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CHEMICAL RESEARCH - RADIATION CHEMISTRY

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REPORT FOR MONTH ENDING MARCH 15, 1945

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Abstract

The pH of the P-9 moderator in CP-3 has dropped in a period of several months to 4.52. Titration curves seem to rule out the likely inorganic acids, for K_a is about 6.2×10^{-6} . The effect may be attributable to the growth of an organic acid from organic contaminants (2001).

The 100 ev yield of H_2 in UNH solution experiencing fission decreases with exposure from ~ 4 to ~ 1.5 . The yield of O_2 depends upon standing time. Yield is independent of variations in anion concentration through small ranges of the latter. Fe^{+3} ion has no appreciable effect. The 100 ev yield for hydrogen is slightly less in sulfate solution (~ 1.2) at long exposures. In the latter, Ce^{+4} increases the yield of H_2 as well as the yield of O_2 . The phenomena are explainable on the basis of a back-reaction involving peroxide. Acidic gas is produced both in nitrate and in sulfate solutions. Dilatometer studies on UNH solution indicate that after an initial period during which the concentration of H_2 in solution increases while peroxide is also being produced, the rate of production of H_2 is a linear function of exposure (2215).

Recently received samples of intensely exposed graphite show $\Delta R/R_0$ of $\sim 3.6 - 3.8$, with no evidence of further large change, and values of $\Delta R/R_0$ of ~ 2.1 , also with no evidence of further significant change. On the other hand, the values of $(R_{1000}-R_0)/R_0$ seem still to be increasing although, unfortunately, no data are as yet procurable on the most intensely exposed samples. The thermal resistivity ($1/k$) is now over 17 times its initial value, with no indication of a great falling-off. The evidence is that decomposition of the graphite is still occurring at a significant rate (2301).

The behavior of electron-bombarded samples of $BaCl_2$ and $Ba(NO_3)_2$ has been investigated for the purpose of understanding the so-called effervescence of intensely radioactive samples of such materials on dissolution in water. Anhydrous $BaCl_2$ becomes gray to black under intense electron bombardment. Solution in water yields hydrogen plus an equivalent amount of oxygen plus oxidizing agent in the solution. The phenomenon of hydrogen production is attributable to action of trapped electrons on water with the possible concomitant action of colloidal metal. The production of oxygen plus oxidizing agent is attributable to frozen-in Cl atoms which subsequently react with the water on solution. The explanation suggests that 1 in 150 valence electrons are displaced under these conditions, far above the concentration produced in ordinary F-center formation. $Ba(NO_3)_2$ becomes yellow, then white, under intense electron bombardment. Solution in water yields mainly oxygen with about 3% hydrogen. The oxygen yield does not correspond exactly to the NO_2^- yield. The deviations are not yet explained. The probable mechanism involves the formation of the NO_3 radical and its subsequent decomposition. In the most intense bombardment $\sim 21\%$ of the nitrate was converted to the reduced form without any apparent falling off in the yield as a function of exposure (2303).

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320 MLC 2001: Service work - M.G. Bowman, C.J. Hoshanadel, A.J. Miller

The pH of the P-9 moderator of the CP-3 machine has dropped (over a period of several months) to 4.52. This low pH is undesirable since corrosion might be accelerated. At Dr. Zinn's request we have determined the concentration of the acid and prepared a solution of ammonia in P-9 to add to the machine to raise the pH to 6.3.

The titration curve of 25 ml of the P-9 with 0.00618 N sodium hydroxide solution (carbonate free) is shown in Figure 1. The curve is characteristic of a weak monoprotic acid. The concentration of the acid is found to be 1.73×10^{-4} . For an acid of formula HX, the ionization constant is

$$\frac{(\text{H}^+) (\text{X}^-)}{(\text{HX})} = K_a$$

From the pH and concentration of the acid solution we may write

$$K_a = \frac{(10^{-4.52})^2}{1.73 \times 10^{-4} - 10^{-4.52}} = 6.4 \times 10^{-6}$$

When the acid is half neutralized, the values of (X^-) and (HX) are nearly equal. K_a is then equal to (H^+) . From the titration curve this is found to be $10^{-5.23}$. This alternative computation gives K_a equal to 5.9×10^{-6} .

No tests to identify the acid have been made, but it appears probable that it is an organic acid. This conclusion is suggested by the strength of the acid, as well as by conjecture concerning the source of the acid. The K_a value rules out the expected inorganic acids. It seems more probable that small amounts of organic contaminants from pump packing, pipe cement, etc. would yield acid in the radiation field than that unknown inorganic impurities could enter. Qualitative tests will be made later.

