work. No previous magnetic work seems to have been done on other chromous complexes.

The authors wish to acknowledge the kind assistance of Dr. Charles D. Coryell, whose generous coöperation has made the magnetic measurements possible.

Summary

Three new complex compounds of divalent chromium have been prepared: monopyridino chromous acetate, chromous anthranilate, and chromous 8-hydroxyquinolate. The magnetic properties of a number of other chromous complexes have been studied. The free ion and the ammonia, ethylenediamine, and thiocyanate complexes contain four unpaired electrons with presumably ionic bonds being formed. The chromocyanide complex has two unpaired electrons, indicating octahedral covalent bond formation.

LOS ANGELES, CALIFORNIA RECEIVED DECEMBER 31, 1940

[JOINT CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY,* NO. 86, AND THE GEORGE EASTMAN LABORATORY OF PHYSICS,† MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Radioactive Determination of the Relative Abundance of the Isotope K^{40} in Terrestrial and Meteoritic Potassium[1]

BY W. C. SCHUMB,* R. D. EVANS† AND W. M. LEADERS*

The use of radioactive substances in determining ages of rocks and other geological formations is well known. In the present work, the age of the potassium atoms in the Pultusk meteorite in relation to the age of potassium atoms in the earth has been determined by the use of the long-lived beta emitter, potassium, *viz.*, K^{40}. This was accomplished by the separation and comparative study of the specific activity of potassium chloride obtained from the meteorite and from a pure terrestrial sample.

The Pultusk meteorite is listed in von Niessl and Hoffmeister's[2] catalog of fireballs as having an hyperbolic orbit. More recent work, however,[3] has led to the opposite opinion, indicating that the meteoritic fragment used is of solar system origin and not extra-solar as previously supposed.

This work is based on the assumption that the abundance ratios of the isotopes of each element are the same at the time of their formation, no matter where in the universe the formation occurred. A number of investigations of isotopic abundance ratios have been made on meteorites[4] and in no case has the ratio obtained differed from that found for the corresponding element in terrestrial material. In the case of the Pultusk meteorite, the isotopic abundance ratio of O^{16} to O^{18} has been determined[5] and is reported as the same as that found for terrestrial oxygen; and the same is true[4] for the ratio of $U^{238}:U^{235}$.

The chemical separation of potassium is based on the low solubility of potassium perchlorate in alcohol as compared with other perchlorates. The only hindering feature is the even lower solubility of rubidium perchlorate in alcohol. The presence of an appreciable amount of rubidium would make this method inoperative, because of the radioactivity of the rubidium isotope, Rb^{87}, but when the amount of rubidium is 1% or less of the potassium present, the method should be applicable.

The Geiger–Müller counter used in the radioactivity measurement was of the "bell" type (Fig. 1). Except for minor changes, the amplifier circuit, power supplies, and drum camera-galvanometer recorder used in this work are the same as those developed by Evans and Alder.[6] The finely ground potassium chloride was placed in a cylindrical well in a small brass disk (D in Fig. 1) and leveled by shaking and rocking. This is brought into close proximity to the thin (21 micron) mica window of the counter. Nearly all of the salt used in such a determination can be recovered effectively and used again. In this manner, one-half gram of salt can be used in dozens of measurements.

Chemical Method.—The procedure used in the separation of the potassium from the meteorite was an adaptation of a method given by Morgan[7] and later by Green.[8]

After the meteoritic sample of about 10 g. had been thoroughly disintegrated by treatment with 47% hydrofluoric acid and the excess hydrogen fluoride removed, the large iron and magnesium content was precipitated by

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(1) From a thesis submitted by W. M. Leaders in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Massachusetts Institute of Technology, June, 1940.

(2) Von Niessl and Hoffmeister; *Denksehr. d. Akad. Wiss. Wien, Math. natw. Kl.*, **100**, 1-70 (1926).

(3) C. C. Wylie, *Science*, **9**, 264 (1939).

(4) *Cf.* Schumb, Evans and Hastings, THIS JOURNAL, **61**, 3451 (1939), and other references given therein.

(5) Manian, Urey and Bleakney, *ibid.*, **56**, 2601 (1934).

