

the more stabilizing electrolyte in a sol the greater its stability. A sol formed by dilution of a pure, relatively instable preparation is proportionately more stable than a sol formed by dilution of an impure highly stable preparation. This explains Sorum's observation that the purer a sol, the less the precipitation values of electrolytes fall off with dilution.

Only a fortuitous combination of circumstances as regards nature of sol, purity of sol, and adsorbability of precipitating ions of a given valence, can give precipitation value-sol concentration curves that are in accord with Burton and Bishop's rule.

7. Burton and Bishop's rule may be restated as follows: For a given sol, the *proportionate* increase

in stability toward precipitating electrolytes on dilution, is in general greater for electrolytes with univalent precipitating ions than for electrolytes with multivalent precipitating ions; and is greater the higher the purity of the original sol.

8. Ostwald's rule that the activity coefficient of various precipitating ions is a constant at their precipitation value, does not apply to the observations herein reported at any concentration of sol. The divergence from a constant value for the activity coefficients of various precipitating ions at their respective precipitation values is greater if they are calculated from the equilibrium molarities after adsorption than from the total added molarities.

HOUSTON, TEXAS

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## Reactions of High Energy Atoms Produced by Slow Neutron Capture

BY W. F. LIBBY

### Introduction

Slow neutron capture by most nuclei (the principal exceptions are Li, B and U) results in the immediate emission of gamma ray quanta with average energy between 3 and 6 million electron volts,<sup>1,2,3</sup> generally followed by negative or beta radioactivity. (Throughout this report these radioactive atoms will be designated by asterisks, e. g., Mn<sup>\*++</sup> for radioactive Mn<sup>++</sup> ions.) The momentum of the gamma quantum,  $h\nu/c$ , is balanced by a recoil of the emitting nucleus of mass  $M$  in atomic weight units involving the energy  $(h\nu/c)^2/2M$ , i. e.,  $533(E_\gamma)^2/M$  e. v. if  $E_\gamma$  is the gamma energy in MEV. This recoil causes the molecule to explode nearly always. It is these processes that have been investigated in this research by study of the distribution of the resultant radioactivity among the molecules in the system.

There is a possibility that the emission of more than one gamma quantum would lead to partial cancellation of the recoil momenta, reducing the energy of recoil of the nucleus, but the fact that only 8 MEV are available on the average (mass defect of the neutron) and that nearly 2 MEV of this is required for the beta radioactivity, shows that the number of gamma quanta cannot greatly

exceed two. If it did the average energy of the radiation could not be between 3 and 6 MEV. Therefore the cancellation of momenta must be a very improbable occurrence, since the cancellation for two gamma quanta would require that they have identical energies as well as opposite directions. This agrees completely with the experimental results. Since these recoil energies, even in the cases of the heavier elements, considerably exceed chemical bond energies, it is reasonable to expect that in most cases a disruption of the molecule containing the atom absorbing the neutron will result. For example, in the case of Mn, if  $E_\gamma$  is 2, the recoil energy is calculated to be at least 40 electron volts. It is the purpose of this paper to present the results of some experiments on these explosion processes and the following reactions of the very energetic atoms, molecules, free radicals or ions resulting from them. Of course only those particles carrying radioactive atoms actually will be followed. In addition, certain data on isotope exchanges will be presented.

In general the reactions of that fragment of the initial molecule which contains the radioactive atom after the recoil might be of any type involving only the fragments of the recoil and the main molecules in the substance being irradiated. It is certain, however, that no reaction involving

(1) F. Rasetti, *Z. Physik*, **97**, 64 (1935).

(2) R. Fleischmann, *ibid.*, **97**, 242-265 (1935).

(3) S. Kikuchi, K. Fushimi and H. Aoki, *Proc. Phys.-Math. Soc., Japan*, **18**, 188 (1936).

more than one *radioactive* fragment can be important, because the probability of collision is too low. These reactions with the surrounding molecules and non-radioactive fragments will be of two general types. One will require a certain fraction of the energy of recoil in order to proceed and the second will not. The term *activated* will be applied to the first type and *thermal* to the second.

Szilard and Chalmers<sup>4</sup> first demonstrated that the neutron capture recoils separated the struck atoms from the mother molecules so that the radioactivity might be separated and concentrated in those cases where the rate of thermal interchange between the main mother substance and the ejected radioactive atoms is low. Fermi, Amaldi, *et al.*,<sup>5,6</sup> applied similar methods. The later literature includes contributions from Paneth and Fay,<sup>7</sup> Glückauf and Fay,<sup>8</sup> Erbacher and Philipp,<sup>9</sup> and Lu and Sugden.<sup>10</sup> In addition there are many papers concerned either directly or indirectly with the rates of thermal isotopic interchange. Reitz<sup>11</sup> and Rosenblum and Flagg<sup>11</sup> have given reviews of this material.

The methods of investigating the various activated and thermal reactions which follow the recoil expulsions consist in the main in determinations of the fractions of the radioactivity which are found to be removable with various likely carrier molecules which may or may not have been present during the irradiation. The presence of the carrier molecules usually makes little difference, for several reasons, one of which is that they seldom are added in amounts exceeding a small percentage of the target substance. However, in this work the practice has been to add the carrier substances after the exposure. The irradiations generally were made with a 200 mg. Ra-Be source surrounded with water.

### Results and Discussion

**Manganese.**—The result of the recoil in the case of  $\text{MnO}_4^-$  ion might be expected to be the ejection of oxygen atoms or ions. The fragment containing the manganese then probably would react to form  $\text{Mn}^*\text{O}_2$  or to reform  $\text{Mn}^*\text{O}_4^-$  since these

(4) L. Szilard and T. A. Chalmers, *Nature*, **134**, 462 (1934).

(5) E. Fermi, E. Amaldi, *et al.*, *Proc. Roy. Soc. (London)*, **A149**, 522 (1935).

(6) O. D'Agostino, *Gazz. chim. ital.*, **65**, 1071 (1935).

(7) F. Paneth and J. W. J. Fay, *J. Chem. Soc.*, 384 (1936).

(8) E. Glückauf and J. W. J. Fay, *ibid.*, 390 (1936).

(9) O. Erbacher and K. Philipp, *Ber.*, **69**, 893 (1936); *Z. physik. Chem.*, **A176**, 169 (1936).

(10) C. S. Lu and S. Sugden, *J. Chem. Soc.*, 1273 (1939).

(11) O. Reitz, *Z. Elektrochem.*, **45**, 100 (1939); C. Rosenblum and J. Flagg, *J. Franklin Inst.*, **228**, 623 (1939).

are the stabler forms of manganese in neutral or acidic solutions containing excess  $\text{MnO}_4^-$ . The technique therefore is the separation of  $\text{MnO}_2$  from the  $\text{MnO}_4^-$  and the observation of the relative radioactivities. The data obtained are given in Table I and are partially reproduced in Figs. 1, 2 and 3 where the percentage of the radioactivity recovered as  $\text{Mn}^*\text{O}_4^-$ , called the *retention*, is plotted.

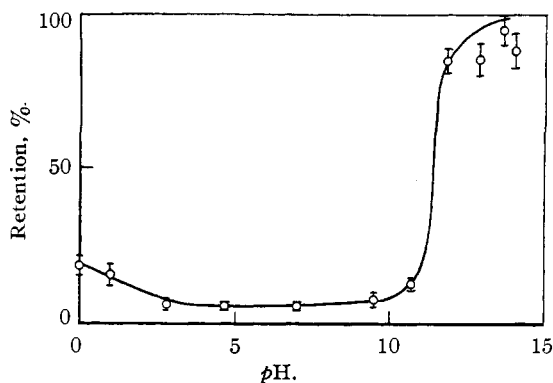


Fig. 1.—Retention vs. pH for  $\text{MnO}_4^-$  solutions.

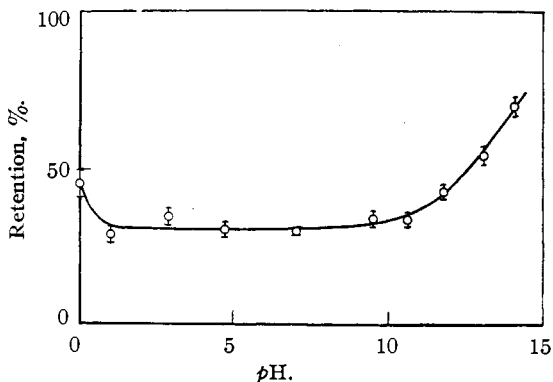


Fig. 2.—Retention vs. pH for solid potassium permanganate exposed and dissolved later in solutions of various pH values.

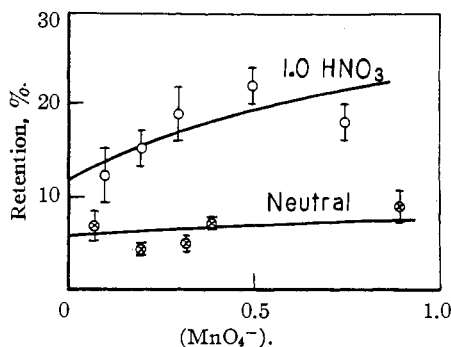


Fig. 3.—Retention in  $\text{MnO}_4^-$  solutions vs. concentration of  $\text{MnO}_4^-$ .

