parallels the titanium and thorium plots, good agreement was obtained for several assumed complexes. This may be the result of the existence of more than one zirconium complex in the equilibrium solutions whereas the calculations were made for a single complex. The calculated pK values for the higher pH range show a larger variation. All the calculations for zirconium which gave reasonable agreement are listed in Table IV.

TABLE IV

pK VALUES OF ASSUMED COMPLEXES

pH	Zr-Ci_2^{-2}	Zr-OCi^-	Zr-OCi_2^{-4}	Zr-OCi_3^{-7}	ZrO-HCi^0	ZrO-$(HCi)_2^{-2}$	ZrO-$(HCi)_3^{-4}$
Region where Zr C values parallel Ti and Th C values							
1.59	23.96	12.03	21.27	30.72	8.30	14.01	19.71
1.73	24.24	12.30	21.25	30.19	8.81	14.25	19.70
1.83	23.89	12.05	20.70	29.35	8.66	13.91	19.16
1.88	24.11	12.11	20.71	29.21	8.86	14.02	19.18
1.86	24.31	12.48	21.04	29.60	9.11	14.31	19.51
1.95	24.16	12.42	20.72	29.02	9.14	14.17	19.19
Range:	0.42	0.45	0.57	1.70	0.84	0.40	0.55
Region of non-parallel C values							
2.28	23.53	12.08	19.43	26.78	9.13	13.54	17.94
2.84	23.02	11.98	17.81	23.64	9.59	13.03	16.47
4.08	22.73	11.90	15.02	18.15	10.75	12.73	14.71
5.39	25.21	13.21	14.88	16.55	13.38	15.22	17.05
Range:	2.48	1.31	4.45	10.23	4.25	2.49	3.23

From these data it seems that within the pH range studied, the predominant complexes are $TiCi_2^{-2}$ and $ThCi_2^{-2}$. The data for zirconium are less readily interpreted, but $ZrO(HCi)_2^{-2}$ seems to predominate at the lower pH values and $ZrOCi^-$ at the higher.

(2) **Elution Experiments.**—The fact that both pH and temperature have a significant effect on the ion-exchange equilibrium is illustrated by the elution experiments. Without the temperature control jacket on the ion-exchange column, erratic shifts in the peaks of the elution curves were observed. The large pH effect is shown by the lack of separation of titanium and zirconium in a short resin bed at pH 2.0, while at pH 1.5 the titanium is held by the resin so strongly as to interfere with an efficient separation.

The elution with radioactive titanium as shown in Fig. 3 may be interpreted as follows. The titanium which appeared early in the elution is probably due to a colloidal form of titanium which passed through the resin bed without being held by the resin. The fact that the radioactivity was concentrated in the later part of the elution indicates that the peculiar shape of the elution curve is probably due to the partial separation of the isotopes of titanium. This is in agreement with the observation of Brewer[16] who reported a preferential desorption of the light isotope of potassium when a column of potassium-containing zeolitic greensand was eluted with a sodium chloride solution. Taylor and Urey[17] have also shown that in the exchange of potassium and ammonium in zeolites the heavier isotope is taken up more readily and is more difficult to replace.

[16] A. K. Brewer, THIS JOURNAL, **61**, 1597 (1939).

[17] T. I. Taylor and H. C. Urey, *J. Chem. Phys.*, **6**, 429 (1938).

NEW BRUNSWICK, N. J.

RECEIVED AUGUST 7, 1951

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY]

Recoil Reactions with High Intensity Slow Neutron Sources. II. The Retention of Radiobromine by Crystalline $KBrO_3$[1]

BY J. W. COBBLE AND G. E. BOYD

Retention of radiobromine as bromate, during bombardment of crystalline $KBrO_3$ in the Oak Ridge graphite pile, increased from an apparent zero-time value of 9 ± 1% to a limit of 32 ± 1% after 16 hr. irradiation. With the temperature at −195° during irradiation, the retention was 13 ± 1% beyond five minutes. Heating the irradiated $KBrO_3$ above 80° or exposing it to an energetic gamma ray source (Co^{60}) returned the radiobromine to bromate at a rate dependent on the temperature or source intensity, respectively. No simple rate law could describe the thermal back-reaction; the radiation-induced reaction obeyed a first order velocity equation and showed an activation energy of *ca.* 8 kcal./mole. Theoretical estimates were made of the retention from "cage" effects and from the chance cancellation of γ-ray recoils. The constant retention observed in long-time neutron bombardments was attributed to a steady state between the rate of production of separable Br^{82} and the rate of its recombination to bromate by pile γ-rays and fast neutrons.