(6) Evans and Alder, *Rev. Sci. Instruments*, **10**, 332 (1939).

(7) J. J. Morgan, *Ind. Eng. Chem.*, **13**, 225 (1921).

(8) M. M. Green, *ibid.*, **15**, 163 (1923).

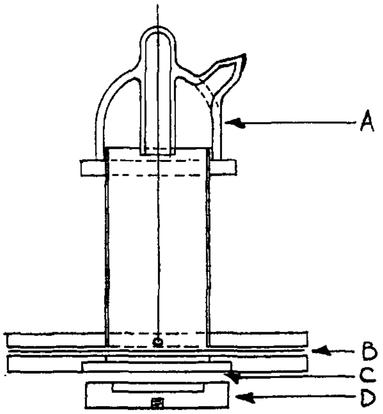

Fig. 1.—"Bell" type Geiger–Müller counter and sample holder in half section. The counter is filled with dry air at a pressure of 60 mm. of mercury. All parts are of brass except A which is a glass top cemented to the tube. B is the mica window held in place with machine screws and picein cement. C is machined to receive the sample holder D and ensures uniform geometry to the sample and counter system. The window aperture in C is one inch in diameter.

ammonium hydroxide and ammonium bicarbonate. The filtrate from this separation is evaporated to dryness in platinum and the excess ammonium salts carefully decomposed. The residue is then treated with perchloric acid in the manner of Morgan and Green. This treatment is repeated until a constant weight of the final perchlorate indicates the purity of the product. The potassium perchlorate obtained from several of these separations is combined and submitted once more to the perchloric acid-alcohol separation to ensure uniformity of the final product, which is then transferred to a quartz dish and decomposed at 550°,[9] leaving the chloride.

Great care was exercised in the choice of reagents in order that none would be used that had come into contact with any terrestrial potassium during its preparation.

Samples Used.—The terrestrial samples of potassium chloride used in this work were Merck C. P. reagent.[10] The meteoritic samples of potassium chloride were separated from the center portion of specimens of the Pultusk meteorite obtained from the Field Museum of Natural History, through the courtesy of Dr. C. G. Gregg and Mr. H. W. Nichols.

A spectroscopic analysis was made on both samples of potassium chloride used. The results of these analyses showed that the terrestrial sample was very pure (99.8 + %) and contained less than 0.01% rubidium. The meteoritic potassium chloride had an estimated upper limit of 0.75% impurity, the major impurity being calcium. Since rubidium is about 30 times more active than potassium, the 0.15% present could account for a 4.50% increase in the observed count if *all* the available rays were detected. Not more than 50% can be detected, however, due to the 21-micron mica window which has a stopping power equivalent to 50,000 volts and excludes those beta rays of rubidium which have less than this energy. Therefore, the rubidium present could not account for more than 2.25% error. Since this is within the 2.9% statistical error, no correction was made in the subsequent calculations for the presence of rubidium.

Calculations and Results.—Data obtained from the counting rate meter consisted of two parts: (1) combined count of a weighed sample of potassium chloride and background; and (2) count of background alone. Four runs of five minutes each were made on each sample,

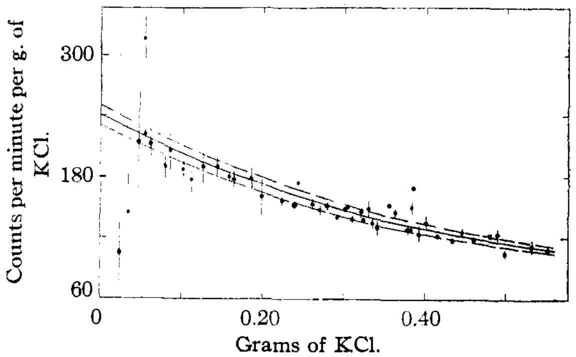

Fig. 2.—The ordinates were obtained by dividing the observed counts per minute of a given sample by the sample weight. The tails are indications of the probable error of each point.