TABLE I  
EXPERIMENTS ON MANGANESE

No.	Experiment	Result, % retention
1	0.2 M KMnO <sub>4</sub> , phosphate buffers at pH 6.8	5 ± 1
2	.2 M KMnO <sub>4</sub> , 0.5 N NaOH	94 ± 5
3	.25 M KMnO <sub>4</sub> , 1 N NaOH	88 ± 6
4	.2 M KMnO <sub>4</sub> , 0.079 N NaOH	85 ± 5
5	.2 M KMnO <sub>4</sub> , .1 M Na <sub>2</sub> CO <sub>3</sub>	85 ± 5
6	.2 M KMnO <sub>4</sub> , .1 M Na <sub>2</sub> CO <sub>3</sub> , 0.067 M NaHCO <sub>3</sub>	12 ± 2
7	.2 M KMnO <sub>4</sub> , .0021 M Na <sub>2</sub> CO <sub>3</sub>	7.3 ± 1
8	.18 M KMnO <sub>4</sub> , .4 M HAc, 0.4 M NaAc	4.9 ± 1
9	.2 M KMnO <sub>4</sub> , .1 M HNO <sub>3</sub>	19 ± 2
10	.2 M KMnO <sub>4</sub> , .1 M HNO <sub>3</sub> , 0.4 M HAc	17 ± 2
11	.2 M NaMnO <sub>4</sub> , 1 N HNO <sub>3</sub>	15 ± 2
12	.2 M NaMnO <sub>4</sub> , .1 N HNO <sub>3</sub>	14 ± 2
13	.39 M KMnO <sub>4</sub>	7 ± 6
14	.048 M KMnO <sub>4</sub> , .1 M NaHCO <sub>3</sub>	10.6 ± 2
15	.90 M NaMnO <sub>4</sub> , .5 M HAc, 0.5 M NaAc	9 ± 2
16	.07 M NaMnO <sub>4</sub> , .5 M HAc, .5 M NaAc	7 ± 2
17	.16 M KMnO <sub>4</sub> , 4.2 M NaNO <sub>3</sub> , .07 M HAc, .07 M NaAc	10 ± 2
18	.1 M KMnO <sub>4</sub> , 1 N HNO <sub>3</sub>	12 ± 3
19	.3 M KMnO <sub>4</sub> , 1 N HNO <sub>3</sub>	19 ± 3
20	.5 M NaMnO <sub>4</sub> , 1 N HNO <sub>3</sub>	22 ± 2
21	.75 M NaMnO <sub>4</sub> , 1 N HNO <sub>3</sub>	19 ± 2
22	.01 M NaMnO <sub>4</sub> , 1.0 M NaNO <sub>3</sub> , .4 M Na <sub>2</sub> CO <sub>3</sub>	35 ± 5
23	.1 M NaMnO <sub>4</sub> , .9 M NaNO <sub>3</sub> , .4 M Na <sub>2</sub> CO <sub>3</sub>	38 ± 5
24	1.0 M NaMnO <sub>4</sub> , .4 M Na <sub>2</sub> CO <sub>3</sub>	43 ± 6
25	0.083 M KMnO <sub>4</sub> in acetone, filtered through wet MnO <sub>2</sub> , for extraction	1 ± 1
26	Solid KMnO <sub>4</sub> exposed at 25°, dissolved after exposure in neutral water at 25°	28 ± 5
27		30 ± 5
28		32 ± 5
Solid KMnO <sub>4</sub> exposed at 25°, dissolved in buffered solutions of various pH values		
29	pH 0	44 ± 2
30	pH 1	28 ± 3
31	pH 2.9	34 ± 3
32	pH 4.7	30 ± 3
33	pH 9.5	34 ± 3
34	pH 10.6	34 ± 3
35	pH 11.7	43 ± 3
36	pH 13	55 ± 3
37	pH 14	71 ± 3
38	Solid KMnO <sub>4</sub> exposed, then dissolved in 1 N HNO <sub>3</sub>	39 ± 2
39	Solid KMnO <sub>4</sub> exposed, then dissolved in 2 N H <sub>2</sub> SO <sub>4</sub>	42 ± 4
40	Solid KMnO <sub>4</sub> exposed, then dissolved in 1 M H <sub>3</sub> PO <sub>4</sub>	29 ± 3
41	Solid KMnO <sub>4</sub> exposed in liquid air, then dissolved in water	50 ± 5
42	Solid KMnO <sub>4</sub> exposed, then dissolved in acetone and allowed to stand 20 minutes	28 ± 3
43	Solid KMnO <sub>4</sub> exposed, then dissolved in acetone and allowed to stand 80 minutes	31 ± 3
44	0.28 M Na <sub>2</sub> MnO <sub>4</sub> approximately 0.3 M NaOH exposed, then acidified with HAc, MnO <sub>2</sub> filtered off and counted as MnNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O, filtrate was reduced and counted as MnNH <sub>4</sub> PO <sub>4</sub> ·H <sub>2</sub> O	Activity in MnO <sub>2</sub> = 85 ± 5% MnO <sub>4</sub> = 15 ± 5%
45	0.028 M Na <sub>2</sub> MnO <sub>4</sub> , 1.1 M NaOH, exposed, then acidified to 0.2 N H <sup>+</sup> and MnO <sub>2</sub> filtered off and half of filtrate reduced with SO <sub>3</sub> <sup>2-</sup> to MnO <sub>2</sub> . Precipitates were counted.	Activity in MnO <sub>2</sub> = 85 ± 3% MnO <sub>4</sub> <sup>-</sup> = 15 ± 3%
46	0.2 M KMnO <sub>4</sub> (slightly alkaline to insure approximately 50% retention) was exposed, split into three equal parts. One portion was made 0.1 N H <sub>2</sub> SO <sub>4</sub> , another 0.1 N NaOH, and the third was left neutral. After 130 minutes the retention values were determined.	For 0.1 N H <sub>2</sub> SO <sub>4</sub> , 45 ± 3% retention, neutral, 41 ± 3% retention, 0.1 N NaOH, 36 ± 3% retention
47	0.94 M MnSO <sub>4</sub> , 1 M H <sub>2</sub> SO <sub>4</sub> , exposed, successive MnO <sub>2</sub> precipitates were made by addition of small amounts (1.6%) of MnO <sub>4</sub> <sup>-</sup> . All activities were equal.	Formation of valences higher than +4 was less than 1%.

TABLE I (Concluded)

No.	Experiment	Result
48	1 M MnSO <sub>4</sub> , neutral. Treated as in Expt. 47.	Formation of valences higher than +4 was less than 1%.
49	Solid Mn(OH) <sub>2</sub> , exposed, dissolved in dilute H <sub>2</sub> SO <sub>4</sub> and treated as in Expt. 47.	Formation of valences higher than +4 was less than 1%.
50	Interchange between MnO <sub>4</sub> <sup>-</sup> and MnO <sub>4</sub> <sup>-</sup> tested by mixing equal volumes of 0.4 M Mn*O <sub>4</sub> <sup>-</sup> and 0.4 M MnO <sub>4</sub> <sup>-</sup> in 1 N OH <sup>-</sup> . After one minute excess Ba <sup>++</sup> was added to precipitate BaMnO <sub>4</sub> which was centrifuged off. Filtrate of MnO <sub>4</sub> <sup>-</sup> was reduced to MnO <sub>2</sub> and two precipitates were counted.	Complete interchange in two minutes.
51	Approximately 2 g. of finely powdered MnO <sub>2</sub> was shaken with 5 cc. of 0.1 M Mn*O <sub>4</sub> <sup>-</sup> in 0.5 N OH <sup>-</sup> for 1/2 hour.	Activity in MnO <sub>2</sub> was less than 3% of that in MnO <sub>4</sub> <sup>-</sup> . No interchange in 1/2 hour involving more than about 100 molecular layers on the surface of the MnO <sub>2</sub> .
51 <sup>a</sup>	600 cc. of colloidal MnO <sub>2</sub> containing 1.06 × 10 <sup>-6</sup> mole (prepared by adding equivalent amounts of 1% H <sub>2</sub> O <sub>2</sub> to 0.02 M KMnO <sub>4</sub> and diluting) mixed with 2 cc. of radioactive manganous chloride containing 1.8 × 10 <sup>-6</sup> mole. After 67 hours the sol was coagulated with HNO <sub>3</sub> , the MnO <sub>2</sub> filtered off and counted, and the filtrate Mn <sup>++</sup> precipitated and counted. The precipitates were determined gravimetrically. The active atoms were Mn <sup>54</sup> (310 days half-life) which decays by K capture and γ ray emission. Sol particles were less than 10 <sup>-6</sup> cm. in diameter, as shown by centrifuging.	Activity of Mn <sup>++</sup> = 89 ± 8% Activity of MnO <sub>2</sub> = 11 ± 8% Little if any interchange.

<sup>a</sup> This experiment was performed by Mr. Arthur W. Adamson.

Fermi, Amaldi, *et al.*,<sup>5</sup> and D'Agostino<sup>6</sup> report concentrating the 2.5-hr. Mn<sup>56</sup> isotope by irradiation of an aqueous solution of potassium permanganate and removing most of the activity simply by filtering the solution through paper. Presumably the activity remained in a thin deposit of manganese dioxide on the paper. Polissar<sup>12</sup> showed that no rapid thermal interchange occurs between Mn<sup>++</sup> or MnO<sub>2</sub> and MnO<sub>4</sub><sup>-</sup> under ordinary conditions.

