

The increase in calcium concentration has no definite effect on the film potential at this low pH .

(3) The experiments described in this letter, when compared with those at a pH of 9.4, prove that the pH of the solution is one of the primary factors which determine the film potential.

The data of Langmuir and Schaefer⁸ indicate that our monolayer at $(10)^{-4}m$ Ca^{++} consists of 27 molecules of stearic acid to 73 of calcium stearate. We have used still higher concentrations of the ion in the solution to increase its proportion in the film. It is of interest to determine the relation between the concentration of the hydroxyl ion in the solution, the Ca^{++} ion in the monolayer, and the film potential of the X multilayer.

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¹ William D. Harkins and Richard W. Mattoon, *Phys. Rev.* **53**, 911 (1938).

² Eliot F. Porter and Jeffries Wyman, Jr., *J. Am. Chem. Soc.* **60**, 1083 (1938).

³ Irving Langmuir and Vincent J. Schaefer, *J. Am. Chem. Soc.* **58**, 284 (1936).

Chemical Separation of Nuclear Isomers

Many examples of nuclear isomers are now known, and it is of interest to have methods to find possible genetic relationships between the isomeric states of the same nucleus. For instance, this can be readily accomplished by standard methods if the lower level has a longer life than the upper. But for the opposite case the problem is much more difficult because a transient equilibrium is reached soon and the only apparent period is that of the parent.

An actual *separation* of two genetically related isomers of a nucleus can be performed by the following artifice in some cases: Consider the case in which the element having the isomers can give compounds suitable for the application of the Szilard-Chalmers¹ method of concentration and prepare initially such a compound from a mixture of the two isomers. When the isomer in the upper state decays to the lower state the nucleus emits a gamma-ray and recoils. The energy of recoil may be sufficient to knock the decayed atom out of the compound and the daughter activity may then be separated as in the Szilard-Chalmers method.

However, if the energy of the transition gamma-ray is of the order of magnitude of 100 kv, as one might expect,²⁻⁴ the recoil for elements of medium and high atomic weight would not be sufficient to break an ordinary chemical bond. Fortunately the gamma-ray is highly internally converted and the recoil from the conversion electron is higher than that from the corresponding gamma-ray so that recoil energies comparable to chemical bond energies are obtained.

Even if the recoil energy is insufficient to break the bond, the method does not necessarily fail because the energy given to the bond may suffice to create an activated condition within the molecule such that it may undergo chemical reaction upon collision with some other kind of molecule

deliberately introduced for this purpose. The daughter activity will then be found in the product of the chemical reaction.

We have used this method to separate the 18-minute and 4.4-hour isomers of Br^{80} . The separation was fairly complete and showed definitely that the 18-minute period is formed from the 4.4-hour period.

About one liter of ethyl bromide was irradiated for three hours with slow neutrons from the Berkeley cyclotron and the radioactive bromine was removed as solid sodium bromide. Radioactive tertiary butyl bromide was synthesized by saturating tertiary butyl alcohol with hydrobromic acid generated from the sodium bromide. Five grams of the butyl bromide were introduced into 200 cc of aqueous methyl alcohol (75 mole-percent methyl alcohol) at $0^{\circ}C$ where it underwent chemical reaction with both the methyl alcohol and the water liberating hydrobromic acid. In this manner the butyl bromide molecules which contain a bromine nucleus which has recoiled can react to liberate hydrobromic acid. Under the experimental conditions chosen this type of activation occurs much more frequently than the spontaneous activation due to thermal agitation, and hence there is a large enrichment of the radioactivity of the lower isomeric state (18 minutes) in the reaction products. The chemical reaction was allowed to proceed for about three times the radioactive half-life of the lower state and then, after first extracting the unreacted butyl bromide with benzene, silver bromide was precipitated from the aqueous methyl alcohol.

In Fig. 1, *a*, is shown the decay curve of such a concentrate effected four hours after the end of the bombardment. The first reading was taken 27 minutes after the precipitation of the silver bromide. The activity evidently has two periods, a short one of 18-minute half-life shown in curve *b*, due to the recoil atoms, contaminated with an activity

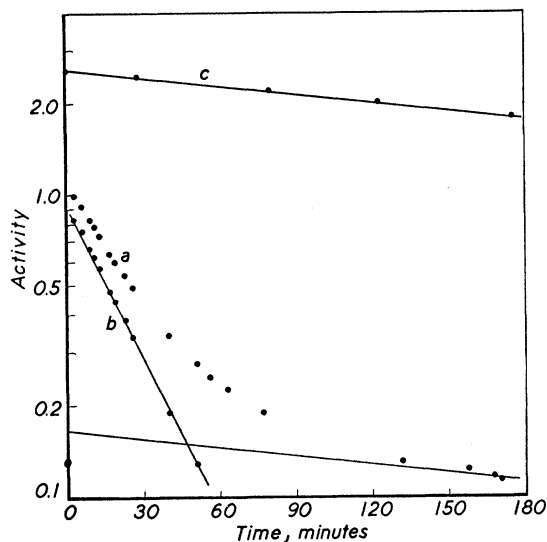


Fig. 1. (*a*) Decay curve of bromine extracted from 4-hour activity of Br^{80} . (*b*) Curve *a* corrected for long-lived tail (18-minute half-life). (*c*) Decay curve of the bromine activity from which the extraction was made.