320 MLC 2002: Handbook - J. Royal, A. Novick, L. Treiman, A.O. Allen

Progress in organization of data continues slowly. The Section is handicapped in this subject by shortage of secretarial help.

322 MLC 2215: Effect of radiation on water and aqueous systems

Gas evolution from uranyl solutions (C.J. Hoshanadel, A.J. Miller, R. Livingston, M.G. Bowman).

Experimental Procedure. The uranyl solutions are de-aerated and sealed into ampoules of 11-15 cc volume. They are exposed in side-hole No. 8 of the CP-3 pile. After exposure the ampoules are broken open and the gas pumped from the solution, through a dry ice trap, for analysis. At least

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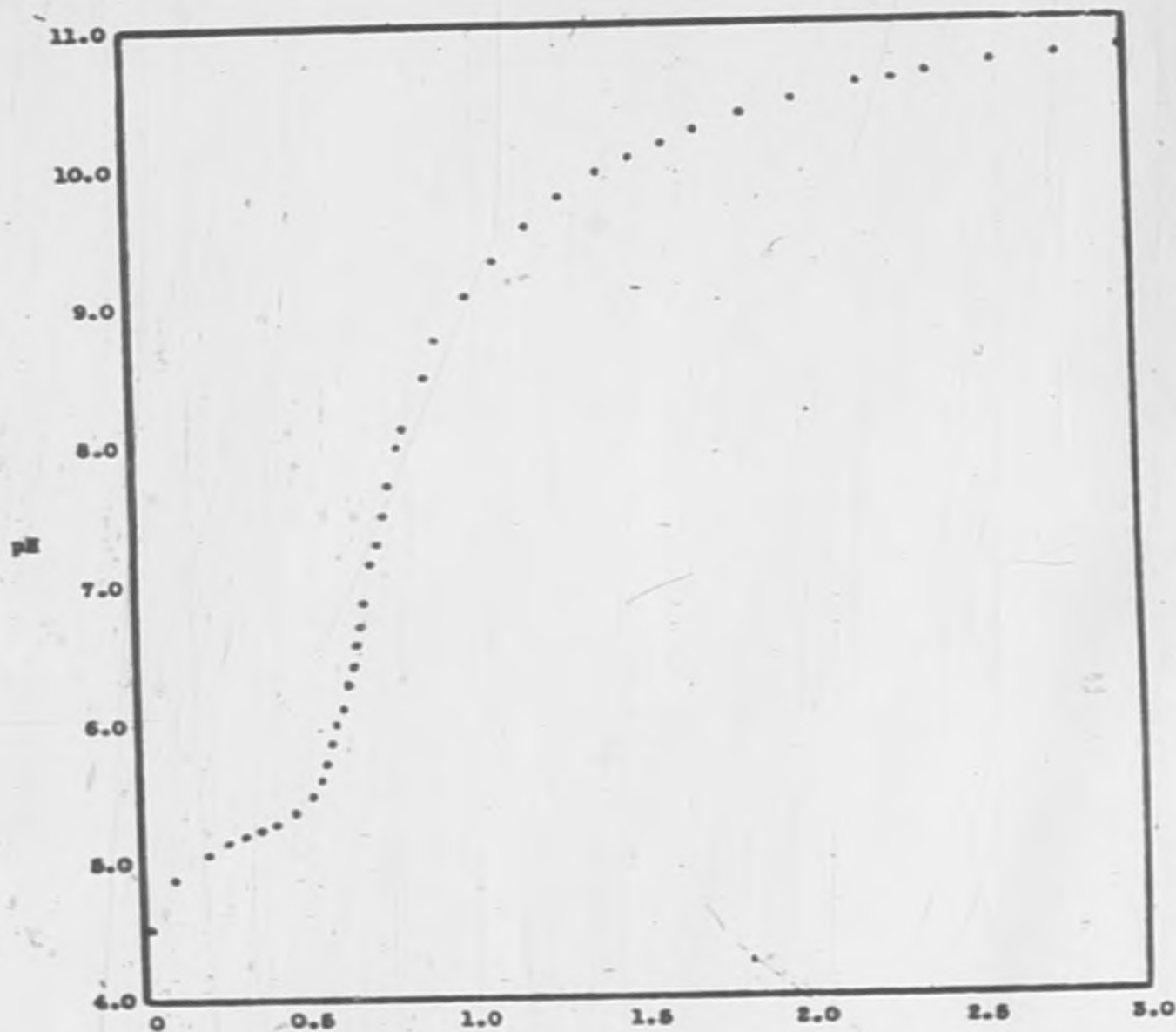


Fig. 1. Titration of 25 ml of P-9 moderator from CP-3.

