THE RADIOACTIVITY OF THE ALKALI METALS

I. JOCELYN PATTON[1] WITH L. J. WALDBAUER[2]

The radioactivity of potassium and rubidium was first reported by Campbell and Wood (1) in 1906. Of the remaining alkali metals, lithium and sodium have been consistently reported inactive, while the activity of caesium is still doubtful (2). Numerous investigations have since been undertaken to determine the origin of the activity of potassium and rubidium, but the question is still undecided, as a careful scrutiny of the experimental evidence discloses many contradictions.

Three theories have been advanced to account for the radioactivity of the two alkali metals, viz.,

I. The activities of potassium and rubidium are due to a disintegration of the atoms of these elements;

II. A missing radioactive element of this series (atomic number 87) causes the apparent activity;

III. The beta rays emitted are not of radioactive origin, i.e., from the nucleus, but are comparable to the photo-electric effect.

The arguments that have been adduced in favor of I are:

a. Potassium and rubidium salts from various sources have an activity which is proportional to the percentage of potassium or rubidium present. The experimental evidence which has been brought forward in support of this argument is, however, exceedingly doubtful.

b. The beta rays emitted from potassium and rubidium are of different intensities and penetrating powers.

c. All attempts to isolate a new element from any potassium or rubidium salts have completely failed. A possible excep-

---

[1] Research student of the Research Council of Canada at McGill University, Montreal, Canada.

[2] Instructor in Chemistry, Lehigh University, Bethlehem, Pa.

tion may be found in Ebler's (3) "radioactive amalgam," which will be described later.

The principal objections to this theory are:

a. The number of beta rays emitted by either potassium or rubidium is very small, compared to the number emitted by any of the elements of the three well-known radioactive series. This objection is somewhat weakened by the findings of Hahn and Rothenbach (4) and Hoffmann (5), who found that the activity of metallic rubidium to metallic uranium is as 1:15.

b. The atomic numbers of the two "active" alkali elements are so low that it seems improbable that the nuclei of these elements actually break down due to their instability.

c. Caesium is not active, or only slightly so, yet its atomic number is considerably higher than either of the other alkali metals.

d. If potassium and rubidium are active, one would expect their disintegration products to be isotopic with calcium and strontium respectively, in accordance with the Soddy-Fajans disintegration law (loss of an electron from the nucleus shifts the element one group to the right in the Periodic Table.) No isotopes of calcium or strontium which could have been produced from the various isotopes of potassium and rubidium have been found.

In addition to the objections to the first theory, there is an argument in favor of the second theory, viz., that there is a missing element of atomic number 87, which is in all likelihood an alkali element. From its position between radon and radium, one would expect this missing element to be radioactive. It is a significant fact that the only group of elements containing an unknown member which, if existent, would be radioactive, is the only one whose other members show radioactivity. On the other hand, there is an objection to this theory too, in addition to the arguments in favor of the first, and that is that the missing element of Group I would be more nearly related to caesium than to either potassium or rubidium, and hence should be found associated with caesium rather than with either or both of the others. Nevertheless, the best-known caesium mineral, pollux, has been consistently reported as "inactive."

Objections (*a*) (*b*) and (*d*) to theory I might be considered as arguments in favor of theory III, while objection (*c*) would be an argument against this theory. This will be further discussed later.

In order to form a background for the discussion of the three theories, it will be necessary to give a fairly comprehensive review of all the literature dealing with the radioactivity of the alkali metals.

Campbell and Wood (1) found variations in the activity of various potassium salts (all derived from the Stassfurt deposits), but concluded that the discrepancies were due to the varying absorption of the rays from the bottom layers of material, due to the different densities of the salts. On attempting recrystallization of the salts, it was found that the activity of the mother liquor was 1 to 2 per cent lower than that of the crystals in some cases, and had the same activity in others. In a later paper, Campbell (6) states that he failed to observe or produce any difference in the activity of different samples of the same potassium compound. McLennan and Kennedy (7) examined a large number of compounds, and found that the activity varied from compound to compound, depending on the source. Unfortunately, these investigators assumed that the purity of all their compounds, even of those designated "commercial," was 100 per cent, and made their calculations on this basis. Had the percentage of potassium been determined for each sample, their results might have been of some value. In the case of the samples of potassium cyanide, analyses were made, and it is interesting to note that there actually was a variation in the activity of the potassium.

