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Electrostatic Radionuclide Separation

A New Version of Rutherford's "Thorium Cow"

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As early as 1900, E. Rutherford (*1*) reported on the discovery of a gaseous α-radioactive substance emanating from thorium compounds. In a second paper in the same journal (*2*) he described a simple device to concentrate the daughter products by precipitation on a charged electrode [Fig. 1].

This device, which was later called "thorium cow," may be used in a number of instructive experiments in the undergraduate laboratory. These experiments, which will be described hereafter, produce results which are of practical and theoretical value in undergraduate instruction. They may also be used in lecture demonstrations.

Experiment 1

Successive α-decay of the partial chain

$$^{220}\mathrm{Rn} \xrightarrow[55.6\ \mathrm{s}]{\alpha} {}^{216}\mathrm{Po} \xrightarrow[0.15\ \mathrm{s}]{\alpha} {}^{212}\mathrm{Pb}$$

Part of the Th ($4n$) decay series relevant to this work is given in Figure 2.

^{220}Rn decays with a half-life of 55.6 s to ^{216}Po. This in turn decays with a half-life of 0.15 s to ^{212}Pb. If therefore a carrier-gas containing ^{220}Rn is introduced into a cloud chamber these two decay events show up as two α-tracks, forming a "V."

Procedure

Approximately 500 mg ThO_2 (see below) is placed into a small glass tube (ID 4–5 mm, 5 cm long) and kept in place by means of two cotton or glass wool wads. One end of the glass tube is connected to a rubber hose which leads into the sensitive region of a continuous cloud chamber. The other end of the tube is connected to a small rubber ball. When the rubber ball is squeezed, the air in its interior is expelled and passes over the thorium compound into the cloud chamber, carrying the ^{220}Rn which has accumulated over the thorium salt. After initial turbulence around the gas entry, the cloud chamber atmosphere calms down, and a large number of α-tracks are observed (Fig. 3), which spread across the whole interior of the chamber. Because of the short half-life of ^{220}Rn, the number of α-tracks diminishes rapidly within the next 2–3 min, so that individual events may be studied more leisurely (Figs. 4 and 5). The V-shaped tracks observed are explained easily below.

The α-decay observed occurs according to the following general scheme

$$^{A}_{Z}\mathrm{X} \rightarrow {}^{A-4}_{Z-2}\mathrm{Y} + \alpha \qquad (1)$$

where A = number of nucleons, and Z = atomic number. The reaction energy Q may be calculated as follows:

$$Q = (m_n[{}^{A}_{Z}\mathrm{X}] - m_n[{}^{A-4}_{Z-2}\mathrm{Y}] - m_n[{}^{4}_{2}\mathrm{He}]) \cdot c_0^2 \qquad (2)$$

where also

$$Q = E_\alpha + E_\mathrm{Y} \qquad (3)$$

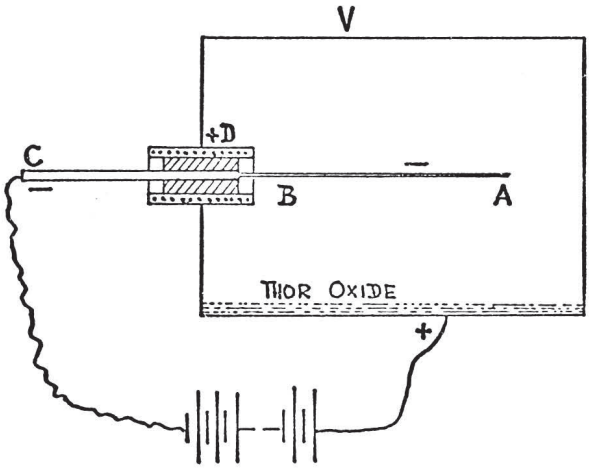

Figure 1. Rutherford's first depositing apparatus (thorium cow) from reference (*2*).

