

J. N. BRØNSTED MEMORIAL ISSUE

*(Dedicated to the memory of the great scholar and experimenter,
the late Professor J. N. Brønsted)*

The Application of Brønsted's Method of Isotope Separation to the Study of the Natural Radioactivity of Potassium

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The late Professor Brønsted has shown a great interest in the application of his method of isotope separation to the determination of the isotope (or isotopes) responsible for the natural radioactivity of potassium. This fact induced the author to present a survey of these investigations.

The first separation of isotopes was carried out by Aston¹. He started from 100 ml of neon and obtained, by diffusion through ripe clay, after thousands of operations two extreme fractions of 2 to 3 ml, showing the densities 20.15 and 20.28. When continuing the work by means of an automatic apparatus which was expected to permit a much more effective separation, the separation of neon isotopes achieved was only half of that attained previously, although the apparatus performed the mechanical operations of diffusion many thousands of times in a satisfactory manner. This failure was very fortunate since it induced Aston² to give up the plan of separating isotopes on a preparative scale and to concentrate on the much more accurate analysis of positive rays in proving the existence of isotopes among the elements in general, which he succeeded in accomplishing to such a remarkable extent. While the proof of the existence of isotopes was established through Aston's work it seemed to be of importance to carry out a separation on a preparative scale and to compare the result with that expected on the basis of theoretic considerations. This work was carried out by Brønsted and assoc.³

BRØNSTED'S METHODS OF SEPARATION

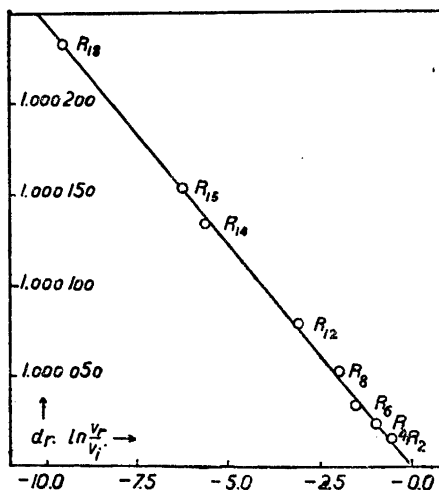
Two different methods were introduced. a) Separation by making use of the difference in the evaporation velocities of isotopes (ideal distillation); b) a fraction of the mercury vapour penetrates through narrow openings in the condensation space, where the lighter isotope is found in a relatively larger

amount than in the ordinary mercury (effusion method). Even if we disregard the small difference of the vapour-pressure of two isotopes we can expect evaporation under suitable conditions to lead to a livelier exchange between the lighter than between the heavier atoms in the two phases. The former have, namely, in accordance with their smaller mass (m_1), a velocity (v_1) $\sqrt{\frac{m_2}{m_1}}$ times as great as the latter — the mass and velocity of which we will denote by m_2 , and v_2 — respectively, and thus in the time-unit $\sqrt{\frac{m_2}{m_1}}$ times as many molecules of the lighter as of the heavier isotope will be transferred from the liquid into the vaporous stage, and vice versa. As long as evaporation under usual conditions is considered, we are not able to utilize the quicker movements of the lighter molecules to an appreciable extent for the purpose of separating isotopes, because the quicker evaporation in the case of the lighter molecules is just counterbalanced by a quicker re-condensation. We can, however, prevent this effect by suppressing one of the two compensating processes. This is most easily accomplished by allowing the liquid to evaporate in a vacuum and placing a well cooled glass plate over its surface. Now, when the vapour-pressure of the liquid is sufficiently low, each molecule which leaves the liquid will reach the cooled wall before it has had an opportunity of meeting other molecules and being thrown back into the liquid. Having reached the cooled wall, it will be held by it, transferred into the solid state, and hindered in re-evaporation. It follows from the above that in the 'ideal distillate' obtained in this way there will be $\sqrt{\frac{m_2}{m_1}}$ times as much of the lighter isotope as in the initial substance, and through repeated 'ideal distillations' of the fractions thus obtained it is possible to carry the partial separation further. When 2700 ml of mercury were distilled, the residual fractions were shown to have the values to be expected from the considerations outlined above, as seen in Fig. 1.

Furthermore, the results of density measurements were corroborated by measurements of the atomic weight of the light and heavy mercury fractions obtained. Brønsted's work was thus the first in which the separation of isotopes on a preparative scale was unambiguously obtained, the claim of separation being based not only on a deviation of the density of a separated sample from that of a normal one, which might be due to the presence of minute impurities, but on a coincidence between the experimental values and those calculated from the kinetic theory of evaporation.

After the method of ideal distillation was successfully used by Brønsted and assoc.⁴ for the separation of the isotopes of chlorine, concentrated solu-

Fig. 1. Separation of mercury isotopes. — Density of mercury plotted as ordinate, the abscissa representing the natural logarithm of the ratio of the remainder and the initial volume.



tions of hydrochloric acid being distilled, attempts were made to carry out a partial separation of the isotopes of potassium. The investigation of the radioactivity of the fractions obtained was expected to elucidate whether the natural radioactivity of potassium is due to the main isotope K 39 or to a minor constituent of the mixed element potassium.