Introduction

In our earlier study[2] of the enrichment of 35.9 h Br^{82} activity by recoil following neutron capture in $KBrO_3$ some evidence was obtained of the presence of thermal and of radiation-induced effects acting to return the radiobromine atoms to bromate. This paper is concerned with a detailed study of these novel and interesting solid state reactions.

Experimental Procedures

The quantity measured was the radiochemical separation, or recovery factor, ϕ_t, defined as the fraction of the total induced bromine activity chemically separable from neutron irradiated $KBrO_3$. The recovery factor so defined is a convenient index of the radiobromine behavior since its value is independent of radioactive decay. It is also perhaps more sensitive than other possible functions to changes in the distribution of activity between bromine and bromate.

The radiochemical separation procedure, radioactivity detection equipment, etc., have been described.[2] Briefly, when neutron irradiated potassium bromate is dissolved in water and bromine is added a large fraction of the radiobromine can be extracted into carbon tetrachloride. Since only bromide, bromine, hypobromite and bromate may co-exist in aqueous solutions, and since the first three of these exchange with one another rapidly and completely, the organic extraction separates all the radiobromine in stable valence forms lower than bromate. A precision of 0.5% was obtained in the estimation of the recovery factor upon the extraction of successive aliquots from a given sample of $KBrO_3$. However, values of ϕ_t were reproducible to only 2% in successive bombardments of the same duration. The majority of the recovery determinations utilized

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[1] Presented before the Division of Physical and Inorganic Chemistry, 119th Meeting, American Chemical Society, April 16-19, 1951, Cleveland, Ohio.

[2] G. E. Boyd, J. W. Cobble and Sol Wexler, THIS JOURNAL, **74**, 237 (1952).