Quoting from McLennan and Kennedy's paper:

> From the results set forth in the table, it will be seen that exceedingly wide variations were found in the potassium content of the various specimens. It will be seen too, that those salts which possessed the greater potassium content also exhibited the higher activities, and that, in the case of the more active, the radioactivities were approximately proportional to the potassium contents of the salts.

The results obtained with the potassium cyanide in this series of experiments, therefore, rather support the view taken by Campbell that the activities of potassium salts are directly proportional to the amount of potassium in them.

McLennan and Kennedy neglected to calculate the A/K values, which have been calculated by the present writers. It will be seen that the conclusions drawn in the lines just quoted are hardly justifiable. The sample exhibiting the highest activity had a percentage of potassium about one-seventh that of the next most active sample, and it is difficult to trace any proportionality whatever between the percentage of potassium and the radioactivity of the salt.

TABLE 1

Activity of potassium cyanide; McLennan and Kennedy (7)

SOURCE OF SALT	RELATIVE ACTIVITY "A"	PERCENTAGE OF K BY WEIGHT	$\frac{A}{K} \times 10^2$
Manufacturer A, No. 1	8.85	52.15	16.9
Manufacturer B, No. 1	1.40	9.44	14.8
Manufacturer C, No. 1	0.15	2.84	5.3
Manufacturer C, No. 2	0.10	2.76	3.6
Manufacturer C, No. 3	0.60	9.57	6.3
Manufacturer C, No. 4	0.00 (slight)	2.36	0.0
Manufacturer C, No. 5	1.47	7.64	19.3

Campbell (6) attributed the variation just mentioned to the fact that the ionization chamber used by McLennan and Kennedy was not protected by the usual aluminium foil, and to the additional fact that the change in the "natural ionization" of the air, due to the admission of fresh air while introducing the new sample, was so large as to preclude consistent results for the activity even of the same sample.

Biltz and Marcus (8) examined samples of potassium salts, extracted from minerals of widely different origins eithers by means of the hydrofluoric acid (9) or J. Lawrence Smith (10) method. They came to the conclusion that potassium salts from any source have an activity proportional to the potassium content of the salt. A close examination of their data fails to reveal any great constancy, as table 2 will show.

Biltz and Marcus make the interesting statement that, on precipitation of the sulfate sample obtained from spodumene as $BaSO_4$, the activity of the sample disappeared. It seems strange that radium (to which they attribute the high activity) could have been carried along with the K_2SO_4. It is a well-known fact that $BaSO_4$ has the property of adsorbing small amounts of substances as it precipitates, and it might easily have carried down some unknown active substance. It would be well to investigate spodumene again, and the writers have experiments on this mineral in view.

TABLE 2

Potassium sulphate; Biltz and Marcus (8)

SOURCE	% K	ACTIVITY	ACTIVITY/1%K
K_2SO_4 Kahlbaum	44.87	7.4	0.167
Carnallite (lying)	44.87	7.3	0.162
Rocksalt (Hartsalz)	44.2	7.1	0.160
Carnallite (hanging)	44.87	7.5	0.167
Orthoclase	27.0	4.35	0.161
Muscovite	32.7	5.4	0.165
Lepidolite	19.6	3.3	0.168
Leucite (Vesuvius)	27.4	4.8	0.175
Leucite (Albanian Mts.)	34.0	5.8	0.171
Spodumene (impure)	0.4	0.3	0.75
Spodumene (purified)	0.4	0.05	——calc. 0.125
Beryl (Norway)	7.0%K	1.0	(0.14)
trace Rb	5%Cs		