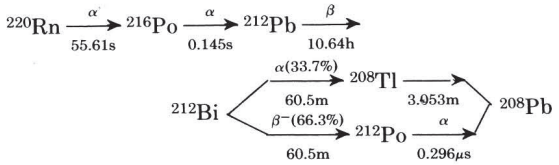

Figure 2. Part of the ^{232}Th decay series of interest in this work.

In accordance with the classic laws of preservation of momentum and energy, E_α and E_Y may be defined as follows:

$$E_\alpha = Q \cdot \frac{m_n[{}^{A-4}_{Z-2}\mathrm{Y}]}{m_n[{}^{4}_{2}\mathrm{He}] + m_n[{}^{A-4}_{Z-2}\mathrm{Y}]} \qquad (4)$$

and

$$E_\mathrm{Y} = Q \cdot \frac{m_n[{}^{4}_{2}\mathrm{He}]}{m_n[{}^{4}_{2}\mathrm{He}] + m_n[{}^{A-4}_{Z-2}\mathrm{Y}]} \qquad (5)$$

Numerical evaluation of eqns. (4) and (5) shows that approximately 98% of the energy Q is dissipated to the α particle, but only approximately 2% to the resulting daughter nucleus. This daughter nucleus undergoes a recoil; however, its track is so short that it is barely visible in the cloud chamber before the second α-decay takes place. Even though the α-decay energies of ^{220}Rn (6.288 MeV) and ^{216}Po (6.7783 MeV) differ by only 0.5 MeV, the tracks of the two successive α's usually appear to have a different length, probably due to the different

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Figure 3. Cloud chamber photograph with many α-tracks.

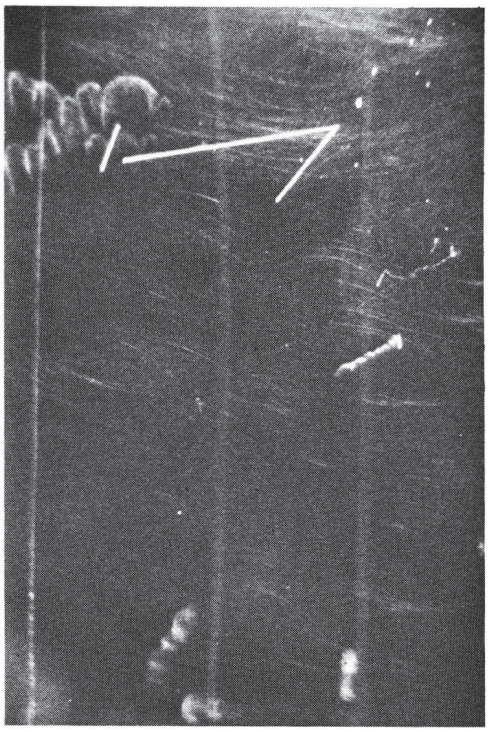

Figure 4. Cloud chamber photograph taken 2 min later than Figure 3—few α-tracks, one of them V-shaped.

observation angle, or because the particle causing the shorter track escapes from the sensitive region of the cloud chamber.

Experiment 2. Carrier-free Isolation of ^{220}Rn Daughters

Since the recoil nuclei formed in the ^{220}Rn α-decay are electrically charged,[2] they may be collected on a suitable surface, having the appropriate charge. The yield is different, depending on whether the wire or the body of the chamber (Fig. 1) is chosen as the cathode. A carrier-free isolation of the ^{220}Rn granddaughter ^{212}Pb, and its greatgranddaughter ^{212}Bi may be carried out using the apparatus developed by B. Heinrich (*3*) or that by R. Schwankner (*4*, *5*). Since the ^{220}Rn granddaughter may be continuously "milked" from the setup, the latter is sometimes referred to as a "thorium cow."