The procedure used in the study of all permanganate and manganate solutions was to expose the solutions by inserting the glass enclosed Ra-Be source into the solution or to place the solution near the source in a water tank. In a few cases the solutions were filtered with a paper filter several times to remove the reduced radioactivity as MnO<sub>2</sub>. In most cases, however, the solution was made slightly acidic with nitric or sulfuric acid and a small amount of Mn<sup>++</sup> (less than 1% of MnO<sub>4</sub><sup>-</sup> present) was added to give a precipitate of manganese dioxide before filtration. In the case of potassium permanganate solutions the procedure of filtering directly was found to be nearly as efficient in removing the activity as the use of carrier. Probably this was due to slight manganese dioxide formation by reaction with the water and the filter paper. In all cases re-

peated filtrations were made until no further activity was removed. The first precipitate usually contained more than 95% of the extractable activity. However, in the experiments where solid potassium permanganate was irradiated and then dissolved it was found necessary to use the Mn<sup>++</sup> carrier procedure to extract the activity in less than four or five filtrations. The irradiated solution was divided into two approximately equal portions, one of which was purified for extractable activity in the way described above. This purified solution and the original solution were then compared in activity either by placing in a jacket surrounding an ordinary Geiger-Müller counter<sup>13</sup> or by completely reducing the MnO<sub>4</sub><sup>-</sup> to MnO<sub>2</sub> or to Mn<sup>++</sup> (which was precipitated as MnNH<sub>4</sub>PO<sub>4</sub>·H<sub>2</sub>O) and counting the two precipitates with an ordinary solid wall counter. Care was taken to ensure that the same amount of MnO<sub>4</sub><sup>-</sup> was present in the two solutions finally counted, so that errors due to absorption of the beta radiation in the solutions or precipitates themselves would cancel.

The first point to be considered is the completeness of the initial explosion reaction, whatever it may be. Experiment 25 shows that MnO<sub>4</sub><sup>-</sup> in acetone showed zero retention and Fig. 1 shows

(12) M. J. Polissar, *THIS JOURNAL*, **58**, 1372 (1936).

(13) A. R. Olson, W. F. Libby, F. Long and R. S. Halford, *ibid.*, **58**, 1313 (1936).

that variation of the  $pH$  from 8 to 12 in aqueous solutions caused nearly a 100% change in the percentage retained. The acetone result can be explained as a consequence of an excitation of the  $MnO_4^-$  caused by the recoil rather than a complete ejection of part of the  $MnO_4^-$ . However, in the case of aqueous solutions the presence of 0.01  $M$   $OH^-$  changes the retention from about 7% for neutral solution to nearly 100%. The curve in Fig. 1 (Expts. 1-12) in the region of highest  $pH$  values is drawn above the actual points to partially correct for the reduction of  $MnO_4^-$  which occurs in alkaline solutions, probably due to traces of  $MnO_2$ . This would have lowered the retention values. The curve probably approaches 100% quite closely in 0.1  $N$  or 1  $N$   $OH^-$  solutions. The values in the acid range fluctuated considerably from experiment to experiment, but the average value represented by the curve is probably accurate to 5% even in these solutions. It is very difficult to imagine the  $MnO_4^-$  ion retaining its internal activation long enough to meet an  $OH^-$  in 0.01  $M$   $OH^-$  solution and thereby have its whole fate changed. Under these conditions it should have struck on the average more than 5000 water molecules before the  $OH^-$  approach occurred. An ion as simple as  $MnO_4^-$  hardly could retain through so many collisions sufficient energy to allow it to oxidize water (as it must do in neutral solution). The alternative explanation of *explosion* in at least 95% of the cases therefore is adopted.

It seems extremely probable that no manganese molecules or ions of oxidation number above +4 formed by explosion of  $MnO_4^-$  or  $MnO_4^{\cdot-}$  can reduce  $H_2O$  or  $OH^-$ . The justification of this consists in the assignment of values for the energies of hydration and for the bonds involved which are consistent with those for known systems. Such considerations show that a strongly reducing intermediate of this sort is very improbable.

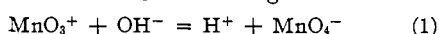
This assumption requires that any elevation of the valence of the radioactive fragments must be accomplished by  $MnO_4^-$  in competition with hydration and reduction reactions with  $H_2O$  and its ions. Such oxidations by or interchanges with  $MnO_4^-$  must necessarily increase in importance with the concentration of  $MnO_4^-$  because of the chance of reaction with  $MnO_4^-$  rather than with  $H_2O$  or  $H^+$  and  $OH^-$  ions is increased. The possibility of forming  $Mn^*O_4^-$  by oxidation processes depends on the rapid electronic interchange be-

tween  $MnO_4^{\cdot-}$  and  $MnO_4^-$  (Expt. 50). This accomplishes the +6 to +7 change in valence of the radioactive molecule. The data shown in Fig. 3 (Expts. 13-21) and in Table I, Expts. 22, 23 and 24, show that  $MnO_4^-$  concentration effects are small in neutral and alkaline solutions, but are somewhat larger in strongly acid solutions. Because of these facts the processes causing retention by intervention of  $MnO_4^-$  must be relatively unimportant and the conclusion is drawn that *in nearly all cases the result of the recoil is the formation of fragments containing +7 manganese directly and therefore not requiring reaction with  $MnO_4^-$  to form  $Mn^*O_4^-$* . The chances of being reduced before they can be hydrated to  $Mn^*O_4^-$  are decreased by increasing the  $OH^-$  concentration until at about  $pH$  12 the chance of hydration is nearly unity. The small variation of retention with  $MnO_4^-$  concentration indicated in Expts. 22, 23 and 24 may be evidence that some of the fragments are reduced but in the case of the 0.1  $M$  and 1.0  $M$   $MnO_4^-$  solutions (Expts. 23 and 24) the change may be attributed to ionic strength effects on the  $pH$  of the solution when 0.9  $M$  sodium nitrate is replaced with 0.9  $M$  sodium permanganate. It is interesting to notice that these experiments with 0.4 sodium carbonate and 1  $M$  sodium nitrate show lower retentions than Expt. 5, with 0.1  $M$  sodium carbonate alone with the  $MnO_4^-$ . This corresponds to the expected reduction of  $pH$  due to increase in ionic strength.

Figure 2 (Expts. 26-40) presents data obtained by irradiating solid potassium permanganate and dissolving it in aqueous solutions of various  $pH$  values. The similarity of the curves in Figs. 1 and 2 indicates that at least 40% of the activity in the case of irradiated solid potassium permanganate which later is dissolved in solutions of various  $pH$  values acts in a way very analogous to that in which most of the activity behaves in the case of the irradiated solutions. The reactions in the case of the solid being dissolved after irradiation certainly are thermal. At least several minutes have elapsed since the neutral recoil has occurred in all cases. The recoil process itself cannot well require more than  $10^{-12}$  second; therefore the similarity indicates that even in the case of the solution the *reactions determining the variation of retention with  $pH$  are thermal* in character also. This is in agreement with the point that 0.01  $M$   $OH^-$  solution could hardly have enough  $OH^-$  ions present so that the majority of the particles carry-

ing radioactive manganese atoms could encounter an  $\text{OH}^-$  before losing both their recoil energy and internal energy of activation by collision with water molecules.

The nature of the intermediates produced by the primary explosion probably is such that they have +7 manganese, and can react with 0.01  $M$   $\text{OH}^-$ , 0.2  $M$   $\text{MnO}_4^-$  solution, but not with neutral 0.2  $M$   $\text{MnO}_4^-$  to form  $\text{MnO}^*_{4^-}$ . Mild reducing agents immediately convert them to  $\text{Mn}^*_{\text{O}_2}$  or  $\text{Mn}^{*++}$ . However the acetic acid in 0.4  $M$  acetic acid does not reduce them (Expts. 9 and 10) more than the acid aqueous solution itself would. In addition,  $\text{NO}_3^-$  (Expt. 17 compared with others),  $\text{HSO}_4^-$  (Expts. 38 and 39) and  $\text{H}_2\text{PO}_4^-$  (Expt. 40) all fail to affect the course of the reaction with the aqueous environment in any way. In fact, together all these experiments indicate that the ions and molecules other than  $\text{H}_2\text{O}$ ,  $\text{MnO}_4^-$ ,  $\text{H}^+$  and  $\text{OH}^-$  have little effect on the phenomena in the case of aqueous solutions. At least they do not control the fate of more than 5 or 10% of the activity. The four possible intermediates satisfying the requirements mentioned above are  $\text{MnO}_3^+$ ,  $\text{MnO}_2^{+3}$ ,  $\text{MnO}^{+5}$  and  $\text{Mn}^{+7}$ . All of these probably will be at least as powerful oxidizing agents as  $\text{MnO}_4^-$ , which is itself strong enough to oxidize  $\text{H}_2\text{O}$  in neutral solution.<sup>14</sup> In addition they probably would be much more rapid in their action because their structures are simpler. On the other hand, they certainly will strongly attract negative ions and in the case of  $\text{OH}^-$  should hydrate in so doing to form  $\text{MnO}_4^-$  according to



as a typical case. This explains the rise in retention with increasing  $p\text{H}$ . At lower  $p\text{H}$  values the oxidation of water probably proceeds, causing nearly zero retention. The data of Fig. 3 show that in neutral solutions there is no appreciable increase in retention with  $\text{MnO}_4^-$  concentration. This might be taken as evidence that  $\text{MnO}_3^+$  is not the principal ion formed because it seems likely that the charge attraction would promote the interchange