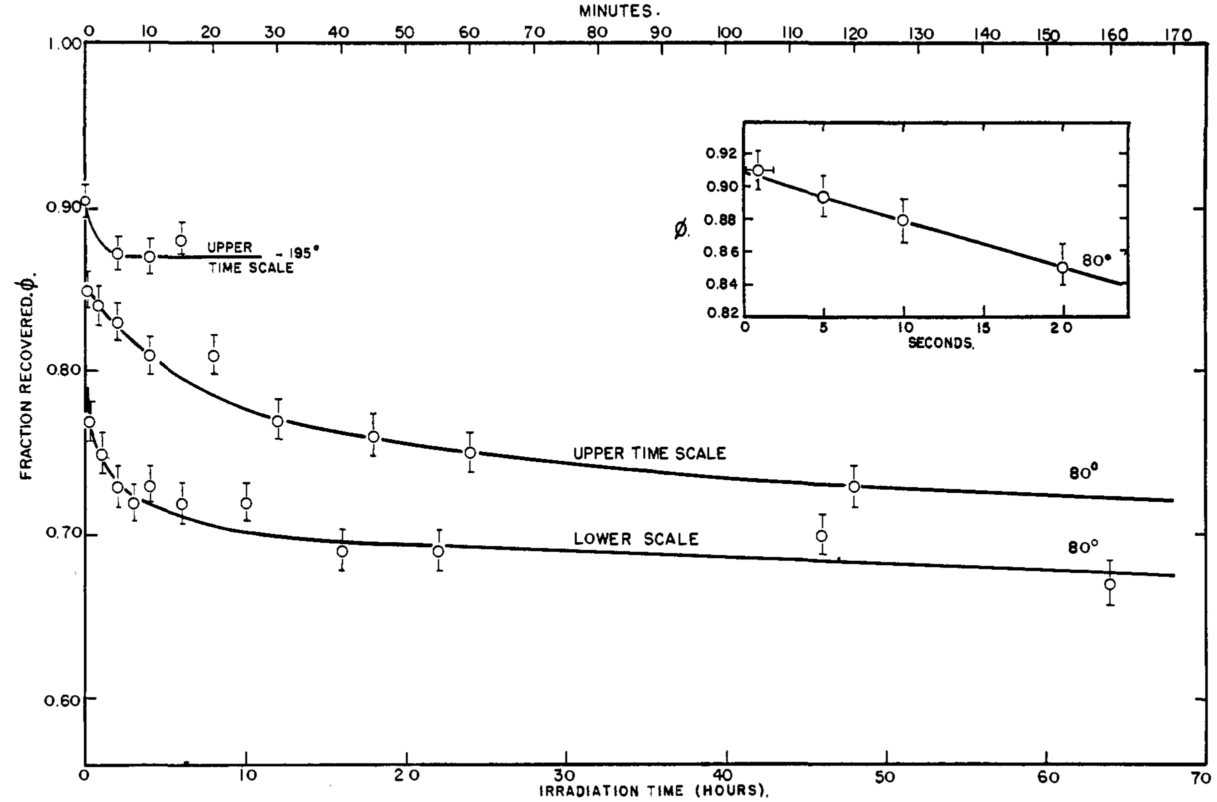

Fig. 1.—Variation of the recovery of radiobromine from $KBrO_3$ with time of exposure to a high intensity neutron source.

the 35.9 h Br^{82} activity, except for the irradiations up to twenty minutes duration which employed the 18 m Br^{80}. In these latter cases chemical separations were performed within a few seconds after bombardment so as to measure only that 18 m activity formed *directly* by neutron capture. The ϕ_t values derived using both bromine radioisotopes when plotted against time gave a single smooth curve within the stated experimental error (Fig. 1).

An attempt was made to use a bromide–bromate separation method based on the fractional precipitation of AgBr and $AgBrO_3$ previously described by Libby[3] and more recently employed by Berne.[4] Great difficulty was experienced in preventing coprecipitation and/or thermal exchange reactions, and, after a number of studies in which labeled bromate or bromide were employed, this procedure was discarded as being too inaccurate.

The radiation decomposition of $KBrO_3$ to form bromide also was measured as previously described.[2] The extent of the decomposition was used as a gamma radiation monitor for the experiments in which the radiation-induced reaction of radiobromine was determined. Other studies showed that the bromide produced was directly proportional to the γ-ray source intensity and increased linearly with the irradiation time. Thus, 4.71×10^{-3} p.p.m. of bromine was formed per roentgen of Co^{60} γ-radiation. The micropotentiometric titration method used to estimate bromide in bromate was accurate to within $\pm 3\%$ and was reliable down to about 10 p.p.m. of bromide in bromate in the presence of a 25 p.p.m. blank.

Neutron bombardments were conducted in the Oak Ridge graphite pile in a thermal flux of 6.7×10^{11} n/cm.^{2}/sec. The gamma ray intensity at this same position was approximately 8000 R/min. and the temperature about 80°. A Co^{60} source was used for the pure gamma irradiations; intensities up to 16,000 R/min. could be attained by varying the position of the sample with respect to the source.

Recovery Variations in Pile Bombardments.—Several determinations of the change of radiobromine recovery with time of neutron irradiation were made in addition to those reported earlier. A summary is afforded by Fig. 1 which shows that the recovery falls relatively quickly during the first 15 hours after which it appears to remain constant. In view of the rapid initial drop in ϕ_t, it was of interest to discover if a complete recovery would be observed in very short irradiations. As may be seen, this was not the case. The recoveries for irradiations of one up to 20 seconds duration may be extrapolated to a zero time value of 0.91 ± 0.01.