An Erlenmeyer flask with narrow neck is coated on its inside surface with strips of aluminum foil. The individual strips have to be in electrical contact with each other, and should project for ~2 cm beyond the rim of the flask's neck. The "collar" formed in this manner is turned down on the outside and is fixed to the wall of the flask with a clean wire loop. An anode wire is soldered to this loop, and then the whole aluminum collar is insulated with plastic tape. The exchangeable, well-insulated cathode assembly consists of a rubber stopper equipped with a well-centered hole, into which a banana plug is inserted and connected to the cathode wire. A crocodile clamp connected to a piece of Pt foil is clamped to this plug (see Fig. 6). For safety reasons, the required high voltage [0.1 to 1 kV] is connected to the apparatus by means of a 100 kΩ resistor which is connected in line with the apparatus. Finely divided (ground) ThO_2 is recommended as the emanating material; coarse ThO_2 or other Th compounds have a considerably lower emanating power, so that they have to be converted to a highly emanating source (*5*).

Since the emanating power of the ThO_2 may differ within a wide range depending on its previous history and on several other parameters (deposition voltage, geometry of the assembly, size of Pt-electrode), we have constructed an apparatus which allows a continuous measurement of the ^{212}Pb deposit and its daughter. This apparatus may be considered as a modified "thorium cow," which is equipped with a side arm through which a continuous measurement and reading of the cathode deposit activity is possible throughout the whole deposition period. This technique also allows us to measure the equilibrium value (saturation value), which is attained by competition between deposition value and decay value for the predetermined parameters.

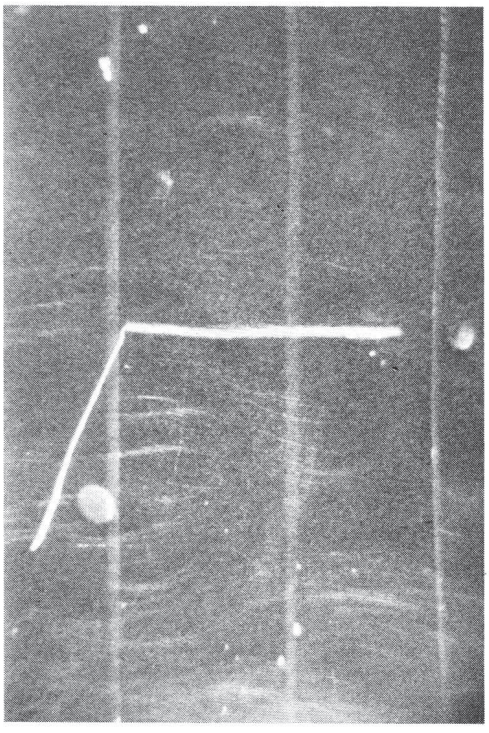

Figure 5. Cloud chamber photograph with another typical V-shaped α-track.

Using a 200-ml wide-necked Erlenmeyer flask, we obtained the following optimum values for the individual parameters: DC high voltage: 500–600 V; emanating substance: ~10 g of ThO_2; area of cathode: ~3 cm^2; saturation time ~70 hr; recommended minimum deposition time 24 hr. If more than one experiment is planned with the ^{220}Rn daughter products de-

[2] Due to strip-off effect by collision with air molecules.

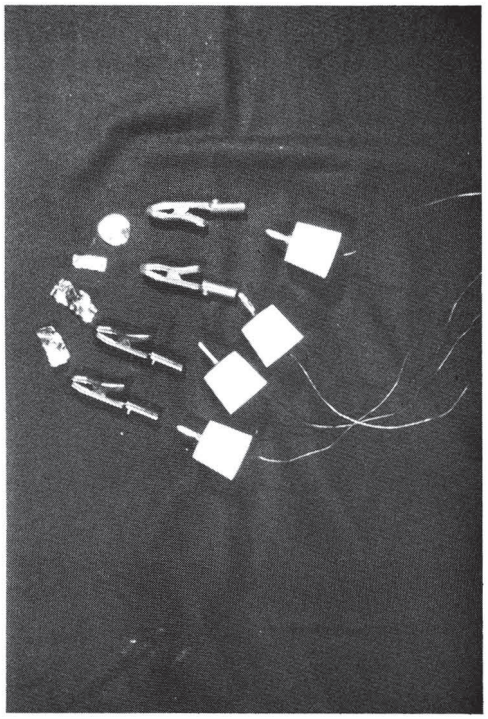

Figure 6. Exploded view of depositing apparatus.