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one-fourth of the water from the solution is distilled into the dry ice trap to ensure complete removal of the gases from the solution. Frequently more of the water is evaporated, and occasionally all of the water is evaporated.

The gas is analyzed in the following steps:

1. Pumped over ascarite and anhydrous to remove acid gas (very little moisture comes through the dry ice trap).
2. Pumped over white phosphorus to remove oxygen.
3. Pumped over hot copper oxide to remove hydrogen, and then over anhydrous to remove water.

Experience has shown that the removal of the hydrogen is practically complete. The percentage of acid gas in the analyzed sample seems to depend on the amount of solution evaporated from the ampoule. The percentage of oxygen also shows a rather random variation, depending somewhat upon the length of time the samples stand, after exposure, before the gas is pumped off. This would be expected since the hydrogen peroxide is known to decompose on standing in uranyl solutions. It is apparent, however, that lower oxygen percentages are obtained in short bombardments, and also that uranyl sulfate solutions give less oxygen than uranyl nitrate solutions, with equivalent exposure.

The data for 0.2 molar uranyl nitrate solutions are listed in Table 1. G values for hydrogen yield have been computed. The energy absorption has been determined by the activity of the Ba fission product, using 170 mev per fission. The data for the 0.2 molar uranyl sulfate solutions are listed in Table 2. The values of G for hydrogen production versus total number of fissions per cc for both the uranyl nitrate and uranyl sulfate solutions are plotted in Figure 2.

The following generalizations are suggested:

- (1) The rate of H_2 formation is most rapid at the start of a bombardment. The rate becomes more constant as the reaction proceeds. It is possible that there is some back-reaction with hydrogen peroxide, or that dissolved molecular hydrogen enters into some back-reaction and that saturation of the solution leads to a steady rate.
- (2) Fe^{+3} ion has no appreciable effect.
- (3) The anion concentration seems to have little effect, at least in low concentration ranges.

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Table 1

Sample No.	Total no. fissions per ml	Conc. of added substances	Vol of gas per cc of soln.	% acidic	% SO_2	% H_2	% inert	hrs exp.	O_2
UN-4	2.98×10^{11}	0.3 M $\text{Fe}(\text{NO}_3)_3$	0.0432	0.4	36.3	55.8	8.6	4.5	1.3
9	0.6	+ 0.5 M HNO_3	0.015	7.3	22.9	63.2	6.6	1.8	2.5
10	0.53	0.1 M $\text{Fe}(\text{NO}_3)_3$	0.014	5.2	27.9	60.8	6.1	1.8	2.5
11	0.66	0	0.015	5.7	10.7	78.0	5.6	1.85	2.8
12	3.15	0	0.038	4.1	17.1	78.6	0	8.87	1.6
13	2.38	0	0.030	4.0	15.8	80.2	0	8.87	1.6
14	0.11	0	0.0031	14.1	0	81.7	4.2	0.35	3.6
16	0.75	0	0.015	8.7	9.6	81.7	0	2.32	2.6
18	1.20	0	0.018	8.2	20.0	71.8	0	3.75	1.7
19	1.74	0	0.019	5.0	14.1	80.9	0	3.75	1.4
21	4.53	0	0.025	7.3	12.4	80.4	0	12.05	0.7
25	2.10	0.3 M KNO_3	0.033	16.2	19.6	64.5	0	5.2	1.6
26	1.89	0	0.024	10.3	14.8	74.9	0	5.2	1.5
27	1.72	0	0.024	16.1	16.0	67.9	0	5.2	1.5
28	1.85	0.3 M $\text{Fe}(\text{NO}_3)_3$	0.042	12.0	37.1	47.5	2.5	5.2	1.7

Table 2

Sample No.	Total no. fissions per ml	Conc. of added substances	Vol of gas per cc of soln.	% acidic	% SO_2	% H_2	% inert	hrs exp.	O_2
US-1	1.76×10^{11}	0.45 M Na_2SO_4	0.015	19.2	0	76.5	2.0	5.2	1.1
2	1.69	0	0.015	14.1	0	85.9	0	5.2	1.2
3	1.98	0.11 M $\text{Ce}(\text{HSO}_4)_4$	0.13	6.9	57.4	35.7	0	5.2	3.9

(4) Ce^{+4} ion has a large adverse effect. Not only is the H_2 formation increased, but the O_2 formation is increased to a larger extent. Apparently, very powerful oxidizing agents will give greater gas formation through their reaction with substances that favor back-reaction. Possibly, also, hydrogen peroxide plays a role in back-reaction.