It seems probable to the author that most of the activity is distributed among the four ions listed, most of it belonging to those bearing either one or three positive charges. The principal reason for this conclusion is that there hardly seems to be

(14) W. M. Latimer, "Oxidation States of the Elements," Prentice-Hall, New York, N. Y., 1938.

enough energy in the expected 40 to 100 electron volts from the average recoil to produce  $\text{Mn}^{+7}$  ion. (The author is indebted to Professor W. M. Latimer for this point.) It may be that the interchange reaction (2) is slow enough not to be able to compete with the oxidation of  $\text{H}_2\text{O}$  whereas the  $\text{OH}^-$  reaction (1) can. It is interesting that in acid solution there seems to be a small dependence of the retention on  $\text{MnO}_4^-$  concentration. One might guess that the abundance of  $\text{H}_3\text{O}^+$  in 1  $N$   $\text{H}^+$  solutions reduces the chance of contact of  $\text{H}_2\text{O}$  with the positively charged oxidizing ions just enough to allow reaction (2) to have some effect. Such effects have been discussed previously in kinetic studies (*cf.* M. H. Gorin<sup>15</sup> on the  $\text{Cl}^-$  catalysis of the reduction of  $\text{Fe}^{+++}$  by  $\text{Sn}^{++}$  due to formation of the weak salts).

With respect to  $\text{MnO}_4^-$ , Expts. 44 and 45 prove first that the retention by  $\text{MnO}_4^-$  in alkaline solutions is not nearly as high as in the case of  $\text{MnO}_4^-$  (in fact less than 25% under conditions of 100% retention for  $\text{MnO}_4^-$  solutions) and that less than 25% of the cases lead to  $\text{MnO}_4^-$  formation because the rapid interchange (Expt. 50) between  $\text{MnO}_4^-$  and  $\text{MnO}_4^-$  would transfer the activity to  $\text{MnO}_4^-$  immediately. Despite certain evidence in the literature from measurements at low concentration that such  $\text{MnO}_4^-$  solutions should contain a considerable concentration of  $\text{MnO}_4^-$ , direct test by precipitation of  $\text{BaMnO}_4$  with excess  $\text{Ba}^{++}$  and centrifuging showed the  $\text{MnO}_4^-$  concentration to be low (less than 5% of  $\text{MnO}_4^-$ ). The  $\text{MnO}_4^-$  test was made by means of the violet color of the liquor after removal of the  $\text{MnO}_4^-$ . In all cases it was very faint. There was insufficient  $\text{MnO}_2$  present before the  $\text{Ba}^{++}$  was added to allow an equilibrium shift. Though a slow rate may be involved here, it is more probable that the system needs further study at higher  $\text{MnO}_4^-$  concentrations and higher ionic strengths.

It seems probable that in explosions of such violence if the recoils caused lower valence ions or molecules to form in the case of  $\text{MnO}_4^-$  they should in general produce some of the same character with respect to the oxidation and hydration reactions as those produced from  $\text{MnO}_4^-$ . The great difference between the two cases indicates that the  $\text{MnO}_4^-$  products are mainly of +7 valence which could not be produced from  $\text{MnO}_4^-$  by the ejection of any ordinary atoms or ions. It is possible that in the case of  $\text{MnO}_4^-$  some re-

(15) M. H. Gorin, THIS JOURNAL, 58, 1787 (1936).

duction occurs in the primary step (by the ejection of oxygen atoms or less probably ions), though of course the follow reactions may be responsible for the low retention.

With respect to the possibility that dissolved oxygen in the case of the  $\text{KMnO}_4$  solutions is acting to oxidize the small amount of reduced Mn up to  $\text{MnO}_4^-$  in alkaline solution which might then interchange with  $\text{MnO}_4^-$  to leave the activity in the  $\text{MnO}_4^-$  and so account for the alkaline rise in retention, Experiment 46 is crucial in showing that no significant change in the distribution of the activity occurs if after irradiation a solution is made alkaline and allowed to stand in the air for over two hours. It follows therefore that the *rise in the alkaline range is not due to oxidation of small amounts of relatively stable lower valence forms of manganese containing most of the activity*. In other words, in the case of the solutions, variations of pH after irradiation have no effect. *All the determining reactions occur during irradiation and before the activity reaches any stable form, i. e.,  $\text{MnO}_4^-$ ,  $\text{Mn}^{++}$ ,  $\text{MnO}_2$  or  $\text{MnO}_4^=$ .* All of the experiments in which alkaline solutions were irradiated serve as further checks of this point because they all were acidified after radiation before the standard analysis.

The situation in the case of the irradiated solid seems to be different from that of the solutions in that about 30% reformation of  $\text{MnO}_4^-$  and 30% reduction to lower valence states appear to occur, probably due to direct reaction with the surrounding ions in the crystal. The residual 40% of the activity appears to be left trapped in the crystal as some of the +7 ions discussed above, which on being dissolved in aqueous solutions act just as they do in the case of the irradiated solutions. Experiment 41 shows that the retention as  $\text{MnO}_4^-$  in the case of solid potassium permanganate irradiated at liquid air temperature with neutrons cooled by paraffin immersed in the liquid air has risen from 30 to about 50%, constituting strong evidence that the phenomena even in the solid are largely determined by reactions which follow the initial explosion and of which a good fraction are thermal in character.

Experiments 47, 48 and 49 show that elevation of +2 Mn to any higher valence than +4 does not occur, because  $\text{Mn}^*\text{O}_2$  would have been formed. Experiment 51 shows that manganese dioxide does not interchange with  $\text{Mn}^{++}$  under these conditions at all readily. Experiment 50

shows that  $\text{MnO}_4^=$  and  $\text{MnO}_4^-$  interchange very rapidly, presumably by the transfer of a 3d electron from the  $\text{MnO}_4^=$  ion to the  $\text{MnO}_4^-$ , since the two ions appear to be nearly identical in other ways. Any other mechanism seems quite improbable because *all atomic interchanges between similarly charged ions* studied so far have been found to be slow. For example  $\text{CO}_3^=$  and  $\text{OH}^-$ <sup>16</sup> show very slow interchange of O atoms. In addition  $\text{SO}_4^=$  and  $\text{SO}_3^-$  ions,<sup>17</sup> the arsenate and arsenite (20) ions,  $\text{PO}_4^=$  and  $\text{PO}_3^=$  (19) and the other phosphate and phosphite ions are all so slow as not to have given observable interchanges in a few hours in ordinary solutions.

In conclusion, the experiments described indicate that:

1. The  $\text{MnO}_4^-$  ions in solution are disrupted in nearly every instance to form one or all of the ions  $\text{Mn}^*\text{O}_3^+$ ,  $\text{Mn}^*\text{O}_2^{+3}$ ,  $\text{Mn}^*\text{O}^{+5}$  and  $\text{Mn}^{*+7}$ . The ion  $\text{Mn}^*\text{O}_3^+$  probably is the most important.
2. These ions oxidize  $\text{H}_2\text{O}$  rapidly and in neutral and dilute acid solutions this is the predominant reaction.
3. In alkaline solutions they combine with  $\text{OH}^-$  ions to form  $\text{MnO}_4^-$  again at a rate much faster than the  $\text{H}_2\text{O}$  oxidation. None of the series  $\text{NO}_3^-$ ,  $\text{H}_2\text{PO}_4^-$  or  $\text{HSO}_4^-$  seems to be able to accomplish this hydration nearly so readily.
4. In strong acid solutions the interchange  $\text{Mn}^*\text{O}_3^+ + \text{MnO}_4^- = \text{MnO}_3^+ + \text{Mn}^*\text{O}_4^-$  seems to be able to compete with the oxidation reaction.
5. When solid potassium permanganate is irradiated at room temperature about 30% of the activity returns to  $\text{MnO}_4^-$ , about 30% is permanently reduced and about 40% appears to be left trapped in the solid as the ions of +7 valence which, on being dissolved in aqueous solutions, proceed to act just as they do in the case of irradiated solutions.
6.  $\text{MnO}_4^-$  and  $\text{MnO}_4^=$  interchange an electron (probably 3d) with great ease.

**Phosphorus.**—The thermal exchange between phosphate and phosphite in neutral, strong acid, and strong alkaline solutions has been shown by Wilson<sup>18</sup> to be very small. Wilson's analytical technique was used in this work. To the irradiated solution, or solution made by dissolving the irradiated solid, the acid or salt of different valence was added and separated. The amounts of

(16) G. A. Mills and H. C. Urey, *THIS JOURNAL*, **61**, 534 (1939).

(17) H. H. Voge and W. F. Libby, *ibid.*, **59**, 2474 (1937); H. H. Voge, *ibid.*, **61**, 1032 (1939).

(18) J. N. Wilson, *ibid.*, **60**, 2697 (1938).