decaying in the same manner as the starting substance, whose decay is shown in curve *c*. This small long-lived tail, which we followed for 24 hours, arises from the bromide liberated in the spontaneous chemical reaction. By repeating the experiment, but with an elapse of 26 hours between the end of the bombardment and the beginning of the chemical reaction, a decay very similar to curve *a* was obtained. These two runs also showed that the upper state (parent substance) was decaying with a half-life of approximately four hours. By comparing curves *b* and *c*, and by taking into account that curve *b* started 27 minutes after the end of the chemical reaction, it can be seen that most of the nuclei in the upper state decay by falling to the lower state from which the observed disintegration electrons are emitted.

DeVault and Libby have applied our method of separation to other bromine compounds and will report their findings shortly.

We wish to thank Professor E. O. Lawrence for his interest and encouragement in this work. Thanks are also due to the Research Corporation for continued support.

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Evidence for Gamma-Radioactivity of 4.5-hour Br^{80} from Radiobromate

In the course of work on the chemistry of the decomposition of bromoform caused by the recoil from the neutron-capture gamma-radiation, it was noticed that the radioactive bromine persisted in coming out of the molecule over a long period of time after the irradiation ceased. This remained unexplained until Dr. E. Segrè (cf. preceding Letter to the Editor) proposed a method of separation of nuclear isomers and that the 4.5-hour Br^{80} isomer was converted to the 18-minute form by emission of a soft highly forbidden gamma-ray. It was found that most of the activity in the later extracts decayed with the 18-minute half-life although no 18-minute bromine not grown from the 4.5-hour isomer could have been present in the bromoform extracted at the time.

Simultaneously with the later experiments on bromoform, work on the chemistry of the neutron-capture gamma-ray recoil for bromate ion gave evidence for the effect which was considerably more definite because it was possible to purify the BrO_3^- solution completely for bromine of lower valence by precipitation of AgBr from BrO_3^- solution 2.5 molar in NH_4OH .

Figure 1A is a typical decay curve for a AgBr precipitate

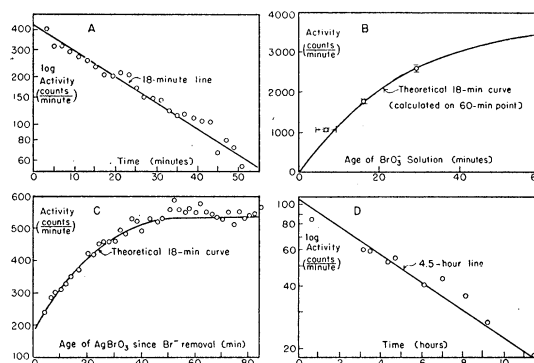


FIG. 1. Growth and decay curves. A, decay of AgBr precipitate; B, growth curve for AgBr precipitates; C, growth curve for AgBrO_3 purified for Br^- ; and D, decay of AgBr activity with 4.5-hour mother BrO_3^- .

obtained from a mother BrO_3^- solution which had stood several hours so the 18-minute activity originally present when removed from the neutron source (200 mg $\text{RaBr}_2 + \text{Be}$ powder) could have been present to less than five percent of the activity found. Apparently very little of the 4.5-hour activity was present in these precipitates. Figure 1B is a plot of the activities of AgBr precipitates obtained from a single mother BrO_3^- solution which had stood various times since its last purification for Br^- . The solid line is the theoretical 18-minute growth curve. Figure 1C is a plot of the activity of a AgBrO_3 precipitate (obtained by acidifying the ammoniacal solution) which was purified for Br^- at zero time. The solid line is the 18-minute growth superimposed on an initial activity of 160 counts per minute. This initial activity must have been due to 18-minute Br^{80} still remaining in the BrO_3^- after the activation by the kick from the electron ejected by the converted soft gamma-ray or to beta-radiation from the 4.5-hour body itself, or to both. However, the curve does show that unless the 4.5-hour beta-rays are softer than about 500 kv (this was determined by the thickness of the sample and the wall of the counter) at least 75 percent of the 4.5-hour body must decay by the gamma-emission process. Further, in view of the fact that experiments with BrO_3^- showed the efficiency of the much more powerful neutron gamma-ray recoil in destroying the ion to be only 80 percent approximately, it seems probable that most, if not all, of the initial 25 percent activity is due to retention of 18-minute activity in the BrO_3^- rather than to 4.5-hour beta-emission. Of course this indicates that the 4.5-hour body is practically a pure gamma-ray emitter, unless it has beta-radiation softer than about 500 kv.

Figure 1D shows the activities of AgBr precipitates obtained at various times from a given mother BrO_3^- solution. The solid line is the theoretical 4.5-hour decay curve.

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