TABLE 3

Activities of the minerals examined; Biltz and Marcus

MINERAL	%K	ACTIVITY	ACTIVITY/1%K
Orthoclase	7.2	1.5	0.208
Muscovite	8.1	1.1	0.136
Lepidolite	6.3	1.1	0.175
Leucite (Vesuvius)	5.5	2.0	0.364
Leucite (Albanian Mts.)	8.7	1.9	0.218
Spodumene	0.12	1.5	12.5
Beryl (Norway)	0.07	0.0	——

Henriot (11) has made the statement that his potassium chloride and sulfate samples had an activity proportional to the potassium content. He did try recrystallization, vaporization, etc., in an attempt to change the activities of the sample, but unsuccessfully. Elster and Geitel (12) tried fractional crystallization and fractional electrolysis, using a mercury cathode, but were also unsuccessful in changing the activity of the potassium chloride sample.

Strong (13), using the photographic method, found that some old samples of potassium compounds collected by Rowland were radioactive, but that potassium sulfate of recent manufacture was not nearly so active. Levin and Ruer (14), using the same method, found all samples of potassium salts active. Hoffmann (5), using a highly refined electrical method, found that the activity of potassium salts is proportional to the potassium content. Recently Harkins and Guy (15) measured the activities of potassium and rubidium salts and reached the same conclusion. Practically all of these investigators assumed the purity of their salts to be 100 per cent simply because the manufacturers claimed this purity.

Rubidium salts were first investigated by Campbell (16) who used the sulfate prepared by Kahlbaum, and found this active. McLennan and Kennedy (7) reported an exceedingly slight activity, but, as has been pointed out, their results are entirely untrustworthy. Strong (13), Levin and Ruer (14), and Büchner (17) all found rubidium salts active, using the photographic method. Henriot (11), Hahn and Rothenbach (4), Hoffmann (5), and Harkins and Guy (15) all verify this statement, using electrical methods. Hahn and Rothenbach measured the activities of several samples of rubidium salts of various ages, viz., one of recent date, prepared by Kahlbaum, one sample 11 years old, one 21 years old, and several rubidium alum samples, but found no variations in the activity. As they point out, rubidium is a rather difficult substance to work with, as there are no representative rubidium minerals, although the element is fairly widely scattered in nature.

All authors are agreed that lithium and sodium are possessed of no activity, although McLennan and Kennedy (7) did report an active sample of rocksalt. Caesium has been reported as inactive by all authors but Zwaardemaker (2). He bases his conclusion on the fact that commercial caesium preparations produce physiological effects similar to those produced by well-known beta radiators. The effect is probably due to an active impurity. Ringer (18) states caesium to be inactive.

Campbell (1), from their absorption in tinfoil, concluded that the beta rays from potassium are heterogeneous. McLennan and Kennedy (7) reached a similar conclusion. Henriot (11) concluded that the beta rays from K_2SO_4 and from KCl are homogeneous, although the curve obtained by plotting the ionization current as ordinates against the weight of tinfoil used as abscissae did not give a simple exponential curve. By using a two-term exponential equation he found that the curve corresponded to two types of beta rays, the softer ones being 10 per cent of the total. In spite of his own experimental evidence, he concluded that the beta rays from potassium are homogeneous, and attributed the softer radiation to secondary rays emitted by the tinfoil screen. Harkins and Guy (15) apparently found the beta rays from potassium homogeneous.

Henriot (11), Hoffmann (5) and Harkins and Guy (15) found that the beta rays from rubidium are heterogeneous, Hahn and Rothenbach (4) apparently did not observe any heterogeneity, as they did not mention it. Rothenbach's papers were destroyed after his death, and thus most of the experimental results were lost before Hahn could publish them. Hoffmann gives 347 cm.^{-1} as the absorption coefficient of the harder rays in aluminium, and 900 cm.^{-1} for the softer radiation. Harkins and Guy state that the absorption coefficient decreases from 593 to 522 as the thickness of the aluminium foil increases from 0.0017 to 0.0051 cm.

