from commercial sources. It is possible that the air reduction processes used in isolating the neon could have resulted in fractionation of the isotopes and that the fractionation effect was different in the various samples investigated. If this were true, one might expect a better correlation between the Ne^{21}/Ne^{20} and Ne^{22}/Ne^{20} ratios from sample to sample. It appears more likely that experimental errors of one kind or another were present in much of the work. The fact that the mass span of the neon isotopes is nearly ten percent of the mass means that systematic errors leading to mass discriminative effects could assume serious proportions. Also, the very low abundance of Ne^{21} makes it difficult to measure this isotope accurately.

As can be seen from Tables II and IV, the earlier work of the author on krypton and xenon[8] is in good agreement with the more recent work of Lounsbury and his co-workers.[9] However, the present determinations do not agree with either of these older measurements. In view of the care taken in all three researches it appears to be worth looking for sources of systematic error unknown to the investigators. It is seen from the

TABLE IV. Comparison of mass spectrometer readings for xenon and argon standard A V.

	$A^{36}/A^{40} \times 10^5$	$(Xe^{128}/Xe^{136})^{3+} \times 10^4$
	1081	2149
	1080	2137
	1075	2145
	1079	
	1079±0.9	2144±3
	1096±1.5	2164±4

	Xe^{124}/Xe^{136} $\times 10^5$	Xe^{126}/Xe^{136} $\times 10^5$	Xe^{128}/Xe^{136} $\times 10^4$	Xe^{129}/Xe^{136} $\times 10^3$
	1084	1006	2172	2983
	1078	1004	2158	2960
	1084	1017	2155	2985
Av.	1082±1.3	1009±2.7	2162±3.6	2979±5.6
Corr.	1084±4	1010±4	2164±4	2981±8
Dibeler *et al.*[a]	1136	1091	2149	2952
Lounsbury *et al.*[b]	1064	985	2147	2938
Nier[c]	1049	982	2121	2927
Nier (recalculated)[d]	1098	1020	2186	3004

	Xe^{130}/Xe^{136} $\times 10^4$	Xe^{131}/Xe^{136} $\times 10^3$	Xe^{132}/Xe^{136} $\times 10^3$	Xe^{134}/Xe^{136} $\times 10^3$
	4596	2389	3035	1179
	4566	2376	3010	1173
	4607	2396	3043	1178
Av.	4590±8.3	2387±4	3030±6.7	1177±1.3
Corr.	4594±11	2388±5	3032±7	1177±2
Dibeler *et al.*[a]	4100	2343	3020	1174
Lounsbury *et al.*[b]	4540	2378	3016	1178
Nier[c]	4540	2363	3009	1176
Nier (recalculated)[d]	4644	2406	3054	1184

[a] See reference 11.
[b] See reference 9.
[c] See reference 8.
[d] See discussion at end of present paper.

TABLE V. Comparison of mass spectrometer readings for mercury and krypton, mercury and xenon.

	Kr^{80}/Kr^{86} $\times 10^4$	$(Hg^{198}/Hg^{202})^{2+}$ $\times 10^4$	$(Hg^{199}/Hg^{202})^{2+}$ $\times 10^4$	$(Hg^{200}/Hg^{202})^{2+}$ $\times 10^4$	$(Hg^{201}/Hg^{202})^{2+}$ $\times 10^4$	$(Hg^{204}/Hg^{202})^{2+}$ $\times 10^4$
	1299	3370	5640	7756	4448	2305
	1297	3357	5637	7748	4429	2300
	1299					
Av.	1298±0.5	3363±5.2	5639±1.1	7752±2.7	4439±6.4	2302±1.7
Corr.	1308±6	3370±7	5648±6	7761±5	4441±7	2299±2.4
	Xe^{128}/Xe^{136} $\times 10^4$					
	2128	3348	5622	7701	4389	2300
	2136	3347	5657	7782	4440	2308
	2145					
Av.	2136±3.3	3347±0.5	5639±12	7743±27	4415±14	2304±2.7
Corr.	2164±4	3361±3	5657±12	7759±27	4420±14	2299±3
Average[a]		3362±3	5650±5	7761±5	4437±6	2299±2
Hibbs[b]		3371	5693	7773	4448	2301
Nier[c]		3420	5761	7869	4459	2270
Nier (recalculated)[d]		3386	5718	7753	4448	2281

[a] Two sets of data assumed independent except for dependence upon A^{36}/A^{40} ratio in original standard.