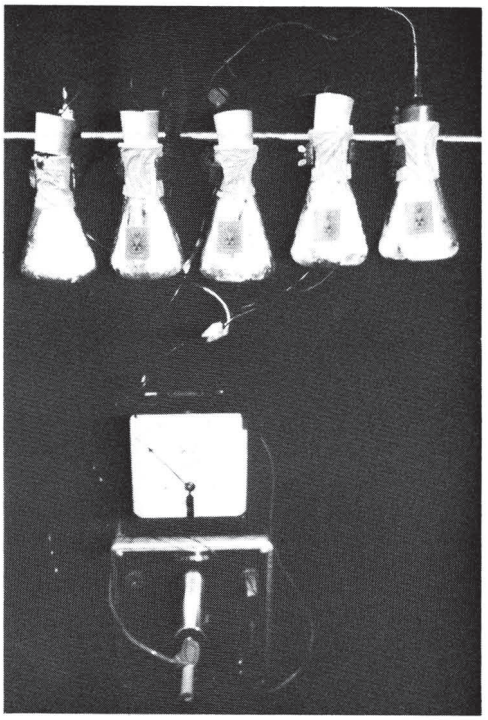

Figure 7. Five depositing units in operation.

posited, several of the "thorium cows" may be connected in parallel to a high voltage line (Fig. 7). Using the "thorium cow" we obtained carrier-free ^{212}Pb—an ideal nuclide for many laboratory experiments on the undergraduate level. One has to take into account, however, that after ~8 hr this nuclide is in equilibrium with its daughters. For this reason, a Pt electrode which has been exposed for sufficient time, and is then left off the "thorium cow" for approx. 8 hr may be used for identification of the ^{212}Pb. After this time, the β activity of the deposit, which may be measured in a Geiger counter, is proportional to the ^{212}Pb amount present. The half-life obtained from the β measurement is 10.6 ± 0.5 hr (recommended measuring time: 5 days, 2–3 measurements per day). Residual activity observed after 5 days is due to contamination with ThO_2 dust and is to be subtracted from the individual measurements.

An electrode exposed in this manner and "cooled" for a few hours may also be used to demonstrate the ^{208}Tl recoil. Approximately one-third of the ^{212}Bi formed on the electrode surface undergoes α-decay [6.05, 6.09 MeV], in which the daughter nucleus undergoes a relatively large recoil, which may be calculated from the law of conservation of momentum:

$$E_R = \frac{m_\alpha}{m_R} \cdot E_\alpha \tag{6}$$

where E_R = energy of recoil daughter nucleus, m_R = mass of recoiling nucleus, E_α = energy of emitted α-particle, and m_α = mass of emitted α-particle. In the particular case discussed here

$$E_R = \frac{4}{208} \cdot 6 \text{ MeV} = 0.115 \text{ MeV} \tag{7}$$

According to B. Heinrich (*3*, p. 160) this energy is sufficient to propel the daughter nucleus over a distance of up to 0.2 mm in the air.

The loaded electrode is wrapped tightly in thin aluminum foil. After 30 min the foil is removed and is placed under the counter. The inside, which was exposed to the ^{208}Tl recoil nuclei, is placed facing the sensitive area of the counter. The ^{208}Tl is identified from its decay curve with the half-life of 3.1 ± 0.7 min. Since the recoil activity collected is small (a few thousand ^{208}Tl nuclei at the most are collected), it is recommended to use a low background counter, if such is available. Using the ^{212}Pb isolated from the "thorium cow," a number of classical microchemical experiments are possible, in which the nuclide is used both with and without carrier (*5*). The experiment described here is the confirmation of Hahn's adsorption rules. One has to keep in mind that a precipitation reaction with a very small amount of a radioactive nuclide cannot be carried out, unless a large amount of a suitable carrier is present, or co-precipitation, adsorption or similar phenomena are utilized in scavenging a carrier free radioisotope. This is easily explained by the following rough estimation.