Since the pile neutron irradiations were necessarily conducted at 80°, it also seemed important to know if the recovery was temperature dependent. The bombardments 5, 10 and 15 minutes long, respectively, were conducted with the $KBrO_3$ submerged in liquid nitrogen. At −195° (Fig. 1) the recombination back to bromate was effectively quenched after less than five minutes.[5] Even at liquid nitrogen temperatures it appears that a fraction of the recoils were sufficiently reactive to recombine to bromate within a few minutes after their formation. In another experiment in which $KBrO_3$ was irradiated for 30 minutes at −195° a recovery of 0.87 was found upon subjecting an aliquot to an immediate analysis. If, however, the irradiated crystals were allowed to warm up to room temperature, the recovery fell to 0.78. An otherwise identical irradiation conducted outside the liquid nitrogen bath at about 80° gave 0.77.

The relatively constant recovery for long bombardments (Fig. 1) suggested[2] that a steady state was established between the rate of radiobromine formation and the rate of its thermal and radiation induced return to bromate. To gain some indication of the fast neutron and γ-ray contributions several bombardments were made in which $KBrO_3$ was wrapped either in sufficient cadmium to remove virtually all thermal neutrons, or, in an amount of lead to reduce the γ-ray intensity by threefold. In all cases the changes in the recoveries were quite small; a slight, although possibly not significant, increase in the recovery was found with lead, while cadmium gave a distinct, unexpected lowering of ϕ_t. It was possible, nevertheless, to conclude that γ-rays, either from pile or produced locally by neutron capture in Cd, must influence the recovery.

Thermally Induced Recombination of Recoil Radiobromine.—Previously,[2] excepting for very short times, the re-

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[3] W. F. Libby, THIS JOURNAL, **62**, 1930 (1940).

[4] E. Berne, *J. Chem. Soc.*, Supplement 2, S338 (1949).

[5] A sample irradiated for five minutes at the same time as the one in liquid nitrogen but maintained at the surrounding pile temperature gave the expected recovery of 0.83.

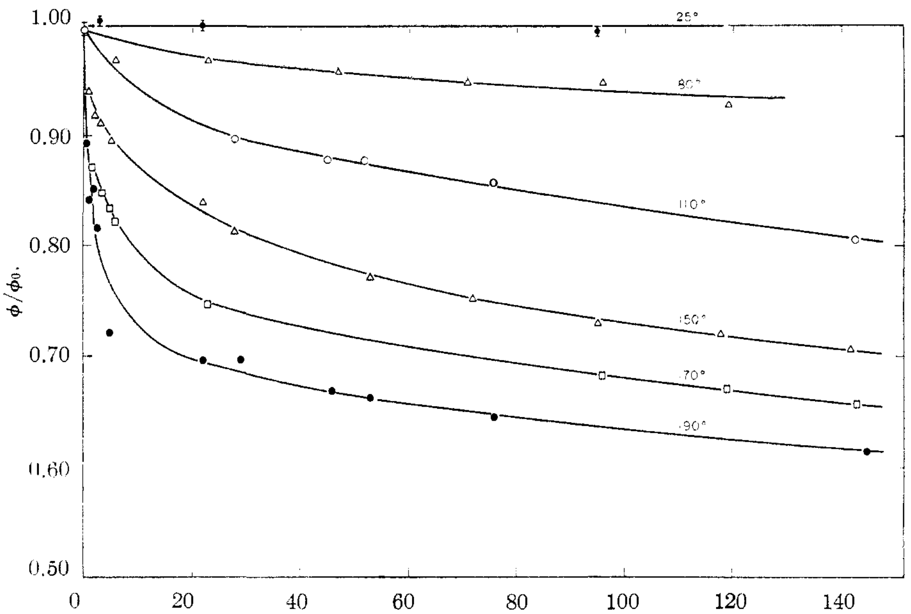

Fig. 2.—Variation of the relative recovery (ϕ/ϕ_0) of 35.9 h Br^{82} with time of heating of neutron irradiated $KBrO_3$.