[b] Ratios given here computed from Hibbs' percentage abundances. Hg^{196} percentage abundance (not included in above table) was given as 0.16±0.03. See also reference 12.

[c] See reference 8.

[d] See discussion at end of present paper.

data in Tables II and IV that the older determinations differ from the present in that, in general, the relative abundances of the light isotopes are lower. This suggests a mass discriminative effect. In all but the most recent work on isotope abundances no effort was made to correct for possible mass discriminative effects produced by the "leak" used to introduce gaseous samples to the mass spectrometer. The assumption usually made was that the mass spectrometer diffusion pumps pumped off molecules at a rate inversely proportional to the square root of their masses and that somehow or other the inlet leak admitted gases in the same manner and hence no correction had to be made. It is now clearly recognized that the leak may have either molecular or viscous flow, or for that matter, anything between these two extremes.[10] Leaks used in earlier work usually consisted of a length of fine bore glass capillary drawn from glass tubing of larger diameter. The nature of the flow through a capillary depends upon the pressure, length, diameter, and upon whether or not the bore is uniform. In the author's earlier work on krypton and xenon the leak flow was assumed to be molecular. If the flow were actually viscous, the heavier isotopes would have too high an abundance relative to the lighter ones in the spectrometer. In the last rows of Table II and IV the author's earlier data have been "corrected" on the assumption that the leak flow may have been viscous. It is seen that the author's new results for both krypton and xenon lie between his "original" and "corrected" values. Thus it appears to be attractive to assume that the leak used in the earlier work came closer to being a viscous than a molecular leak. The close agreement between the author's earlier work and that of Lounsbury and his co-workers suggests that a similar situation may have existed also in the latter investigation. These speculations are, of course, based on the assumption that the rare gases employed were identical in composition.

The mass spectrometer used by Dibeler[11] and his co-workers employs a carefully designed molecular leak. Hence the gas composition in the mass spectrometer is accurately known. However, the apparatus was not designed specifically for making isotope analyses, and the precision, especially for rare isotopes, does not appear to be as good as the other work cited. Nevertheless, the results seem to agree reasonably well with the author's new work.

In the case of mercury the present results agree very well with both the author's earlier[8] values as well as Hibbs'[12] recent determinations. If a correction factor depending upon the square root of the mass ratio is applied to the author's earlier values the agreement between the new and old data is even better. A correction factor of this sort is possibly justified for the following reason: The author's earlier apparatus was evacuated by two mercury pumps each having it own trap. Ordinarily both traps were immersed in liquid air or dry ice. However, when the mercury determinations were made one of the traps was warmed to around 0°C in order to give a sufficiently high vapor pressure

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[10] A manuscript based on a study of leaks in this laboratory is now in preparation. Published references include: R. E. Honig, J. App. Phys. **16**, 646 (1945); A. O. Nier, Rev. Sci. Inst. **18**, 398 (1947); A. O. Nier *et al.*, Anal. Chem. **20**, 188 (1948). M. G. Inghram, *Advances in Electronics*, Vol. I (Academic Press, New York, 1948).

[11] Dibeler, Mohler, and Reese, J. Research Nat. Bur. Stand. **38**, 617 (1947).