An electrode exposed for a longer period of time in the "thorium cow" may collect up to 0.5 μCi ^{212}Pb, if 10 g ThO_2 is used as the charge.

With a specific activity given by the following formula (*6*)

$$S = \left(\frac{dN}{dt}\right)_{1g} = \frac{\ln 2 \cdot N}{A \cdot T_{1/2} \cdot 3.7 \cdot 10^{10}} \left[\frac{\text{Curie}}{\text{g}}\right] \tag{8}$$

$$= \frac{0.693 \cdot (6.02 \cdot 10^{23})}{211.992 \cdot 10.64 \cdot 3600} \left[\frac{\text{Curie}}{\text{g}}\right] = 1.39 \cdot 10^6 \text{ Curie/g} \tag{9}$$

leads to the quantity of ^{212}Pb contained in 0.5 μCi

$$\frac{5 \cdot 10^{-7}}{1.39 \cdot 10^6} = 3.59 \cdot 10^{-13} \text{ g} = \frac{3.59}{211.992} \cdot 10^{-13} \text{ [Mol]}$$

$$= 1.69 \cdot 10^{-15} \text{ Mol} \tag{10}$$

$$\sim 1.7 \cdot 10^{-15} \text{ Mol.} \tag{11}$$

If this amount is carefully dissolved from the Pt electrode and concentrated to approximately 1 ml solution, the ^{212}Pb concentration is calculated to be $1.7 \cdot 10^{-12}$ Mol/l.

Since the solubility product of $PbSO_4$ is

$$K_{sp}PbSO_4 = [Pb^{2+}] \cdot [SO_4^{2-}] = 1.8 \cdot 10^{-8} \text{ [Mol}^2\text{/l}^2\text{]} \tag{12}$$

the amount of $[SO_4^{2-}]$, which theoretically would be required to reach this value of K_{sp} at the Pb^{2+}-concentration given, would be

$$[SO_4^{2-}] = \frac{1.8 \cdot 10^{-8}}{1.7 \cdot 10^{-12}} = 1.1 \cdot 10^4 \text{ Mol/l (!)} \tag{13}$$

It is immediately clear, that this value [more than 1 ton of SO_4^{2-} per liter!] cannot be realized.

One of the possible ways to scavenge minute amounts of a radionuclide present in the solution is by the adsorption on the surface of some suitable inactive carrier precipitate. However, this phenomenon may also lead to erroneous results in a precipitation. For instance, in 1930 O. Erbacher and B. Nikitin (*7*) found a value of $1.40 \cdot 10^{-4}$g/100 ml H_2O at 20°C for the solubility of $RaSO_4$. Two years later B. Nikitin and P. Tolmatscheff (*8*) found this value to be too low and, by correction for adsorption on glass surfaces, arrived at $2.1 \cdot 10^{-4}$g/100 ml H_2O at 20°C—a much higher value.

Otto Hahn (*9–11*) studied the co-precipitation, co-crystallization, and surface adsorption phenomena in great detail and formulated his well-known precipitation rules, which were discussed in detail in his book "Applied Radiochemistry" (*12*). In this book Hahn formulated his precipitation law as follows:

> An ion, at any desired dilution, will be adsorbed by a precipitate if that precipitate has acquired a surface charge opposite in sign to the charge of the ion to be adsorbed, and if the adsorbed compound is slightly soluble in the solvent involved.

The ^{212}Pb isolated in Experiment 2 may be used to demonstrate this rule as described below.

Experiment 3

If ^{212}Pb is to be co-precipitated on the surface of AgCl by addition of $AgNO_3$ and KCl to the ^{212}Pb solution, two different surface conditions of the precipitating AgCl may be achieved (Fig. 8), depending on whether Ag^+ or Cl^- is added in excess. The $^{212}Pb^{2+}$-adsorption should be much better on the surface of the AgCl-precipitate if its surface would carry negative charge. To test this assumption, the following experiments may be performed.