Campbell (1) estimated that the rubidium rays are 16 times more absorable than those of potassium, while Henriot (7) estimated them to be ten times more absorbable; Harkins and Guy (15) compromise by stating that the rubidium rays are from 10 to 15 times more absorbable than those of potassium. Hahn and Rothenbach (4) concluded that the activity of metallic rubidium is to that of metallic uranium as 1:15; this was confirmed by Hoffmann (5) who found the ratio 1:14. Harkins and Guy (15) state that the activities of rubidium to potassium are in the ratio of 1.39:1.00.

On discovering the heterogeneity of the beta rays from potassium, Campbell (1) attempted to isolate a new element from the potassium salts by means of fractional crystallization, heating in the blowpipe flame, and by electrolysis. In some cases the crystals were more active than the mother liquor by 1 or 2 per cent, but not consistently. If he expected to find a new alkali element, one would expect its salts to be more soluble in water than either KCl or K_2SO_4. Campbell gave up the attempt to fractionate the potassium salts, simply because of the experimental difficulties involved.

Elster and Geitel (19) and Henriot (11) tried fractional crystallization, but also without results. The former investigators also tried fractional electrolysis of KCl using a mercury cathode, but found no difference in the activities of the fractions. It was impossible to crystallize fractionally rubidium salts, because of the small quantities available.

Ebler (3) investigated the sediment from the Max Spring at Dürkheim, Germany, and found it very highly active. At this point, it might be of interest to quote rather fully from his paper:

> This particular spring is the one in whose water rubidium and caesium were first discovered, hence one might hope to find the sixth alkali metal here.
>
> The sediment from the spring is chiefly remarkable for its high radioactivity, its high arsenic content, and the large quantity of it. The spring deposits 20 kgm. of sediment every twenty-four hours.
>
> After solution of the sediment in aqua regia, and removal of all of the elements up to the alkaline earths, it is found that the mother liquor is highly active. On further removal of the alkaline earths, it is found that these are inactive; in other words, the active substance is in the solution which now contains only the alkali metals. In attempting to concentrate the solution of the alkali metals, it was found that the crystals last obtained showed only a weak activity, i.e., much weaker than the original mother liquor would lead one to expect.

When several kilogrammes of the aqueous solution, acidified with hydrochloric acid, were steam-distilled, the distillate was very strongly active, while the steam distilled solution showed only a slight activity. On standing, the latter regained almost all of its former activity, and the former decreased in activity but did not entirely lose it. A portion of the radioactive substance was evidently volatile with steam. A quantitative test showed that the amount by which the mother liquor decreased in activity (from its original value) was equal to the activity of the distillate.

Electrolysis of the radioactive distillate, using a mercury cathode, caused the mercury to become radioactive. On washing the amalgam with water, the mercury became inactive, and the wash-water highly active. When some of the active amalgam was covered with a saturated solution of caesium chloride, it was found that the caesium had formed an amalgam with the mercury. (Care was taken that no CsCl solution adhered to the mercury.) A blank test with ordinary mercury (inactive) showed no trace of a Cs amalgam. Thus the active substance displaced caesium from a salt, yet caesium is the most electropositive of all metals. This could only occur if the unknown metal were more electropositive than caesium.

Practically all of the investigators since the publication of Ebler's paper have dismissed it with a line or two to the effect that Ebler must have been mistaken. It would seem a relatively simple matter either to corroborate or to refute Ebler's claims, yet no one has taken the trouble to do so.

T. W. Richards and Archibald (20) reported that, in the purification of caesium salts (which were the purest obtainable) for atomic weight determinations, no trace of the missing alkali element was observed. Baxter (21) examined pollux (the commonest caesium mineral) from Paris, Maine, for the missing element, but failed to find it. Dennis and Wyckoff (22) examined various fractions of the alkali chlorides obtained from pollux (from Auburn, Main) spectrographically in the red, visible and the ultra-violet regions, but failed to find any trace of the missing alkali element.