TABLE II  
EXPERIMENTS ON RETENTION BY +3 AND +5 PHOSPHORUS

No.	Experiment	Retention (%)
52	Solid $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ , exposed and dissolved in pure water	92 $\pm$ 3 (as +3 phosphorus)
53	Solid $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , exposed and dissolved in pure water	45 $\pm$ 4
54	Solid $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , exposed and dissolved in pure water	52 $\pm$ 3
55	Solid $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , exposed and dissolved in pure water	50 $\pm$ 4
56	Solid $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , exposed and dissolved in 1 <i>N</i> HCl	51 $\pm$ 4
57	Solid $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , exposed and dissolved in 1 <i>N</i> NaOH	53 $\pm$ 4
58	Solid $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , exposed and dissolved in 6 <i>N</i> NaOH	47 $\pm$ 4
59	0.83 <i>M</i> $\text{H}_3\text{PO}_4$	43 $\pm$ 3
60	0.96 <i>M</i> $\text{H}_2\text{PO}_4^-$	54 $\pm$ 8
61	0.32 <i>M</i> $\text{HPO}_4^{2-}$	38 $\pm$ 3
62	0.58 <i>M</i> $\text{PO}_4^{3-}$ , 0.28 <i>M</i> $\text{OH}^-$	32 $\pm$ 2

phosphate and phosphite were adjusted in the two solutions so the masses of the two precipitates would be the same. The irradiations were made by placing the solutions in wax bottles and the solids in small paper packets. The author is indebted to the Radiation Laboratory for the neutron irradiation of these substances. The intensity of the radium-beryllium source was too low to produce convenient intensities. The data are given in Table II.

Experiment 52 shows that there is little gain in oxidation number in the case of solid  $\text{HPO}_3^-$  salt. Experiments 53 to 62 inclusive show that the retention is remarkably independent of environment, the results in the solids and solutions being nearly the same at about 50% retention, except in the case of irradiated alkaline solutions when it dropped somewhat.

The small effect of environmental changes on the retention of activity by +5 phosphorus in its various forms suggests that in this case, as opposed to that of +7 Mn discussed previously, the initial recoil determines the retention while the following thermal or activated reactions are quite unable to change the result. In aqueous solution +3 phosphorus in its various ordinary forms is thermodynamically unstable with respect to the reduction of water and formation of +5 phosphorus. It is not surprising therefore that water should oxidize the unstable intermediate +4 states to +5 phosphorus. In the case of +3 phosphorus produced by the recoils, hydration might occur more rapidly than oxidation to form the ordinary metastable ions or molecules. If the recoils produced on the average about half as much +3 phosphorus as higher valence states, the data would be explained. It is rather interesting that in the case of  $\text{MnO}_4^-$  it was decided that the MnO bond generally was broken to form -2 oxygen

fragments while in the case of the P-O bond in the +5 phosphorus molecules at least half of the processes appear to involve expulsion of O or much less probably -1 oxygen. This is in agreement with the probable difference in bond type.

**Arsenic.**—Wilson and Dickinson<sup>19</sup> have shown that thermal interchange does not occur at a detectable rate at 100° between +3 and +5 arsenic in aqueous solutions. Their method of separation of arsenate and arsenite was used in this work.

TABLE III  
EXPERIMENTS ON RETENTION BY +3 AND +5 ARSENIC

No.	Experiment	Retention in original valence state (%)
63	Solid $\text{H}_3\text{AsO}_4$ , exposed and dissolved in water	93 $\pm$ 10
64	Solid $\text{As}_2\text{O}_3$ , exposed and dissolved in approximately 1 <i>N</i> NaOH	100 $\pm$ 2
65	3 <i>M</i> $\text{H}_3\text{AsO}_4$	100 $\pm$ 3
66	1.5 <i>M</i> $\text{Na}_2\text{HASO}_3$	96 $\pm$ 2
67	Solid $\text{H}_3\text{AsO}_4$ , exposed and dissolved in 6 <i>N</i> $\text{H}_2\text{SO}_4$	75 $\pm$ 15
68	Solid $\text{H}_3\text{AsO}_4$ , exposed and dissolved in 6 <i>N</i> NaOH	75 $\pm$ 15

Experiments 64 and 66 show that the +3 state retains its activity almost completely in either the solid state or in the alkaline solution. Experiments 63, 65, 67 and 68 substantiate a similar conclusion for the +5 state. Experiments 67 and 68 were not sufficiently accurate to warrant a definite conclusion that dissolving the irradiated solid  $\text{H}_3\text{AsO}_4$  in strongly acidic or alkaline solutions results in a decrease in the retention.

The complete retention of the activity by both +3 and +5 states of arsenic under all conditions is understandable on the basis of no change in valence during the recoil followed by hydration

(19) J. N. Wilson and R. G. Dickinson, *THIS JOURNAL*, **59**, 1328 (1937).



reactions more rapid than any oxidation or reduction reactions with water. There is less free energy available for these latter processes than in the case of  $\text{MnO}_4^-$  so it is not surprising that hydration should be allowed to proceed. The necessity of assuming expulsion of divalent oxygen in the recoil while +5 phosphorus appeared to eject lower valence oxygen is in line with the somewhat more metallic character of arsenic.

The other possibility that the capture process has insufficient recoil energy is excluded by D'Agostino's<sup>6</sup> successful concentration of most of the activity from irradiated cacodyl. The characteristics of the arsenic neutron capture process are so similar to other cases that it is quite inconceivable that there should be any large difference in the neutron capture recoils in this case from those of the other elements discussed.

**Chlorine.**—D'Agostino<sup>6</sup> reported that both sodium chlorate and perchlorate solutions as well as the solid salts showed no detectable retention. Further experiments were performed to check possible effects of *p*H, etc. The data are given in Table IV.

Experiments 69, 70 and 71 show that  $\text{ClO}_4^-$  has the same retention in 1 *N* nitric acid and 1 *N* sodium hydroxide as in neutral solution, for which it is zero within a few %, in agreement with D'Agostino.<sup>6</sup> They show also that in all three cases less than 10% of the recoils lead to  $\text{ClO}_3^-$

formation. As one might have expected from the considerations of the cases of Mn, P and As, the irradiation of  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$  reveals no retention under any conditions that cannot be accounted for by interchange between lower valence states and  $\text{ClO}_3^-$ . In the case of  $\text{ClO}_4^-$  there is little if any retention even in acid solutions. The expected ejection of lower valence oxygen necessarily leads to reduction of the radioactive molecule. The experiments showed that these molecules either were reduced to  $\text{Cl}_2$  or  $\text{Cl}^-$  by water or interchanged with the carrier  $\text{Cl}_2$  or  $\text{Cl}^-$  added for the separation. In this connection Expts. 69, 70 and 71 showing that the irradiation of  $\text{ClO}_4^-$  produced little if any  $\text{ClO}_3^-$  are interesting in hinting that the valence change may generally have been larger than that for the simple expulsion of a single O atom. On the other hand Expts. 73, 74 and 75 seem to show that the presence of acid during irradiation is considerably more effective in causing retention than its addition after irradiation. This may mean that there is acid catalysis of interchange between  $\text{ClO}_3^-$  and intermediate states which leads to higher interchange rates than those observed between  $\text{Cl}_2$  and  $\text{ClO}_3^-$  and suggests that the intermediate states are not to be identified with  $\text{Cl}_2$  or  $\text{Cl}^-$ . However, the interchange in the case of the irradiated acid solution may be faster simply because the recoiling particles still may have energies considerably

TABLE IV  
RETENTION BY CHLORATE AND PERCHLORATE

No.	Experiment	Activities (in arbitrary units)
69	1.0 <i>M</i> $\text{NaClO}_4$ neutral, exposed, $\text{ClO}_3^-$ added till 0.02 <i>M</i> , then $\text{Cl}^-$ and $\text{Ag}^+$ . Filtrate was reduced with $\text{NO}_2^-$ after being made 1 <i>N</i> in $\text{HNO}_3$ to convert $\text{ClO}_3^-$ to $\text{Cl}^-$ , $\text{Ag}^+$ was then added to precipitate $\text{AgCl}$ .	$\text{Cl}^- = 100 \pm 10$ $\text{ClO}_3^- = 0 \pm 10$
70	1.0 <i>M</i> $\text{NaClO}_4$ , 1 <i>N</i> $\text{HNO}_3$ , exposed in same vessel and position as in Expt. 69. Same treatment.	$\text{Cl}^- = 91 \pm 10$ $\text{ClO}_3^- = 0 \pm 15$
71	1.0 <i>M</i> $\text{NaClO}_4$ , 1 <i>N</i> $\text{NaOH}$ , exposed as in Expt. 64, neutralized, and treated in same way.	$\text{Cl}^- = 94 \pm 10$ $\text{ClO}_3^- = 0 \pm 10$
72	Identical bottles of 0.1 <i>M</i> $\text{NaCl}$ and 0.1 <i>M</i> $\text{NaClO}_3$ , 0.56 <i>N</i> in $\text{NaOH}$ were exposed in the same way, the $\text{ClO}_3^-$ was neutralized and made 0.1 <i>M</i> in $\text{Cl}^-$ , equivalent amounts of $\text{Pb}^{++}$ were added to both solutions and the activities compared.	0.1 <i>M</i> $\text{NaCl}$ precipitate = 100 $\pm$ 15 0.1 <i>M</i> $\text{NaClO}_3$ ; 0.56 <i>N</i> $\text{OH}^-$ precipitate = 100 $\pm$ 15.
73	Two solutions of 1 <i>M</i> $\text{NaClO}_3$ , one pure and the other 2 <i>M</i> in $\text{H}_2\text{SO}_4$ , were exposed in the same way and $\text{AgCl}$ precipitations made after neutralization.	$\text{Cl}^-$ from neutral solution = 100 $\pm$ 2 $\text{Cl}^-$ from 2 <i>M</i> $\text{H}_2\text{SO}_4$ solution = 10 $\pm$ 2
74	1 <i>M</i> $\text{NaClO}_3$ exposed, split into equal portions, one of which was made 6 <i>M</i> in $\text{H}_2\text{SO}_4$ and allowed to stand 23 minutes; $\text{Cl}^-$ and a little $\text{S}_2\text{O}_3^{--}$ then were added to both solutions and $\text{AgCl}$ precipitated.	$\text{Cl}^-$ from neutral solution = 100 $\pm$ 6 $\text{Cl}^-$ from 6 <i>M</i> $\text{H}_2\text{SO}_4$ portion = 99 $\pm$ 6
75	A solution of $\text{Cl}_2^*$ (approximately 0.01 <i>M</i> ) in 2 <i>M</i> $\text{H}_2\text{SO}_4$ was split into two equal portions and one was made 1 <i>M</i> in $\text{NaClO}_3$ and both allowed to stand 72 minutes before $\text{SO}_3^{--}$ and $\text{Ag}^+$ were added to precipitate the $\text{Cl}_2$ as $\text{AgCl}$ .	$\text{Cl}_2$ precipitate = 100 $\pm$ 4 $\text{Cl}_2$ , $\text{ClO}_3^-$ precipitate = 59 $\pm$ 6

