ments. Maximum deviations of k from the mean are, at the lowest ionic strengths, ±12%; at higher ionic strengths, ±4 to 5%. While these errors are higher than desirable, the trend of the results is not obscured.

Extrapolated values of k' the rate "constant" calculated directly from the titrations with no correction, agree well with the values of Soper and Williams. Table IV compares at round values of $\sqrt{\mu}$, k(Soper and Williams), k', k(present investigation) and k(King and Jacobs), all for low persulfate concentration and added uni-univalent salts to make up the ionic strength.

TABLE IV

COMPARISON OF RATE CONSTANTS

$\sqrt{\mu}$	k^a	k'	k^b	k^c
0.03	0.062	0.063	0.098	0.097
.05	.066	.068	.107	.106
.08	.081	.080	.123	.122
.10	.092	.096	.133	.131
.16	.123	.125	.168	.166

[a] Soper and Williams. [b] Knudsen and King. [c] King and Jacobs.

Before an investigation can be made of such "medium effects" as those postulated by Soper and Williams, it is evident that there must be a clear understanding of the normal salt effects. For example, for solutions containing 0.005 molar persulfate, 0.01 molar iodide, Soper and Williams found $k = 0.123$, in excellent agreement with the value 0.125 found by Jette and King,[10] who investigated the rate in this particular solution very thoroughly. Here the iodine rapidly attains such a concentration that no correction need be applied to the titration. For approximately the same solution King and Jacobs found $k = 0.133$ and explained the discrepancy to some direct oxidation of thiosulfate by persulfate. For a second solution of the same ionic strength (0.025) but containing 0.0002 molar persulfate and 0.0244 molar iodide, Soper and Williams found $k = 0.122$. The salt effect in this second solution should evidently be much higher than in the first because most of the ions are univalent. For similar solutions the present investigation gives $k = 0.167$ while King and Jacobs found practically the same. Soper and Williams are in error because the iodine is liberated very slowly in the second solution and large corrections are necessary in all the titrations.

Summary

The titration of iodine with thiosulfate has been investigated in solutions 5×10^{-6} to 7×10^{-5} molar, using starch as the indicator, and empirical "calibration curves" have been established for various concentrations of potassium iodide and nitrate.

The rate of the persulfate–iodide ion reaction has been investigated between the ionic strengths 0.0006 and 0.025, by titrating the iodine formed and applying corrections as indicated by the "calibration curves."

The primary salt effect is found to be in agreement with the predictions of the Brönsted theory. The rate measurements are in excellent agreement with those found previously in this Laboratory by a different experimental method.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

A Mass Spectrographic Determination of the Isotope Abundance and of the Atomic Weight of Rubidium

BY A. KEITH BREWER

Rubidium is one of the most widely distributed of all the elements and yet there are no ores in which it is concentrated more than a few per cent. It is of particular interest in that it is the most radioactive of all the elements outside of the so-called "radioactive elements." The radioactivity consists of a soft beta ray, with no detectable alpha or gamma emission.

The present paper presents (1) a measurement of the abundance ratio of the isotopes of rubidium in various natural sources, (2) a mass spectrographic determination of the atomic weight from these ratios, (3) a study of the disintegration products of the radioactive isotope, and (4) a discussion of the effect of the radioactivity of rubidium on the atomic weight of strontium.

I. The Rb^{85}/Rb^{87} Ratio

Aston[1] assigns $Rb^{85}/Rb^{87} = 3.0$ as the most probable value. Bondy, Johannsen and Popper[2] using rubidium carbonate as a source obtained a

(1) Aston, "Mass Spectra and Isotopes," 1933.

(2) Bondy, Johannsen and Popper, *Z. Physik*, 95, 46 (1935).

ratio of 2.68 ± 0.3. Nier,[3] using metallic rubidium, found 2.68 ± 0.02. Two measurements made in this Laboratory with different mass spectrographs but with the same artificial spodumene emitter prepared from metallic rubidium gave 2.59 ± 0.04[4] and 2.59 ± 0.01 as the most probable value.