(5) The H_2 yield from UO_2SO_4 solution is slightly less than from $\text{UO}_2(\text{NO}_3)_2$ solutions for equivalent exposures.

One run at high intensity has been made by inserting a dilatometer in the thimble of CP-3 and measuring the gas evolved by observing the rise of the liquid level in the capillary.

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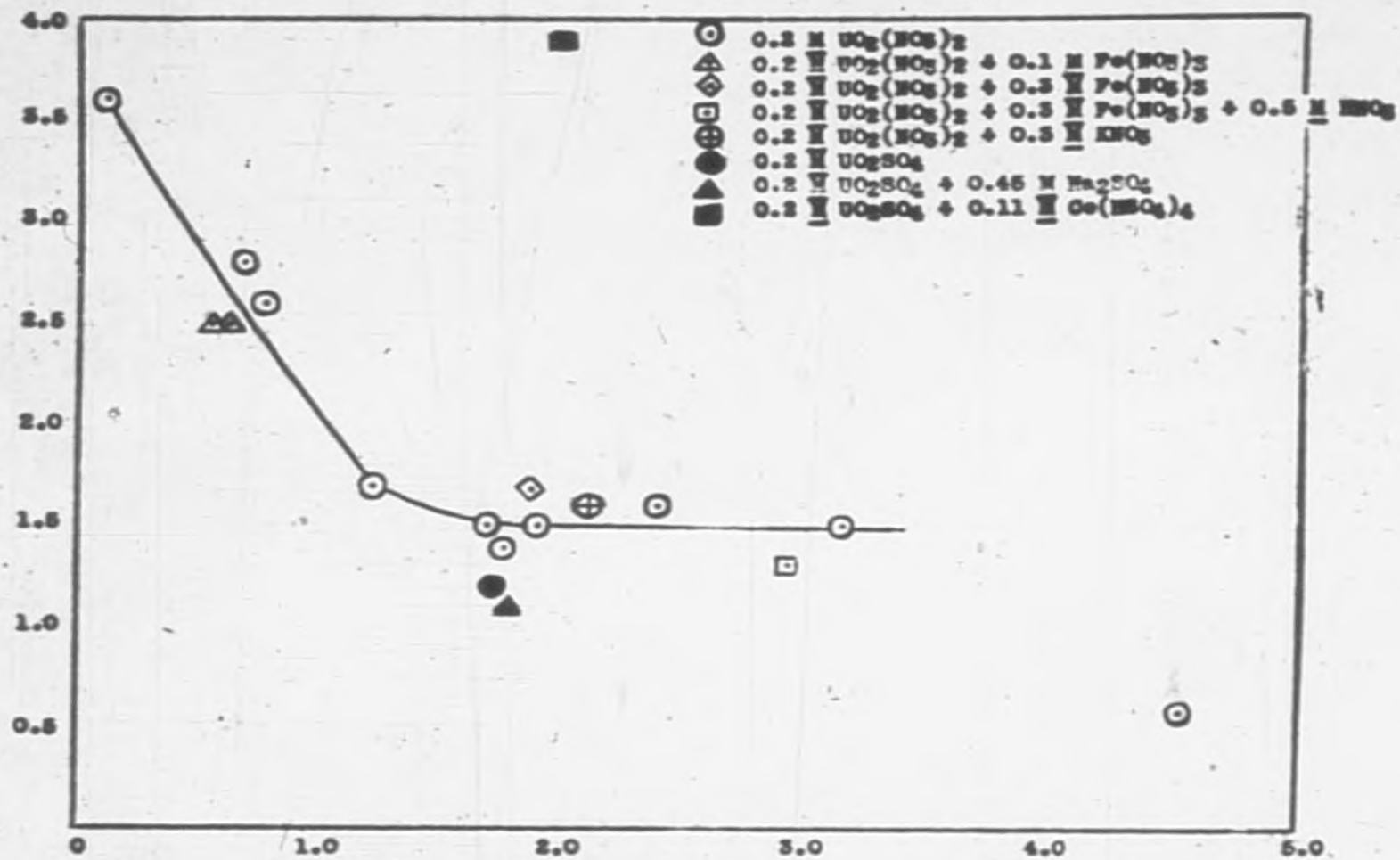


Fig. 2. Fissions per cc $\times 10^{-11}$.