Recently, Druce and Loring (28) have laid claim to the discovery of several of the missing elements, including number 87. They prepared impure rhenium oxide from commercial manganese sulfate, and used this in the usual X-ray method. To quote from their paper: "The method employed consisted in exciting the characteristic X-radiations of the elements present in the sample, spreading these into a spectrum by the Bragg method of reflection at a crystal plane, and recording the lines photographically." Later, they claim to have isolated more of 87 from a sample of pyrolusite, and found the chemical properties of this element resembling the expected ones. Just what the details were, is not stated. Under "Current Topics and Events" in the December 26 issue of *Nature*, a contributor questions the validity of the claims made by Druce and Loring, and points out a number of discrepancies in their statements. The only conclusion to be drawn at the present writing is that the identification of element number 87 is still very doubtful. Certainly nothing definite is known about its radioactive properties.

Zwaardemaker (2) believes the activity of caesium to be due to a higher member of the alkali metal group. Hoffmann (5) investigated pollux and found it inactive. It might be mentioned that Hoffmann's work is extremely accurate, as he eliminated a great many of the usual sources of error in making his measurements.

Lachs (23) was the first to point out that, if potassium and rubidium are radioactive, their disintegration products must be isotopic with calcium and strontium respectively, in accordance with the Soddy-Fajans disintegration law. Hahn and Rothenbach (4) calculated that the half-life of rubidium is 10^{11} years, and that of potassium about three times as great. On this basis, it would be very difficult to detect any calcium isotope of atomic weight 39 or 41, even in potassium minerals of the greatest age. It would be somewhat simpler to detect the strontium isotope of atomic weight 85 or 87, but unfortunately we have no rubidium minerals as such, the rubidium being fairly well scattered. Kossel (24) suggested that only one of the potassium isotopes might be radioactive, and suggested the one of atomic weight 43. As Harkins and Guy (15) point out, no isotope of that atomic weight has been found to exist. Harkins and Guy, on the basis of Harkins' studies on isotopic numbers, are led to believe that the isotope of potassium of atomic weight 40 or 41 is responsible. (The isotope of atomic weight 40 has not been found in positive ray work.) Up to the present only the two isotopes of calcium, atomic weights 40 and 44, have been found by Aston (25); and only two of strontium, 88 and 86 (in the order of their intensities). No systematic investigation of the calcium content of potassium minerals by means of the mass-spectrograph has been published, if, indeed, an investigation of this sort has ever been undertaken.

The objection to the theory that the presence of the sixth alkali metal causes the activity of potassium and rubidium, viz., that one would expect this unknown alkali metal to be associated with caesium, is somewhat weakened by Ebler's findings. The objection is strengthened by the findings of Richards and Archibald, Baxter, and Dennis and Wyckoff.

The objections to the theory that potassium and rubidium are intrinsically active, might be taken as arguments in favor of the theory that the emission of photo-electrons is the cause of the apparent "radioactivity" of these elements. The fact that caesium, the most electro-positive of all of the known elements, is not active in pollux argues against this, as does the fact that lithium and sodium have consistently been reported as "inactive." The photo-electric effect places the alkali metals in the series $Cs > Rb > K > Na > Li$, whereas the radioactivity series is $Rb > K > Cs > Na > Li$. Furthermore, while studying the photographic effect of potassium and rubidium salts, Büchner (17) found that the plates darkened even when Rb_2SO_4 was dissolved in water, and evaporated to dryness in the dark. Later he kept some of his samples in the dark for six months, and found them still "active." This seems conclusive evidence against the "photo-electric" theory of activity.