The mass spectrograph employed in the following experiments was the same, except for several improvements, as that used in obtaining the last results mentioned above. The abundance ratios observed are given in Table I.

TABLE I

Source	Rb^{85}/Rb^{87}
Lepidolite, Stewart mine, Pala, Calif.	2.61 ± 0.01
Lepidolite, San Diego mine, Mesa, Calif.	2.61 ± 0.01
Lepidolite, Himalaya mine, Mesa, Calif.	2.61 ± 0.01
Lepidolite, Katarina mine, Pala, Calif.	2.61 ± 0.01
Zinnwaldite, Morefield mine, Amelid, Va.	2.61 ± 0.01
Rubber seed (*Hevea brasiliensis*), Bayeux, Hali	2.61 ± 0.01
Apple seed, Virginia	2.61 ± 0.01
Artificial spodumene	2.59 ± 0.01

In addition to the above samples a large number of minerals and plant and animal tissues[5] were tested for rubidium. In every case the presence of rubidium was detected, although the concentration was too low for an accurate determination of the abundance ratio; in no instance, however, did the ratio appear to deviate beyond the limits of experimental error from the neighborhood of 2.6. While the artificial spodumene prepared from metallic rubidium appears to have a definitely lower abundance ratio the difference is small and does not appreciably affect the atomic weight. In viewing the results as a whole it is apparent that the abundance ratio in natural sources is very close to 2.61.

II. The Atomic Weight of Rubidium

It is possible to calculate the atomic weight from the isotope abundance ratio provided the packing fraction and conversion factor are known. The packing fraction for rubidium has never been measured, but it can be obtained from that for strontium. Mattauch[6] finds for the packing fraction of strontium, $Sr^{87} = -8.7$ and $Sr^{86} = -9.0$; from these values the packing fractions for rubidium are estimated to be $Rb^{87} = -8.7$ and $Rb^{85} = -8.9$.

The atomic weight of rubidium computed on the basis of the above values for the packing fraction and 1.00027 for the conversion factor is 85.456 for an abundance ratio of 2.61 and 85.457 for a ratio of 2.59. The chemical value of 85.48 recently obtained by Archibald, Hooley and Phillips[7] corresponds to an abundance ratio of 2.45 which is far outside the limits of experimental error.

The principal source of error in the above calculations is doubtless in the value assigned to the packing fraction. For sake of comparison, if Aston's[8] values for krypton, $Kr^{84} = -7.6$ and $Kr^{86} = -7.4$, are used for the packing fraction of rubidium the atomic weight comes out to be 85.465. It does not seem probable that the packing fraction could be in error by more than this amount.

III. The Radioactive Disintegration of Rb^{87}

The first five samples of old mica listed in Table I were furnished by Dr. R. C. Wells of the U. S. Geological Survey. These samples contained about five-tenths of one per cent. of rubidium, but exacting chemical tests failed to show the presence of strontium. Hemmendinger and Smythe[9] have shown that Rb^{87} is radioactive while Rb^{85} is not. Since it seems probable that Rb^{87} upon the emission of a beta particle disintegrates into Sr^{87}, the micas mentioned above should contain strontium. The principal isotopes of strontium are 86, 87 and 88, with abundance ratios close to 10, 7 and 83, respectively; a rare isotope 84 exists in traces.[6,10] Tests were made, therefore, to detect a mass of 87 that was not rubidium. In these tests the impregnated platinum disk sources were glowed at red heat until the emission of Rb^{85} became negligible. The temperature was then raised to white heat and the mass numbers for rubidium and strontium investigated. After a few minutes the mass 85 peak became small while the mass 87 peak became many times larger, the actual ratio of the two peaks depending upon the conditions of the experiment. Since it previously had been found impossible to shift the Rb^{85}/Rb^{87} ratio for pure

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[3] Nier. *Phys. Rev.*, **50**, 1041 (1936).

[4] Brewer and Kueck. *Phys. Rev.*, **46**, 894 (1934); Brewer, *J. Chem. Phys.*, **4**, 350 (1936).