covery of radiobromine was found independent of the time the $KBrO_3$ crystals stood at room temperatures after neutron bombardment. However, the possibility of a thermally activated return of the recoil radiobromine to bromate at somewhat higher temperatures remained to be considered. A number of 2–3-g. samples were irradiated for one hour and then heated in air in a thermostatically controlled furnace. Recoveries were measured on aliquots from the heated, irradiated crystals taken at varying intervals. The onset of a thermal reaction with a threshold at, or slightly below, 80° tending to lower the recovery is clearly indicated by the data in Fig. 2. Evidently, a thermal reaction tending to lower the recovery, ϕ_0, from its initial value of 0.75 can be induced by heating, particularly at and above 80°. Measurements of the total radioactivity contained in successive weighed aliquots taken at various times from crystals kept at 190° showed no change in the activity per gram from that for unheated $KBrO_3$ from the same bombardment. Hence, the decreased recovery with increasing time and temperature (Fig. 2) was not a consequence of a loss of radiobromine by volatilization. It may be further concluded that the radiobromine recoils must be rather firmly trapped in the crystal lattice.

Similar but not so detailed observations on what also appear to be thermal reactions involving radio-recoils in crystals have been made recently on neutron irradiated K_2CrO_4 by Maddock and Green[6] and on $KMnO_4$ by Aten and van Berkum.[7] Broda and co-workers[8] have reported heating curves on neutron-irradiated $KMnO_4$ resembling those of Fig. 2 which indicate a reaction threshold at about 50°.

These experiments appear to support the view that the bromine formed in $KBrO_3$ by recoil following thermal neutron capture is more reactive than the bromine released by the radiation decomposition (*e.g.*, fast neutrons and γ-rays), for there was no "annealing out" of the decomposition products. In fact, although the radiobromine returned to bromate upon heating, the decomposition increased from its initial value of 71 p.p.m. Br at the end of the pile bombardment at a rate of about 1–2 p.p.m. per hour. Although initially the return was quite rapid, in no case could all the radioactivity be recombined; heating at 190° for over 140 hours lowered ϕ_t to only 0.46. The data of Fig. 2 could not be described by any simple chemical rate law, or by a parabolic diffusion rate law. Possibly the recoil species becomes bromate by recombination with oxygen released in the radiation decomposition of the crystal, or by a thermal exchange with unaltered inactive bromate. Another experiment suggested that the rate-controlling step may be the diffusion of either or all reactants initially randomly distributed through the crystals: An annealing sequence at 170° was conducted in which the heating of the irradiated crystals was interrupted for periods up to 16 hours during which time they were maintained at room temperature and then replaced in the furnace. The recovery was a function only of the total time at 170°. Since during a 16-hour quenching period the number of radiobromine atoms (35.9 h Br^{82}) decayed by more than 25%, if the recombination to bromate depended upon the radiobromine concentration, the rate would have been expected to diminish which was not the case.

Above 80° the mechanism responsible for recombination may differ from that for some of the recoils produced in crystals bombarded at −195° and allowed to warm to room temperatures. A characteristic temperature for a loosening of the crystal lattice (Tammann temperature, $T_S = 0.52\ T_m$) can be estimated as about 95° for $KBrO_3$ using 434° as its melting point. Presumably above this temperature the movement of the reactants may be associated with the migration of defects in the crystal.

Radiation Induced Recombination of Recoil Radiobromine.—Although a radiation induced reaction tending to decrease ϕ_t had been indicated, an interpretation of Fig. 1 was made difficult by the fact that in those experiments the rate of formation of decomposition products could not be varied independently of the rate of radiobromine formation. If, however, after neutron irradiation, potassium bromate is exposed to an intense source of energetic γ-radiations, the concentration of decomposition products in the crystal may be increased without changing the amount of radiobromine which will, in fact, diminish owing to its radioactive decay. A series of experiments (Fig. 3) wherein pure crystalline