above thermal values when the interchange occurs. This seems to be quite probable.

A thermal interchange at room temperature between  $\text{Cl}_2^*$  at approximately 0.01  $M$  and  $\text{ClO}_3^-$  at 1  $M$  in 1  $N$   $\text{H}^+$  is definite. The possibility that

the radioactive chlorine atoms leave  $\text{Cl}_2$  to go permanently to some intermediate molecule different from  $\text{ClO}_3^-$  is excluded by the fact that there is no such molecule in the system at concentrations several times that of the  $\text{Cl}_2$ , as would be neces-

TABLE V  
DATA ON RETENTION BY  $\text{BrO}_3^-$

No.	Experiment	Activities
76	Solid $\text{NaBrO}_3$ , exposed, dissolved in pure water and equivalent amount of $\text{KBr}$ added. Solution then was made approximately 1.5 $M$ in $\text{NH}_4\text{OH}$ and excess $\text{Ag}^+$ added to precipitate $\text{AgBr}$ . Filtrate was acidified and more $\text{Ag}^+$ added to precipitate $\text{AgBrO}_3$ .	$\text{AgBr} = 100 \pm 6$ $\text{AgBrO}_3 = 4 \pm 4$
77	2 $M$ $\text{NaBrO}_3$ in 3 $N$ $\text{NaOH}$ , procedure same as in Expt. 76.	$\text{AgBr} = 100 \pm 6$ $\text{AgBrO}_3 = 10 \pm 8$
78	2 $M$ $\text{NaBrO}_3$ , neutral, procedure same as in Expt. 76.	$\text{AgBr} = 100 \pm 6$ $\text{AgBrO}_3 = 10 \pm 8$
79	Two $\text{NaBrO}_3$ solutions (approximately 2 $M$ ), one of which was 1 $N$ in $\text{HNO}_3$ and the other neutral, were exposed in the same way, small amount $\text{Br}_2$ added to each, rapidly extracted with $\text{CCl}_4$ , precipitated as $\text{AgBr}$ and counted.	Neutral solution = 100 $\pm$ 2 1 $N$ $\text{HNO}_3$ solution = 20 $\pm$ 8
80	1.13 $M$ $\text{NaBrO}_3$ was exposed and divided into three equal portions. One part was made 1 $M$ in $\text{HNO}_3$ and 0.012 $M$ in $\text{Br}_2$ and allowed to stand 20 minutes before extracting the $\text{Br}_2$ with $\text{CCl}_4$ and precipitating $\text{AgBr}$ . The second was made 1 $M$ in $\text{HNO}_3$ , allowed to stand 20 minutes, $\text{Br}_2$ added and extracted immediately. The third was made 0.012 $M$ in $\text{Br}_2$ , allowed to stand 20 minutes and extracted.	$\text{Br}_2$ from 1 $M$ $\text{HNO}_3$ , 0.012 $M$ $\text{Br}_2$ solution = 90 $\pm$ 10 $\text{Br}_2$ from 1 $M$ $\text{HNO}_3$ solution = 10 $\pm$ 3 $\text{Br}_2$ from 0.012 $M$ $\text{Br}_2$ solution = 100 $\pm$ 10
81	Same as Expt. 80 except $\text{HNO}_3$ was replaced by $\text{HClO}_4$ and the solution with acid and $\text{Br}_2$ together was omitted.	$\text{Br}_2$ from 1 $M$ $\text{HClO}_4$ solution = 8 $\pm$ 3 $\text{Br}_2$ from 0.012 $M$ $\text{Br}_2$ solution = 100 $\pm$ 4
82	1.13 $M$ $\text{NaBrO}_3$ was exposed, split into five equal portions which were made 0.02 $M$ in $\text{Br}_2$ , allowed to stand various intervals, extracted with $\text{CCl}_4$ , precipitated and counted.	$\text{Br}_2$ from 1 $\frac{1}{2}$ min. = 100 $\pm$ 10 5 $\frac{1}{2}$ min. = 92 $\pm$ 10 10 $\frac{1}{2}$ min. = 92 $\pm$ 10 15 $\frac{1}{2}$ min. = 85 $\pm$ 10 20 $\frac{1}{2}$ min. = 79 $\pm$ 10
83	1.13 $M$ $\text{NaBrO}_3$ was exposed, divided and one portion was made 1 $N$ in $\text{HNO}_3$ , allowed to stand 10 $\frac{1}{2}$ minutes and extracted.	$\text{Br}_2$ from original = 100 $\pm$ 10 $\text{Br}_2$ from 10 $\frac{1}{2}$ min. 1 $N$ $\text{HNO}_3$ solution = 61 $\pm$ 6
84	$\text{Br}_2^*$ was added to 1.13 $M$ $\text{NaBrO}_3$ which was 1 $N$ in $\text{HNO}_3$ till the $\text{Br}_2^*$ concentration was 0.012 $M$ . Different portions were allowed to stand various intervals before extracting and counting.	$\text{Br}_2$ from original = 100 $\pm$ 10 3 min. run = 97 $\pm$ 8 6 min. run = 97 $\pm$ 8 12 min. run = 83 $\pm$ 8 20.5 min. run = 68 $\pm$ 8
85	Same as in Expt. 84 except $\text{HClO}_4$ substituted for $\text{HNO}_3$ .	$\text{Br}_2$ from original = 100 $\pm$ 8 1.5 min. run = 93 $\pm$ 6 5.5 min. run = 93 $\pm$ 6 12 min. run = 88 $\pm$ 6 19.5 min. run = 71 $\pm$ 6
86	1.2 $M$ $\text{NaBrO}_3$ was exposed, made 1.9 $M$ in $\text{H}_2\text{SO}_4$ and allowed to stand 60 $\pm$ 5 minutes at ca. 60°, solution then was cooled, made 1 $N$ in $\text{NH}_4\text{OH}$ and excess $\text{Ag}^+$ added and the $\text{AgBr}$ precipitate filtered and counted. (Its mass showed that the $\text{Br}_2$ concentration due to $\text{Br}^-$ impurity in the acid solution was between $5 \times 10^{-3}$ and $5 \times 10^{-4}$ $M$ .) An aliquot of the filtrate (after several further $\text{AgBr}$ precipitations to show all activity had been extracted) was completely reduced with $\text{KNO}_2$ in acid and $\text{AgBr}$ precipitated.	$\text{BrO}_3^- = 99.5 \pm 0.2$ $\text{Br}^- = 0.5 \pm 0.2$

sary for the activity to leave the  $\text{Cl}_2$  and appear in such a form.

**Bromine.**—The study of the bromine case is complicated by the fact that the 4.5-hr. activity of  $\text{Br}^{80}$  decays by emission of soft internally converted gamma radiation to form the 18-min.  $\text{Br}^{80}$  isomer which emits negative beta radiation.<sup>20,21</sup> The gamma transition effects an expulsion of the bromine atom in many cases which results in the separation of the beta emitting isomer from the parent 4.5-hr. body. (This phenomenon is being investigated further.) In most cases this work was done by allowing all samples to stand at least one hour before measurement so the 18-minute activity would necessarily be in equilibrium with the 4.5-hr. parent. These data generally apply therefore to the neutron capture recoil which is associated with the 4.5-hr.  $\text{Br}^{80}$  isomer. The only exceptions were some of the experiments on thermal interchanges. Professor G. K. Rollefson<sup>22</sup> of this Laboratory has investigated and found a thermal interchange proceeding between  $\text{Br}_2^*$  and  $\text{BrO}_3^-$  in acid solutions. The data given below substantiate and extend his result. Table V gives the data on all the bromine experiments.