[5] Tests were made on most of the samples used in the study of the isotopes of potassium: THIS JOURNAL, **58**, 365 (1936); **59**, 869 (1937).

[6] Mattauch, *Naturwissenschaften*, **25**, 189 (1937).

[7] Archibald, Hooley and Phillips, THIS JOURNAL, **58**, 70 (1936).

[8] Aston, *Proc. Roy. Soc.* (London), **A163**, 391 (1937).

[9] Hemmendinger and Smythe, *Phys. Rev.*, **51**, 1052 (1937).

[10] Sampson and Bleakney, *ibid.*, **50**, 456 (1936).

rubidium by this treatment[4] and since there are no elements of mass 87 except rubidium and strontium, it is evident that the marked enhancement of the 87 peak denotes the presence of Sr^{87}. No peaks were observed for the other isotopes of strontium with masses 84, 86, and 88. The presence of strontium in the mica was confirmed by spectrograms taken by Dr. Eugene Melvin of this Laboratory. It must be concluded, therefore, that the old micas do contain strontium, but only Sr^{87}, and that this strontium is the result of the radioactive disintegration of Rb^{87}. A similar observation has been made by Mattauch,[6,11] who found Sr^{87} in old rubidium micas but was unable to detect the presence of any of the other strontium isotopes, the strontium being estimated to consist of at least 99.5% Sr^{87}.

IV. Possible Effect on the Atomic Weight of Strontium

The question now arises as to how much the atomic weight of strontium may be influenced by the early proximity of rubidium. It seems probable that all strontium produced before the congealing of the earth's crust will be homogeneously mixed. In consequence deviations in the abundance ratio must be looked for in rocks formed subsequent to this time. The uranium-lead ratios[12] indicate that the age of minerals does not in general far exceed 1.5×10^9 years.

The values given in the literature for the disintegration constant of rubidium when converted to apply to Rb^{87} are: Holmes and Lawson[13] 2.48×10^{-11} yr.$^{-1}$, Orban[14] 1.1×10^{-11} yr.$^{-1}$ and Muhlhoff[15] 0.57×10^{-11} yr.$^{-1}$. Assuming an average value of $\lambda = 10^{-11}$ yr.$^{-1}$, which must be correct as to the order of magnitude, the fractional increase in Rb^{87} at 1.5 billion years past is 1.015 compared to the present time as unity.

Goldschmidt[16] gives 420 g. per ton for strontium and 310 g. per ton for rubidium in the earth's crust. The concentration of the isotopes in question becomes, therefore, $Sr^{87} = 29.4$ g. per ton and $Rb^{87} = 86.3$ g. per ton. During the past 1.5×10^9 years 1.2 g. per ton of Rb^{87} have been decomposed and hence 1.2 g. of Sr^{87} have been formed in every ton of the earth's crust. In consequence the atomic weight of strontium has decreased during this time 0.0021 mass unit. It is doubtful if this small change could be detected chemically. In contrast, the strontium formed since the congealing of the earth's crust which is not contaminated by earlier strontium, as is illustrated by the micas investigated, should have an atomic weight of 86.924; this is 0.7 mass unit lower than ordinary strontium.

Summary

The abundance ratio of the isotopes of rubidium in a variety of sources has been measured with the mass spectrograph and found to be $Rb^{85}/Rb^{87} =$ 2.59 to 2.61.

Old micas containing rubidium have been investigated for the isotopes of strontium; only Sr^{87} has been found.

The effect of the radioactivity of Rb^{87} on the atomic weight of strontium is discussed.

The atomic weight of rubidium computed from the isotope ratios is 85.46.

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(11) Hahn, Strassman and Walling, *Naturwissenschaften*, **25**, 189 (1937).

(12) "International Critical Tables," Vol. I, p. 383.

(13) Holmes and Lawson, *Phil. Mag.*, **2**, 1218 (1926).

(14) Orban, *Akad. Wiss. Wien, Ber.*, **140**, 121 (1931).

(15) Muhlhoff, *Ann. Physik*, **7**, 205 (1930).

(16) Goldschmidt, *J. Chem. Soc.*, 655 (1937).