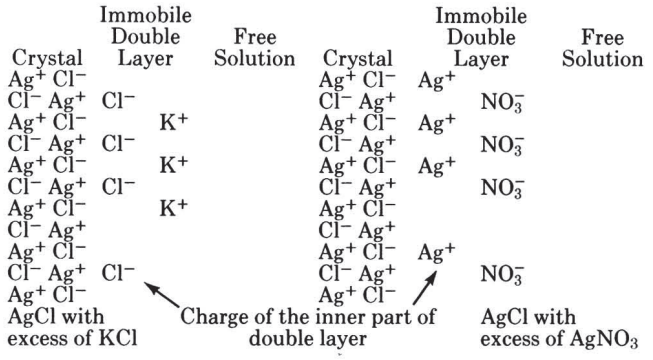

Figure 8. Surface charge conditions in adsorption precipitation of ^{212}Pb (carrier precipitate AgCl).

Procedure

A platinum electrode exposed in the "thorium cow" for at least 24 hr is leached with 12 ml warm HNO_3 (4 *M*). For each experiment, 2 ml of this well-mixed solution are used. The solution is combined with 0.2 *M* $AgNO_3$ solution and 0.2 *M* KCl solution in the sequence given by the Roman numerals I, II, and III in the table, and by adding the amount in milliliters given in this table.

After thorough mixing, the solutions are filtered through a radiochemical filter assembly with removable chimney (*13*),[3] washed with 10 ml dist. H_2O, dried by washing with acetone-ether, and counted with an end window GM counter. (If the filter assembly is not available, a larger filter crucible may be used instead; for counting, the GM end window counter is inserted into the crucible).

The following observation will be made in the experiments type A through E:

Type A. Equivalent amounts of Ag^+ and Cl^- are employed. The surface of the precipitate (resp. precipitated crystals) stays neutral, only little ^{212}Pb adsorption is observed: Low counting rate.

Type B. Excess of Ag^+ causes positive charge on surface of precipitate; no ^{212}Pb-ions will be adsorbed. Only small counting rate due to inclusions is observed.

Type C. Excess of Cl^- causes negative charge on surface of precipitate; ^{212}Pb ion adsorption is strongly favored. Counting rate is strongly increased.

Type D and Type E. In these experiments, the ^{212}Pb solution is added *after* the AgCl precipitation has been made. The ^{212}Pb solution is kept in contact with the precipitate for ~5 min, preferably with stirring. Then, the solution is filtered, the precipitate washed and counted as described before.

In experiment D (Ag^+ in excess) similar results are observed as in experiment B; experiment E (Cl^- ion in excess) shows results similar to those obtained in experiment C. However, the effects observed in B and C are larger than those in D and E since in experiments D and E only the surface of the precipitate is involved in the adsorption, and no inclusion takes place, as in B and C. The same experiments may also be carried out with KBr instead of KCl. The results are even better than in the chloride precipitation. However, if KI is used instead of KBr or KCl, a strong excess of KI causes a decrease of activity, probably due to the formation of the complex $[^{212}PbI_4]^{2-}$ (*3*, p. 162).

It has been demonstrated that even some of the oldest radiochemistry experiments may be updated with modern equipment and are found to be useful in the laboratory courses or in the student demonstrations. Because of the short half-lives of the isotopes involved and very low activities needed for these experiments, no additional precautionary measures are necessary.

Acknowledgment

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[3] In German: *Hahn'sche Nutsche.*

Experiments to Study the Absorption Behavior of ^{212}Pb on AgCl Precipitates

Experiment	$AgNO_3$ (0.2 *M*) ml	[sequence]	KCl (0.2 *M*) ml	[sequence]	^{212}Pb (in 4 *M* HNO_3) ml	[sequence]	Surface charge of precipitate
A	6	[I]	6	[III]	2	[II]	±0
B	10	[I]	2	[III]	2	[II]	+
C	2	[I]	10	[III]	2	[II]	−
D	10	[I]	2	[II]	2	[III]	+
E	2	[I]	10	[II]	2	[III]	−