SEPARATION OF THE ISOTOPES OF POTASSIUM

In their work on the separation of the isotopes of potassium the present author and Lögstrup⁵ distilled about 1 kg of metallic potassium in a pyrex bulb, the bottom of which was heated, while its top was cooled with solid carbon dioxide. The distillation was carried out as calculated from Knudsen's formula

$$p = \frac{G \sqrt{\frac{T}{M}}}{43.7 \times 10^{-6}}$$

where G is the number of grams distilled per second and M is the molecular weight of the potassium vapour, at a temperature of 160° C. The mean free path of potassium atoms was thus shorter than the distance between the warm and the cold surface (< 1 cm). When the potassium residue was reduced to a few ml, the distillation was stopped and the residue shunted to another bulb inserted in the evacuated system. The distillation of the main potassium

fraction was then repeated. The combined residues consisted of 25 g of 'heavy' potassium. This 'heavy' potassium was converted into chloride, purified, and its radioactivity and atomic weight determined.

Potassium contains 93.4 % of K 39 and 6.6 % of K 40. Let us assume that the atomic weight determination indicates that the 'heavy' potassium has a K 41 content increased by 10 %. If K were responsible for the radioactivity of potassium, the activity of the 'heavy' sample would have increased by 10 % as well. If, however, K 39 is the radioactive isotope, the 'heavy' sample should show an activity decreased by 0.71 %. A third possibility is that the isotope K 40 (not yet discovered at the time when the described investigations were started) is responsible for the radioactivity of potassium. In this case, if the atomic weight determination indicates an increase by 10 % in the K 41 content of the sample, the increase in radioactivity will amount to 5 % only.

The atomic weight determination carried out by Hönigschmid and Goubeau ⁶ indicated an increase by 4.8 % in the K 41 content of the 'heavy' sample; radioactive determinations carried out first by using the Hoffmann electrometer indicated a difference of 4.2 % in the radioactivity of the samples and, using the Geiger-Müller tube in extended measurements, a value of 4.43 ± 0.5 % was found (Hevesy ⁷). From these figures it had to be concluded that the radioactivity of potassium is due to its K 41 content.

In view of the fact that the value obtained by Baxter for the atomic weight of *normal* potassium was appreciably lower (39.096) than the value found by Hönigschmid and Goubeau (39.104), Professor Baxter kindly offered to compare the atomic weight of the 'heavy' sample with that of normal potassium. He (Baxter ⁸) found a very much larger increase in the K 41 content of the heavy sample, namely 10.6 %, than did Hönigschmid and Goubeau ⁶. In view of the much greater difference between the increase in the concentration of the isotope 41 in the heavy sample than in the increase of its radioactivity, Baxter's figure leads to the conclusion that the radioactivity of potassium is due to a lighter isotope than K 41 and a heavier isotope than K 39, thus that K 40 is responsible for the radioactivity of potassium. In view of the striking difference between the results obtained by the two greatest authorities in the field of atomic weight determination, it was imperative to attempt another approach.

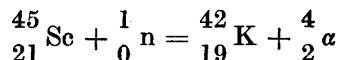
SEARCH FOR CALCIUM 41

From the number of β -particles emitted by 1 g potassium it follows that 1 g potassium produced since the earth-crust solidified about 10^{-4} g calcium. Should the radioactivity of potassium be due to potassium 41, the decay of

this isotope in old minerals would produce detectable amounts of calcium 41. This reasoning induced the separation of calcium of apatite from Bamble, Norway (Hevesy⁹). This apatite of very considerable age has a potassium content of 6.5 % and a calcium content of less than 0.05 %. A decay of minute traces of the potassium present during geological times thus should have produced calcium 41 in sufficient amounts to be discernable in the mass spectrum of calcium isolated from biotite. Aston could not find any indication of the presence of calcium 41 secured in our sample from Bamble apatite. This result suggests that either K 41 is not radioactive or Ca 41 has a short life-time.

ARTIFICIAL PRODUCTION OF K 42

Amaldi and assoc.¹⁴ observed, when bombarding potassium with neutrons, the formation of an artificially radioactive potassium isotope decaying with a period of about 1/2 day. When, later, the same isotope was obtained by bombardment of scandium according to the reaction



the mass-number of the radioactive potassium isotope could be determined to be 42 (Hevesy¹⁰).

The fact that the bombardment of potassium 41 with neutrons leads to the formation of potassium 42 made it quite probable that the ex-terrestrial bombardment of potassium 39 with neutrons leads to the formation of potassium 40 and that the radioactivity of potassium is due to this isotope (Hevesy¹¹).

RESULT OF MASS-SPECTROSCOPIC INVESTIGATIONS

At the time when the above described partial separation of the potassium isotopes was carried out the sensitivity of the mass-spectroscopic method did not suffice to replace the atomic weight measurement of the fractions obtained by mass-spectroscopic determinations. Great progress was, however, achieved in recent years in the field of mass-spectroscopy and during the war Paul and Pahl¹² compared the K 39: K 40 ratio of the 'heavy' fraction obtained by Brønsted's method with that of normal potassium and found an increase of 8.7 % in the K 41 content of the heavy sample. From this figure and from that of the change in the K 39 content of the heavy fraction (— 0.62 %) the extent of concentration of the K 40 content of the sample was inter-

olated. The value obtained for the increase in the K 40 content 4.0 ± 0.5 % compares well with that obtained for the increase in the radioactivity of the sample (4.3 %), showing thus K 40, and this isotope alone, to be responsible for the natural radioactivity of potassium.

Brønsted's method thus permitted the determination of the mass-number of the isotope responsible for the natural radioactivity of potassium.

That potassium 40 is radioactive was also shown by Smythe and Hemmendinger¹³ who prepared minute amounts of K 40 by means of the mass-spectrograph and showed this, and this isotope only, to be radioactive.

SUMMARY

The results obtained in the application of Brønsted's method to the determination of the isotope responsible for the natural radioactivity of potassium are reviewed.

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