[12] R. F. Hibbs, "Mass Spectrometric Measurements of Natural Isotopic Spectra." Report No. AECU-556, August 1949, U. S. Atomic Energy Commission.

for making an analysis. Since the mercury in the trap was that which previously had been distilled over from the nearby pump (the amount distilled being small compared with the total amount of mercury in the pump) one might expect the distillate to be rich in the lighter isotopes. The author was aware of the possibility at the time but hesitated to make the correction since it was by no means clear that the conditions were proper for ideal distillation. The new results would seem to indicate that a correction should have been made. Of course, if the isotopic composition of the mercury used in the several investigations was different the apparent good agreement could be fortuitous. Until such time as the mercury from various sources is shown to have different isotopic compositions it seems best to accept the close agreement as real.

The writer wishes to express his appreciation to Mrs. R. C. Boe for the assistance given in making the many careful measurements and computations required in this work. The construction of the apparatus was aided materially by grants from the Graduate School and the Minnesota Technical research fund subscribed to by General Mills, Inc., Minneapolis *Star-Journal and Tribune*, Minnesota Mining and Manufacturing Company, Northern States Power Company, and Minneapolis Honeywell Regulator Company.

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Study of Electron-Electron Scattering*

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In the course of various cloud-chamber investigations pictures of 98 electron-electron collisions were obtained, in which the primary electrons ranged in energy approximately from 0.05 to 1.7 Mev and the deflections (in the center-of-mass system) exceeded 32°. By means of a statistical test suitable for the systematic evaluation of heterogenous data, a comparison was made of our results with the theory of Møller, relativistic versions of the theories of Mott and Rutherford, and the classical non-relativistic Rutherford theory. Our data discriminate definitely only against the latter theory. When combined with 122 electron-electron collisions observed by Champion, they are consistent only with the first two theories, but are insufficient to discriminate decisively between them.

I. INTRODUCTION

As a by-product of several cloud-chamber investigations carried out in this laboratory, a considerable number of photographs of fast electron-electron scattering events have been obtained. Since the amount of experimental evidence concerning this phenomenon is not very extensive, it was felt worth while to present our findings.

The first studies of this type of collision were made by Bothe[1] and by Wilson[2] using cloud chambers without a magnetic field. The observed cross sections agreed in order of magnitude with the results of a theory by Thomson.[3] Henderson[4] studied the scattering of electrons from RaE in several gases with a scattering chamber (filled with the gas to be investigated) and an ionization-chamber to record the scattered electrons. From the dependence of the scattering on the atomic number, he estimated the contribution made to it by electron-electron scattering.

All subsequent investigations were performed with cloud chambers using a magnetic field. As a source of electrons beta-ray emitters and gamma-ray sources were used. In all cases the energy of the electron before scattering was determined from the curvature of its path in the magnetic field. Some investigators determined the energy of the scattered electron of lower energy while others measured the angles between the directions of the tracks at the point of the collision. Furthermore, the investigations differed in the method used to compare the experimental results of various theories. Williams and Terroux[5] determined the energies of the scattered electrons of lower energy from their ranges. They divided the observed 72 events into four groups depending upon the magnitude of this energy. For electrons with energies between 0.13 and 1.6 Mev before the collision they compared the number of cases in these groups with the number resulting from the theory of Thomson[3] for an average energy of 0.46 Mev. The difference between the experimental and theoretical results is, according to Williams and Terroux, much greater than the experimental and statistical error. According to Hornbeck and Howell,[6] the above results also lead to cross sections which are more than twice

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[1] W. Bothe, Zeits. f. Physik **12**, 117 (1922).

[2] C. T. R. Wilson, Proc. Roy. Soc. **104**, 192 (1923).

[3] J. J. Thomson, Phil. Mag. **23**, 449 (1912). N. Bohr, Phil. Mag. **25**, 10 (1913).

[4] M. C. Henderson, Phil. Mag. **8**, 847 (1929).

[5] E. J. Williams and F. R. Terroux, Proc. Roy. Soc. **A126**, 289 (1929/30).

[6] G. Hornbeck and I. Howell, Proc. Am. Phil. Soc. **84**, 33 (1941).