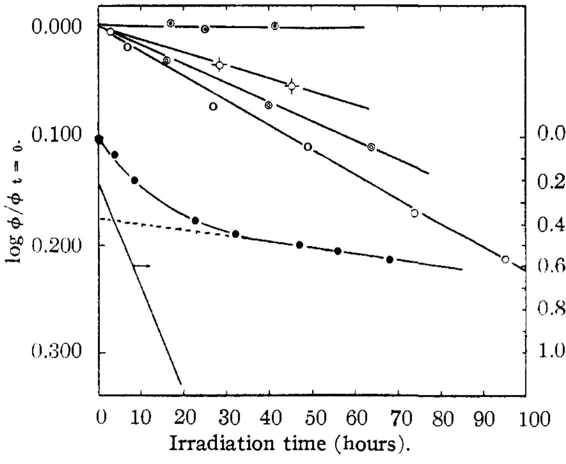

Fig. 3.—γ-Ray induced return of radiobromine to bromate: ⊙, $k = 0$ (−196°; 5200 R/min.); ◇, $k = 4.9 \times 10^{-4}$ hr.$^{-1}$ (10°; 5200 R/min.); ⊛, $k = 7.2 \times 10^{-4}$ hr.$^{-1}$ (10°; 10,000 R/min.); O, $k = 9.8 \times 10^{-4}$ hr.$^{-1}$ (10°; 13,000 R/min.); ●, scale on right axis; —, $k = 0.112$ hr.$^{-1}$ (150°; 16,000 R/min.).

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[6] J. Green and A. G. Maddock, *Nature*, **164**, 788 (1949).

[7] A. H. W. Aten, Jr., and J. B. M. van Berkum, This Journal, **72**, 3273 (1950).

[8] W. Rieder, E. Broda and J. Erber, *Monatsh.*, **81**, 5, 657 (1950).

$KBrO_3$ was first subjected to a one-hour neutron irradiation and then exposed to a Co^{60} γ-ray source showed that γ-radiation alone may produce a significant decrease in radiobromine recovery. Furthermore, (a) the back-reaction obeyed a simple exponential time dependence; (b) the rate was directly proportional to the intensity of the source; (c) the recombination reaction, which may be checked at liquid nitrogen temperature, showed a small positive temperature coefficient corresponding to an activation energy of $\sim$ 8000 cal./mole in the temperature interval between 10 and 150°. As indicated (Fig. 3) the data at this latter temperature were corrected for the change in ϕ_t resulting from the accompanying thermal reaction.

The return of recoiled radiobromine atoms to bromate by γ-radiation is all the more surprising when it is realized that the reverse reaction, the radiation decomposition of the bromate to give bromide at rates varying from *ca.* 25 to 75 p.p.m. Br/hr., occurred simultaneously. Separate experiments further showed the rate of the latter reaction to be temperature independent. These observations again appear to require the conclusion that at least some of the radiobromines are more reactive than the bromide produced by radiation decomposition. However, under the influence of both heat and γ-rays not all of the radiobromines could be made to recombine (Fig. 3); even in the most extreme case ϕ_t did not fall below 0.20.

The reactivity spectrum of the radiobromine recoils trapped in a $KBrO_3$ crystal at the conclusion of a neutron bombardment might perhaps be expected to depend on the length of pile irradiation since the intense γ-radiations (and fast neutrons) also present already will have returned some of the more reactive species to bromate. Such an "aging" of the radiobromine population might be reflected in the pure γ-induced recombination rate. An experiment was conducted in which $KBrO_3$ was irradiated for ten hours and then exposed to the Co^{60} source. No change whatever in the γ-rate was found from that for a one hour neutron irradiation, suggesting that even for the longer bombardment most of the recoils retained sufficient energy to be induced to return to bromate, or, alternatively, that the pile (and Co^{60}) radiations dissipate so much energy in the crystal that all the recoils are subject to recombination.

Discussion

The view that chemical states of radiobromine of varying reactivity are formed and trapped in crystalline $KBrO_3$ irradiated by slow neutrons has appeared to find support in the experimental results given above. Some of the details of the processes leading to these "hot" atoms may now be examined: Upon slow neutron capture both the stable Br^{79} and Br^{81} nuclei contained in $KBrO_3$ are transformed into radioactive types with the simultaneous emission of capture γ-rays. These rays carry away a total energy approximately equal to the neutron binding energy of bromine which is about 9.0 Mev.[9] Upon escaping from the bromine nucleus the capture γ-rays impart recoil momentum whose resultant magnitude will depend upon the details of the emission process. In general the recoil energy will be sufficient to enable the atom to break its chemical bonds with the oxygens of the bromate radical and to escape into the crystal lattice.