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The results are plotted in Figure 3. It is evident that the rate of gas evolution approaches a constant, after the liquid becomes saturated.

The volume of the dilatometer was 0.678 cc and nitrogen was placed in a bulb over the capillary at a pressure of 451 mm of Hg at 25°C.

A slight precipitate was formed during the last exposure period. This is presumably UO_2 .

525 MLC 2303: Effect of radiation on solid compounds

1. Boron nitride: (M.G. Bowman, S. Gordon) Construction of the furnace for preparation of graphitic boron nitride, in quantity, is not completed. The bombardment of the amorphous form is continuing in the low-intensity area of the CP-3 thimble.

2. Electron irradiation of barium salts: (A.O. Allen, J.A. Gheraley) Information reached us that radioactive barium chloride gives considerable effervescence when dissolved in pure water. We have made some irradiations in an attempt to explain this phenomenon. Preliminary results were reported in MUC-MS-373. Results to date are summarized here. Some of the results given in the above memorandum have been revised.

Barium chloride. The dihydrate was thoroughly baked to get rid of all water. Samples were irradiated in a helium atmosphere with 1.25 Mv electrons from the Chicago Van de Graaff. In two runs the amounts of energy absorbed by the salt were respectively 45 and 25 w-hr/g. The salt became dark gray on irradiation, instead of showing the pure color (F band) which ordinarily appears in irradiated salts. After irradiation, the space over the samples was evacuated, and pure water was allowed to enter. Considerable gas was evolved as the salt dissolved, amounting to 0.8 and 0.45 cc/g (atm. pressure, 20°C) in the respective experiments. These amounts are closely proportional to the exposures given. The gases consisted almost entirely of hydrogen and oxygen; the $H_2:O_2$ ratio was 2.6 in the first run and 4.5 in the second. The solution produced in the second run (pH 7.8) reacted rapidly with KI and the amount of oxidizing agent, presumably hypochlorite, was determined to be equivalent chemically to the excess hydrogen, within experimental error (equivalents OCI^- found, 1.8×10^{-5} ; equivalents H_2 , 1.3×10^{-5} ; sum, 3.1×10^{-5} ; equivalents H_2 , 3.0×10^{-5}). Thus if any gas was lost during the irradiation it must have contained equivalent amounts of oxidizing and reducing power.

The formation of gas is ascribed to the existence of trapped electrons in the irradiated material, lodged at a distance from the chlorine atoms from which they were displaced by the bombarding electrons. The salt formed by decomposition of the hydrate is in a highly irregular crystalline state, offering great opportunity for entrapment of electrons at surfaces and irregularities; it is doubtful if conventional F-centers play an important role here. When water penetrates the solid, the electrons (or perhaps colloidal metal) react with it to form OH^- ions and H atoms,