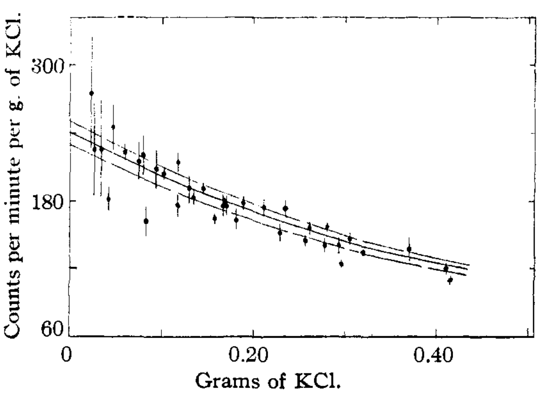

Fig. 3.—Points were obtained in the same manner as in Fig. 2.

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(9) In this procedure we were aided by information made available to us by Prof. G. G. Marvin of this Institute concerning unpublished work on the decomposition of various perchlorates.

(10) Although the manufacturers were unable to trace the source of this potassium chloride, they feel quite certain that it is of German origin. The work of Biltz and Marcus (*Z. anorg. Chem.*, **81**, 369 (1913)) indicates that there is no appreciable difference between the specific radioactivity of terrestrial potassium from a wide variety of mineral sources.

and two runs of five minutes on background were made before and after each sample.

When it was found that the daily averages of the background runs were statistically distributed about a mean value, they were all combined.

The probable errors were calculated from the squares of the residuals, and the calculations on propagation of errors were carried out according to standard procedure.[11]

Figures 2 and 3 graphically represent the data obtained during the course of this work. Figure 2 shows the data for terrestrial potassium chloride and Fig. 3 for the meteoritic samples. The extrapolated intercept for the terrestrial samples is 240 counts per minute per gram of potassium chloride with a probable error of ±10 counts per minute. The extrapolated intercept for the meteoritic samples is likewise 240 counts per minute per gram of potassium chloride with a probable error of ±10 counts per minute. It should be pointed out that the entire curves of Figs. 2 and 3 can be nearly superimposed, further demonstrating the essential equality of the two sets of data irrespective of the extrapolated intercepts.

The ratio of these intercepts gives the ratio of the amounts of K^{40} present, and also determines the relative ages of the two samples. The two intercepts obtained from Figs. 2 and 3 give the ratio, $K_e/K_m = 1.000 \pm 0.029$, showing that within the limit of statistical error, the ratio of the amounts of K^{40} present, and, therefore, the age of the two samples, are the same.

Evans[12] has developed the following equation for determining the difference between the ages in years, which depends upon the mean life of the potassium isotope K^{40}:

$$t_m - t_e = 6.0 \times 10^9 \log (K_e/K_m) \qquad (1)$$

where the subscripts *m* refer to the meteoritic values and subscripts *e* to the terrestrial. Using our ratio of K_e/K_m we find the difference in age to be $(0.0 \pm 7.4) \times 10^7$ years; that is, again the ages of the two specimens are the same within the limit of error.

During the course of this work a total of 93.0411 g. of meteorite was used as a source of potassium. From this material 0.4145 g. of potassium chloride was recovered. This amounts to 0.28% potassium oxide in the rock.[13]

Summary

1. Potassium chloride was separated from a sample of the Pultusk meteorite and its beta activity was compared with that of a terrestrial sample. Spectroscopic analyses indicated the two samples to be of high purity.

2. The results indicate no difference in the proportion of K^{40} present in the two cases and, therefore, no difference in age within the limits of statistical error.

3. A technique in sample mounting has been perfected which is especially useful in cases where a sample of low activity can be obtained in weighable amounts.

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[11] R. T. Birge, *Am. Phys. Teacher*, **7**, 351-357 (1939).

[12] R. D. Evans, *Pop. Astronomy*, **46**, 159-170 (1938).

[13] Although the method used for the extraction of potassium was not 100% efficient, it is reasonable to assume that from 80 to 90% of the total potassium present was finally obtained. Thus, the percentage of K_2O reported here must be slightly lower than the correct value. The only other value reported for K_2O is 0.39% as determined by R. Rammelsberg in 1870.[14]

[14] O. C. Farrington, *Field Museum of Natural History, Geological Series*, **3**, 195-229 (1911).