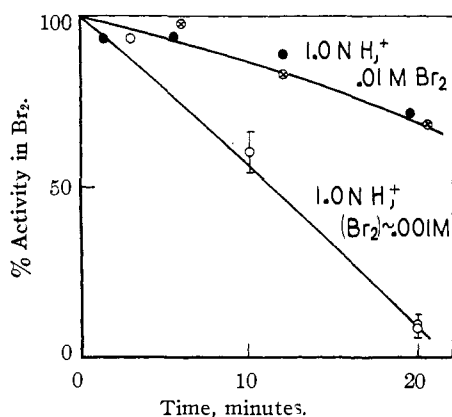


Fig. 4.—Rate of interchange between  $\text{BrBr}^*$  and  $\text{BrO}_3^-$ .

Figure 4 presents the data from Expts. 80, 81 and 82 on the rate of interchange between the species containing the extractable bromine activity (probably  $\text{Br}^-$  or  $\text{Br}_2$  or both) and  $\text{BrO}_3^-$  in 1 *N* acid without carrier bromine. Visual estimate of the concentration of bromine in these solutions, formed by action of  $\text{BrO}_3^-$  and  $\text{H}^+$  on  $\text{Br}^-$  impurity, gave a value of about 0.001 *M*. Experiments 84 and 85 supplied the points for

(20) D. C. DeVault and W. F. Libby, *Phys. Rev.*, **55**, 322 (1939).

(21) E. Segre, G. T. Seaborg and R. S. Halford, *ibid.*, **55**, 321 (1939).

(22) Private communication, unpublished.

the upper curve for the interchange with bromine at 0.01 *M*, the solid circles referring to 1.0 *N*  $\text{HClO}_4$  and the circles with crosses to 1.0 *N* nitric acid. In this connection Expt. 82 is interesting in indicating a slow interchange occurring in the absence of added  $\text{H}^+$  when bromine concentration is 0.02 *M*. Experiment 79 checks these results in showing a retention of about 80% for  $\text{BrO}_3^-$  solutions 1 *N* in acid. There is no evidence here of the retention being higher than the value expected by the thermal interchange rate between  $\text{Br}_2$  and  $\text{BrO}_3^-$ , as there was in the case of  $\text{ClO}_3^-$ . This does not mean, however, that the retention in the case of the irradiated acid solutions does not occur by interchange with molecules or ions of intermediate oxidation number as the  $\text{ClO}_3^-$  evidence indicated. Experiments 76, 77 and 78 indicate low retention in the cases of the irradiated solid sodium bromate and the neutral and alkaline solutions. Experiment 86, performed by Mr. D. C. DeVault, shows that the rate of the interchange increases with temperature. The half-time for interchange must have been about eight minutes or less in this experiment. The data for  $\text{BrO}_3^-$  retention were quite in agreement with those for  $\text{ClO}_3^-$ , no retention being found except in acid solution and this in agreement with thermal interchange.

**Iodine.**—D'Agostino<sup>6</sup> has shown that both solid sodium iodate and neutral solutions have nearly zero retention. He showed also that the addition of chlorine or nitric acid to a solution of sodium iodate before exposure gave nearly complete retention. The solution was boiled in the case of the nitric acid trial. The oxidizing action of chlorine explains the result with chlorine solution, but in view of the results with  $\text{ClO}_3^-$  and  $\text{BrO}_3^-$  the nitric acid result seems to be due mainly to interchange between lower valence iodine molecules or ions and  $\text{IO}_3^-$  occurring in acid solution. To check the prediction of thermal interchange Expt. 88 of Table VI was performed.

Experiment 88 indicates the existence of an interchange between  $\text{I}_2$  and  $\text{IO}_3^-$  in acid, probably even more rapid than in the case of  $\text{ClO}_3^-$  and  $\text{BrO}_3^-$ . Hull, Schifflett and Lind<sup>13</sup> found the interchange to occur in hot 20 *N* sulfuric acid. Dr. J. W. Kennedy<sup>23</sup> of this Laboratory has studied the rate with some care and obtains results in substantial agreement with the above. From Expt. 88 the conclusion is drawn that the

(23) Private communication.

TABLE VI  
 RETENTION BY  $\text{IO}_3^-$ 

No.	Experiment	Activities
88	Solid $\text{NaIO}_3$ was exposed, dissolved in water, split into two portions, to one of which a little $\text{NaI}$ was added, followed by acidification to 0.3 <i>N</i> in $\text{HNO}_3$ , allowed to stand approximately 3 minutes, and then extracted with $\text{CCl}_4$ and $\text{AgI}$ prepared from the extract. This was repeated. The filtrate and the other portion of the original solution were then precipitated as $\text{Pb}(\text{IO}_3)_2$ and counted.	$\text{Pb}(\text{IO}_3)_2$ from original solution = $100 \pm 10$ $\text{Pb}(\text{IO}_3)_2$ from extracted solution = $60 \pm 10$ Second $\text{AgI}$ precipitate = $8 \pm 5\%$ of activity of first $\text{AgI}$ precipitate.

retention by  $\text{IO}_3^-$  in alkaline solution is nearly zero also.

The data for  $\text{IO}_3^-$  retention like those for  $\text{BrO}_3^-$  are in complete agreement with the hypothesis that iodine reduction occurs in the recoil in nearly all cases and that only in acid solution is the activity able to return to  $\text{IO}_3^-$ , the process then being one of thermal interchange. The thermal interchange between  $\text{I}_2$  and  $\text{IO}_3^-$  seems to be somewhat faster than the  $\text{Br}_2$ - $\text{BrO}_3^-$  process which itself was faster than the  $\text{Cl}_2$ - $\text{ClO}_3^-$  interchange. The interchange rates seem to increase in the same order as the ordinary reactivities of the halate ions, but it remains for further more careful studies of the kinetics of the interchange processes to settle the question of the mechanism.

**Organic Halides.**—Retention by the organic halides generally has been studied by making an aqueous extract with the aqueous solution containing either an excess of a reducing agent or of halide ion (the latter ensures extraction because the interchange between any molecular halogen in the organic layer and the excess halide is rapid). This extracted activity then is compared with the activity of the original irradiated substance or with that of the organic layer from the extraction. In other words, any organic molecules made by

the recoil halogen atoms or ions not identical with the main substance irradiated will remain in the organic layer and be included in the percentage retained. Glückauf and Fay<sup>8</sup> have shown in fact, by direct fractionation, that such molecules are formed in numbers somewhat smaller than the number of the original type reformed. Table VII contains some of their results, together with several obtained by Lu and Sugden<sup>10</sup> and the author.

Glückauf and Fay<sup>8</sup> mention irradiating a 4% (by volume) solution of bromoform in carbon disulfide and finding that no active bromoform was formed in this case. Further experiments of this kind are given in Table VIII.

TABLE VIII

EFFECT OF DILUTION ON RETENTION BY ORGANIC HALIDES

No.	Experiment	Retention (%)
89	Solid $\text{CBr}_4$ , exposed, dissolved in $\text{C}_2\text{H}_5\text{OH}$ , precipitated by adding aqueous $\text{Br}^-$ solution. Activity of $\text{AgBr}$ from aqueous extract and purified $\text{CBr}_4$ were compared. The precipitation was repeated until no further activity was extracted.	$60 \pm 5$
90	Solution of $\text{CBr}_4$ in $\text{C}_2\text{H}_5\text{OH}$ , 1.15 mole per cent., <i>i. e.</i> , 195 atoms for each Br atom.	$28 \pm 5$
91	Solution of $\text{CBr}_4$ in $\text{C}_2\text{H}_5\text{OH}$ , 300 atoms per Br atom, 0.74 mole per cent.	$13 \pm 3$
92	Solution of $\text{CBr}_4$ in $\text{C}_2\text{H}_5\text{OH}$ , 500 atoms per Br atom, 0.45 mole per cent.	$2 \pm 2$
93	Solution of $\text{CBr}_4$ in $\text{C}_2\text{H}_5\text{OH}$ , 3500 atoms per Br atom, 0.064 mole per cent.	$0 \pm 2$
94	Solution of $\text{CHBr}_3$ in $\text{CS}_2$ (50% by volume), 3.1 atoms per Br atom. Extracted with $\text{SO}_3^{--}$ solution and counted in solution counter.	$62 \pm 4$
95	Solution of $\text{CHBr}_3$ in $\text{CS}_2$ (15.5% by volume), 9.5 atoms per Br atom.	$47 \pm 6$
96	Solid $\text{CHI}_3$ , treated by procedure in Expt. 89.	$60 \pm 8$
97	Solution of $\text{CHI}_3$ in pyridine, 6.3 mole per cent., 63 atoms per Br atom.	$25 \pm 4$
98	Solution of $\text{CHI}_3$ in pyridine, 1.1 mole per cent., 340 atoms per Br atom.	$1 \pm 1$

TABLE VII

Halide	Retention (%)	Source
$\text{CH}_3\text{I}$	$56 = 45\text{CH}_3\text{I} + 11\text{CH}_2\text{I}_2$	Glückauf and Fay <sup>8</sup>
$\text{CH}_2\text{Br}_2$	$67 = 43\text{CH}_2\text{Br}_2 + 14\text{CHBr}_3$	
$\text{CHBr}_3$	$69 = 47\text{CHBr}_3 + 19\text{CBr}_4$	
$\text{C}_6\text{H}_5\text{Cl}$	$50 = 35\text{C}_6\text{H}_5\text{Cl} + 15\text{C}_6\text{H}_4\text{Cl}_2$	
$\text{C}_2\text{H}_4\text{Br}_2$	31	Lu and Sugden <sup>10</sup>
$\text{C}_6\text{H}_5\text{Br}$	70	
<i>n</i> - $\text{C}_4\text{H}_9\text{I}$	53	
$\text{C}_6\text{H}_5\text{I}$	65	
<i>n</i> - $\text{C}_4\text{H}_9\text{Br}$	60	This research
$\text{CCl}_4$	45	
$\text{C}_2\text{H}_5\text{Br}$	$75 \pm 5$	
$\text{CHI}_3$	$60 \pm 5$	
$\text{CBr}_4$	$60 \pm 5$	
$\text{C}_2\text{H}_5\text{I}$	$37 \pm 5$	