A number of possibilities are available for the interaction of a recoiling bromine atom with the $KBrO_3$ crystal. Undoubtedly, a large fraction of the recoils will merely suffer momentum loss by inelastic collisions with other atoms in the solid and will come to rest in a non-lattice position. Some of these atoms may possess additional potential energy by reason of the electric charge they retain. There appears to be no *a priori* reason to expect that charged recoils will all end up in an electrically neutral condition for only by chance will they possess the correct spatial and energy requirements for neutralization by the electron bands existing in the crystal.

One type of interaction between a recoiling bromine atom and its surroundings may in part explain the observation that not all of the radioactivity can be recovered even at zero time (*i.e.*, 9 ± 1% of the radiobromines remain combined as bromate). If a recoil after separating from its bromate radical chances to collide with the bromine atom in an adjacent bromate and transfer its momentum completely, the net result will be a radiobromate formed and an inactive bromine lodged in the crystal. An estimate of the probability of this occurrence can be made from simple geometrical considerations based upon the known crystal lattice dimensions for $KBrO_3$.[10] The result is that the "cage" effect will account for a retention of not more than 5%. The observed retention is, however, somewhat larger so that other mechanisms need to be examined.

If in the radiative capture of a neutron by bromine all the binding energy were carried away by a single γ-ray, a recoil possessing energy in an amount (580 e.v.) easily sufficient to break all of the chemical bonds in a bromate radical would be formed. However, recent measurements by several investigators[9,11,12] have shown that several γ-rays are emitted per captured neutron, and that a spectral distribution of energies obtains. With bromine an average of 3.4 quanta per neutron was found. The γ-ray spectrum, which suggested a line structure, showed peaks at 3.2, 5.3, 6.3, 7.3 and 8.0 Mev., the first being the most intense by a factor of three.[9] No angular correlation was observed between successive gammas given off in the usual cascade process following neutron capture. These transitions presumably take place with life-times of 10^{-13} to 10^{-17} sec. which is consistent with the energy and dipolar character of the radiations.[13]

The question then was: If three (or more) γ-rays each having about 3 Mev. energy (or less) are emitted following neutron capture what is the probability that the *resultant* momentum of a bromine atom will exceed its chemical binding energy in bromate? This general problem may be treated as a random walk in momentum space and a standard stochastic procedure may be applied.[14] Computations were carried out for the cases where three, four and six γ-rays of *equal energy* are radiated with the results shown in Fig. 4 where the probability is plotted as a function of the net recoil energy. The stochastic analysis also gives the obvious result that when the number of γ-rays is very large a self-cancellation of their recoils becomes quite probable. Further, given the decay scheme for capture γ-rays, in the absence of angular correlations or other effects, it should be possible to estimate the complete number–energy distribution curve for the recoils.

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[9] B. Hammermesh, *Phys. Rev.*, **80**, 415 (1950).

[10] W. H. Zachariasen, *Matemat. Naturwiss. Klasse*, 7 (1928); *C. A.*, **23**, 1791 (1929).

[11] C. O. Muehlhause, *Phys. Rev.*, **79**, 277 (1950).

[12] B. B. Kinsey, C. A. Bartholomew and W. H. Walker, *ibid.*, **77**, 723 (1950); **78**, 77 (1950).

[13] H. A. Bethe, "Elementary Nuclear Theory," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 13.

[14] S. Chandrasakur, *Rev. Modern Phys.*, **15**, 1 (1943).

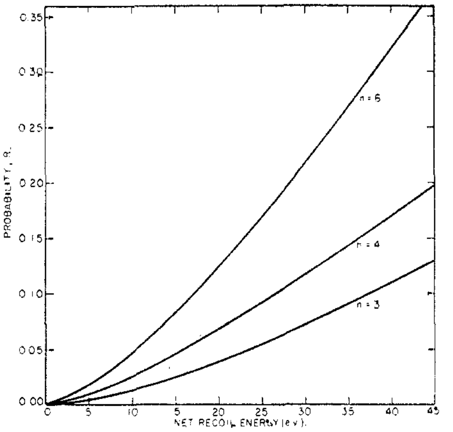

Fig. 4.—Probability that the net recoil from *n* equi-energetic capture γ-rays will be $\leqq E$; $Br^{*82} \rightarrow Br^{82} + n\gamma +$ 8.5 Mev.