None of the alkali metals has been found to emit alpha particles although R. J. Strutt (26) found that a number of beryls contain helium far in excess of that expected from the content of radium or thorium compounds. Piutti (27) examined 26 beryls spectroscopically, and found the helium spectrum well-defined in all of them, although not all of the samples were radioactive. The helium does not seem traceable to the alkali metals, or at least, alpha rays, if emitted by them, are extremely slow, and have not, as yet, been detected.

SUMMARY

From the above review of the literature on the radioactivity of the alkali metals, the following are the only definite conclusions that may be drawn:

a. Lithium and sodium do not show any radioactivity.

b. Potassium and rubidium salts emit heterogeneous beta rays.

c. No alkali metal emits detectable alpha particles.

The following questions still remain unanswered:

a. What are the absorption coefficients in aluminium of the two beta radiations from potassium?

b. What disintegrations cause the heterogeneity of the rays from potassium and rubidium?

c. Is caesium active?

d. Can a sixth alkali metal be isolated from the salts of the others? Is it radioactive?

e. If the sixth alkali element cannot be discovered, do isotopes of calcium of atomic weights 39 and 41, and isotopes of strontium with atomic weights of 85 and 87, exist?

f. What is the source of the helium in the beryls?

BIBLIOGRAPHY

(1) Campbell and Wood, Proc. Cambridge Phil. Soc. **14**, 15, (1906).
(2) Zwaardemaker, Proc. Amsterdam Acad. Sci. **26**, 575, (1923).
(3) Ebler, Zeit. angew. Chem. **21**, 737, (1908).
(4) Hahn and Rothenbach, Physik. Zeit. **20**, 194, (1919).
(5) Hoffmann, Physik. Zeit. **24**, 475, (1923); Zeit. Physik, **25**, 177, (1924).
(6) Campbell, Proc. Cambridge Phil. Soc. **15**, 557, (1908).
(7) McLennan and Kennedy, Phil. Mag. **16**, 377, (1908).
(8) Biltz and Marcus, Zeit. anorg. Chem. **81**, 369, (1913).
(9) Scott, "Standard Methods of Chemical Analysis," 2 ed. D. Van Nostrand and Co., New York, (1917), p. 355.
(10) Scott, ibid. p. 356.
(11) Henriot, Ann. chim. phys. **26**, 54, (1913).
(12) Elster and Geitel, Physik. Zeit. **11**, 215, (1910).

(13) Strong, Am. Chem. Jour. **42**, 147, (1909); Phys. Rev. **29**, 170, (1909).
(14) Levin and Ruer, Physik. Zeit. **10**, 576, (1910).
(15) Harkins and Guy, Proc. Nat. Acad. Sciences **11**, 628, (1925).
(16) Campbell, Proc. Cambridge, Phil. Soc. **15**, 11, (1908).
(17) Büchner, Proc. Amsterdam Acad. Sci. **18**, 91, (1909); Chem. Abstr. **6**, 3226, (1912).
(18) Ringer, Physiol. Abstr. **7**, 83.
(19) Elster and Geitel, Jahrbuch f. Rad. Elek. **10**, 323, (1913).
(20) Richards and Archibald, Proc. Am. Acad. **38**, 443, (1903).
(21) Baxter, Jour. Am. Chem. Soc. **37**, 286, (1915).
(22) Dennis and Wyckoff, ibid. **42**, 985, (1920).
(23) Lachs, Beiblätter Ann. Physik. **40**, 207, (1915).
(24) Kossel, Physik. Zeit. **20**, 265, (1919).
(25) Aston, "Isotopes," 2 ed., Ed. Arnold, London, (1924).
(26) Strutt, Proc. Roy. Soc. A. **80**, 587, (1908).
(27) Piutti, Atti. accad. Lincei, **22**, 140; Chem. Abstr. **7**, 2352, 3076, (1913).
(28) Druce and Loring, Chem. News, vol. 131, Oct. 30, Nov. 6, 13, 20, 30, 1925.
(29) Nature, **116**, 943, (Dec. 26, 1925).