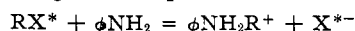
Experiments 89, 90, 91, 92 and 93 show that the formation of organic bromides\* by the bromine atoms or ions ejected is decreased by addition of ethyl alcohol until it reaches zero when there are about 500 atoms per bromine atom in the solution at 0.45 mole per cent. Experiments 94 and 95 together with the retention of 69% for pure bromoform and Glückauf and Fay's<sup>8</sup> observation that a 4% solution of bromoform in carbon disulfide showed no retention (this corresponds to 37 atoms per bromine atom) show that the carbon disulfide atoms are much more efficient in stopping the recoil bromine particles than the atoms in ethyl alcohol. This probably is due to the lightness of the hydrogen atoms. Experiments 96, 97 and 98 present evidence for the dilution effect for iodoform solutions in pyridine, the limiting concentration for zero retention corresponding to about 300 atoms per iodine atom.

The effect on the retention of carbon tetrabromide of dilution with ethyl alcohol obtained in Expts. 89, 90, 91, 92 and 93 shows that the 60% retention in pure carbon tetrabromide probably is not due to a "cage" reaction<sup>24</sup> because the substitution of walls of ethyl alcohol for carbon tetrabromide walls could hardly be expected to completely remove their reflective properties. Stronger evidence for this point is given by the data on the retention of bromoform in carbon disulfide solutions shown in Expts. 94, 95 and the data of Glückauf and Fay.<sup>8</sup> In this case the change of mass of the atoms in the wall is much smaller. A second point is that substitution occurs most readily for other bromine atoms and next most readily for other groups in a molecule containing bromine. Glückauf and Fay's<sup>8</sup> data and the dilution experiments are evidence for this point. If the recoil particles could have reacted with the diluent, an organic halide would have been found which would have appeared in the organic layer and would have prevented the retention from approaching zero at large dilutions when determined by simple aqueous extraction.

A simple explanation of these effects is that the recoiling particles are Br atoms or Br<sup>-</sup> ions of high velocity which on *collision with atoms or groups of nearly equal mass lose large fractions of their energy to be left in the same reaction "cage" with the fragments of the struck molecule.* Reactions then oc-

cur between the stopped Br\* or Br\*<sup>-</sup> and these fragments which result in substitution.

Lu and Sugden<sup>10</sup> have shown that the addition of small amounts of aniline or other organic bases appears to reduce the retention. These results might be expected as consequences of reactions between the aniline and the organic halide molecules formed before they lose all of their energy and return to the unreactive normal state. Lu and Sugden<sup>10</sup> give the equation



It seems that the retention by the organic halides might be reduced in general by either of the methods mentioned:

1. Dilution of the target halide with a solvent consisting of heavy atoms such as carbon disulfide.

2. Introduction of small amounts of substances which will react with activated organic halides to liberate the halogen as halide.

The first of these methods seems to be less promising than the second, because the dilution required increases the bulk of the solution by at least five-fold for an effective reduction in the retention. As Lu and Sugden<sup>10</sup> have pointed out, the second method has very definite possibilities.

The author wishes to thank his colleagues in the Chemistry Department, in particular Professors Lewis, Bray, Latimer and Rollefson for valuable criticisms and suggestions. He is indebted to Mr. D. C. DeVault for some of the experiments and much valuable discussion. It is a pleasure also to acknowledge indebtedness to the Radiation Laboratory for neutron irradiation of the phosphorus and some of the chlorine and bromine samples.

### Summary

1. The neutron capture recoils in the case of MnO<sub>4</sub><sup>-</sup> appear to cause one or two O<sup>-</sup> ions to be ejected.

2. The unstable +7 ions so formed are hydrated rapidly by OH<sup>-</sup> to form MnO<sub>4</sub><sup>-</sup> again in alkaline solution. In neutral or dilute acid solutions they oxidize H<sub>2</sub>O. In strong acid some of them appear to interchange O<sup>-</sup> ion with MnO<sub>4</sub><sup>-</sup>.

3. In the case of solid potassium permanganate at room temperature about 30% of the activity is permanently reduced and about 30% retained as KMn\*O<sub>4</sub>. The residual 40% is trapped in the crystal as the +7 ions which on being dissolved in water solutions act just as they do in the case of the irradiated solutions. At liquid air tem-

(24) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

perature the percentage retained in the crystal as  $\text{KMn}^*\text{O}_4$  has risen to about 50%.

4. A rapid interchange of a  $3d$  electron occurs between  $\text{MnO}_4^-$  and  $\text{MnO}_4^+$  ions.

5. In the case of  $+5$  phosphorus molecules and ions the recoils seem to eject oxidized oxygen leaving  $+3$  phosphorus about half of the time. The retention of activity is near 50% under all conditions.

6. Both  $+3$  and  $+5$  arsenic appear to expel  $-2$  divalent oxygen. The retention is nearly 100% under all conditions.

7. All the halate ions appear to be reduced by expulsion of  $-1$  or atomic oxygen, further substantiating a rough rule that the results of the

recoils will correspond to *distribution of the bonding electrons among the products about as they are distributed in the bonds broken.*

8. The halate ions interchange with the molecular halogens in acid solution, the rates increasing from chlorine to iodine. Perchlorate ion does not interchange rapidly with chlorine.

9. The organic halides have high retentions in the pure state due to collisions between the recoiling  $\text{X}^*$  particles and the halide molecules transferring the energy to non-radioactive atoms, generally halogens, and leaving the residual free radical or ion in the same reaction "cage" with the stopped  $\text{X}^*$  particle.

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## Some Properties of Monoethanolamine and its Aqueous Solutions

BY R. E. REITMEIER, V. SIVERTZ AND H. V. TARTAR

Because of the varied and extensive use of monoethanolamine a more complete knowledge of its properties may be of considerable use. This paper affords data on the melting point, boiling point, refractive index, also the density, surface tension, parachor, and the surface tension of aqueous solutions over the temperature range 25 to  $80^\circ$ .

**Purification of Monoethanolamine.**—Samples from two sources, Eastman Kodak Company and Carbide and Carbon Chemicals Corporation, were subjected to fractional distillation, washed repeatedly with ether, and then crystallized from an ethyl alcohol solution. This was followed by fractional distillation, care being taken to prevent absorption of carbon dioxide. Two successive crystallizations and distillations gave, from each original sample, a product with constant melting point  $10.51^\circ$  (cor.). The boiling point was  $171.1 \pm 0.1^\circ$  at 760 mm. pressure; previous values reported are  $171.1^{11}$  and  $170.5^{12}$ .

As a further check on the purity of the monoethanolamine, it was analyzed by potentiometric titration against standard hydrochloric acid using a quinhydrone electrode and by weight titration using methyl orange indicator; the results were 99.97 and 99.96%, respectively.

The refractive index was found to be 1.4539 at  $20^\circ$  by the use of an Abbe refractometer.

**Density, 25 to  $80^\circ$ .**—Density determinations were made at  $10^\circ$  intervals from 25 to  $80^\circ$  with ordinary pycnometers which had very careful volume calibration. A water-bath controlled to within 0.05° of the desired temperature was

used. The monoethanolamine was freshly distilled before each determination. Results from the use of three 25 ml. pycnometers were compared; agreement within 0.005% was deemed satisfactory.

The results, tabulated in Table I, show the absolute density to be a linear function of the temperature. This relationship between density and temperature ( $^\circ\text{C}.$ ) is expressed by the equation,  $d = 1.03188 - 0.0008038 t$ . The average deviation of the points in Table I from values calculated by this equation is 0.000077.

TABLE I

DENSITY OF MONOETHANOLAMINE FROM 25 TO $80^\circ$	
Temperature, $^\circ\text{C}.$	Density
25	1.01170
30	1.00773
40	0.99983
50	.99182
60	.98366
70	.97551
80	.96749

**The Surface Tension of Monoethanolamine from 25 to  $80^\circ$ .**—The surface tension of monoethanolamine was determined using the capillary rise method. The capillaries were made of Pyrex glass according to the design of Richards and his co-workers<sup>3</sup> and were fitted with ground glass stoppers to prevent the absorption of carbon dioxide and water vapor. The capillary tubing was inspected for uniformity of bore, and the radii of the capillaries were determined by the method of Harkins and Brown.<sup>4</sup> The values for the radii were checked by determining the capillary rise of water in the capillaries,

(1) Trusler, *Ind. Eng. Chem.*, **21**, 685 (1929).

(2) McClure, *Ind. Eng. Chem., News Ed.*, **17**, 149 (1939).

(3) Richards and co-workers, *This Journal*, **37**, 1656 (1915).

(4) Harkins and Brown, *ibid.*, **41**, 449 (1919).