To apply the foregoing considerations to the bromine recoil problem an estimate must be made of the binding energy for bromine in bromate. The not unreasonable magnitude of 8–9 e.v. can be derived by taking three times the value for the Br–O covalent single bond (1.9 e.v.)[15] and increasing this somewhat to allow for resonance stabilization. This energy must be increased further, for not all the net recoil energy will be available[16] to rupture the bromine–oxygen bonds in bromate. The fraction utilized will be $3\ M_O/M_{BrO_3} = 0.38$, where M_O and M_{BrO_3} are the oxygen and bromate masses, respectively. The "effective" binding energy is thus about 25 e.v. Accordingly (Fig. 4), in about 5% of the neutron captures the bromines will not escape from their bromate radicals. This estimate is surely an upper limit and must be reduced perhaps by as much as one-half, for spectral measurements[9] indicate that the *compound* bromine nucleus decays only about one-half the time with three equi-energy γ-rays.

The foregoing treatment will be invalidated if the assumptions do not hold. If, for example, the time between consecutive γ-rays is appreciably longer than 10^{-14} sec., a bromine nucleus, which will achieve a recoil velocity of 1.1×10^6 cm./sec. from a 2.8 Mev. γ-ray, may move sufficiently (~1–2 Å.) to escape from the bromate radical altogether before the emission of a second γ-ray. The possibility of internal conversion of the capture γ-rays is under active investigation, and several reports[17,18] have been made of low energy electrons apparently associated with neutron capture. It has been proposed that low lying, low energy capture states having lifetimes of the order of 10^{-10} sec. are of common occurrence. However, some important details remain to be established: Measurements of capture γ-conversion electrons coincidence rates are needed to demonstrate that the low energy electrons reported are truly emitted as a part of the γ-ray cascade following neutron capture. Information on the number of electrons per capture will permit an evaluation of the importance of γ-ray conversion to chemical bond rupture. If every capture in bromine were accompanied by a low energy electron bond rupture would be expected even if there should be a self-cancellation of the recoils from the capture γ-rays. Further, an appreciable fraction of the trapped recoils might bear a positive charge so that the observed retentions may be determined to some extent by charge induced effects. Yield measurements[19,20] of charged recoils seem to indicate that in some isotopes approximately half of the neutron captures give rise to charge production ascribable to internal conversion.

General stochastic considerations based on the admittedly as yet incompletely known level structure in bromine for the emission of capture γ-rays suggest that radiobromine atoms are formed with differing initial recoil energies. In addition, perhaps as many as 25% possess a positive charge at the start.[19] The details of the manner in which the recoils lose their kinetic energy and come to rest in solid $KBrO_3$ within a few ångströms of their origin are not known. A number of chemical tests designed to establish the valence states of the recoil bromines trapped in the crystal lattice were performed with unsatisfactory results owing to the rapid and complete exchange which all of the lower oxidation states undergo. It has, however, been demonstrated that these recoils are reactive to varying degrees which at least is consistent with the vitro that they are trapped with varying amounts of potential energy. The effect of thermal annealing may be interpreted as a loosening of the crystal lattice sufficiently to allow for the chemical recombination of a diffusing radiobromine with the decomposition products in the crystal which also may diffuse. The characteristics of the radiation induced return of radiobromine to bromate suggest the occurrence of an exchange reaction between a trapped bromine atom and an adjacent bromate radical excited or ionized by gamma rays. A zero activation energy would be expected for such a mechanism while actually a small energy was observed so that vibrational or rotational degrees of freedom may also be required for the over-all reaction.

Acknowledgment.—The authors gratefully acknowledge the helpful suggestion of Dr. M. E. Rose that the problem of the likelihood of the self-cancellation of recoil momenta following γ-emission in cascade could be attacked using stochastic methods.

Oak Ridge, Tenn. Received August 6, 1951

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