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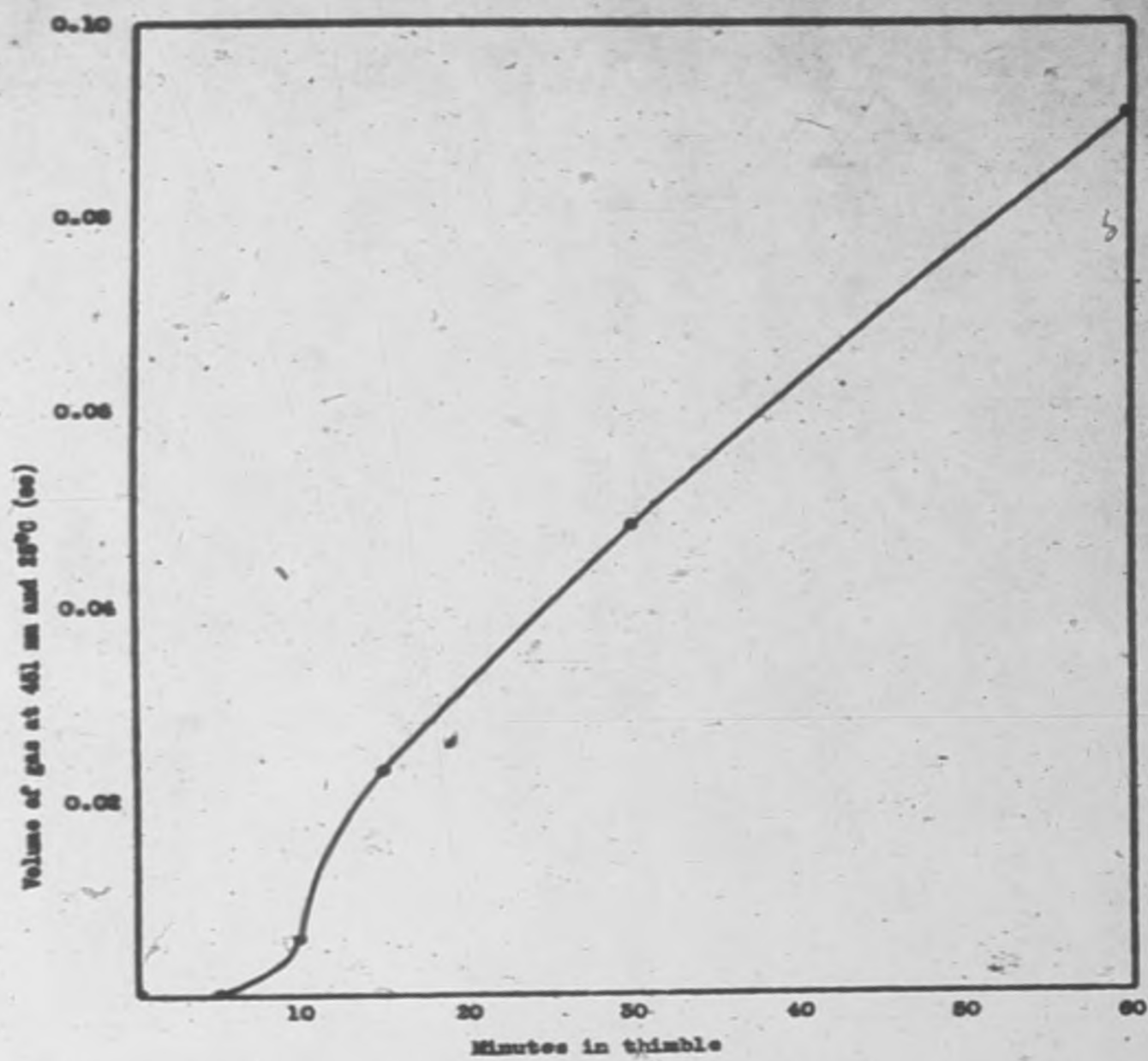


Figure 3.

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which yield H_2 ; the Cl atoms may react with water to yield oxygen and HCl, or with one another to give Cl_2 (which remains in solution as hypochlorite, since the amount of alkali formed must be equivalent to the amount of chlorine).

Barium nitrate. This salt was first irradiated in a closed system, as with the chloride; the space was then evacuated and water was admitted. The gas evolution was much greater than with the chloride; an exposure of only 1.1 w-hr/g gave 0.9 cc of gas/g. The gas contained 5% H_2 ; the balance contained no acid gas (i.e., no NO_2 or NO) and presumably consisted entirely of oxygen. A quantity of nitrate was found in the solution, roughly equivalent to the amount of oxygen evolved.

A quantity of salt spread out on a pan in the open air was then irradiated. Samples were taken from time to time, placed in a closed tube and evacuated; water was admitted, the quantity of gas formed was measured and the pH and the nitrite content of the solutions were determined. Energy was not absorbed uniformly by the salt during the course of the experiment, since the thickness of the salt layer varied as well as its distribution on the pan with respect to the electron beam. Roughly, the rate of energy dissipation may be taken as 1.5 watts/g. The solutions of irradiated salt (0.1 M) showed a pH of 9-10, which is more alkaline than could be accounted for by hydrolysis of barium nitrite; the alkalinity presumably corresponds to the small amount of hydrogen in the gas. Data on the amounts of gas and of nitrite are given in Table 4.

Table 4.

Formation of gas and nitrite on solution of irradiated barium nitrate.

Irradn. time (hr)	Gas found (Y) (cc/g at 22°C)	NO_2^- found (millieq./g)	% NO_2^- converted to NO_2^-	cc O_2 at 22°C equivalent to NO_2^- found (E)	Ratio gas found to O_2 expected (Y/E)
2.8	5.9	0.85	5.5	5.1	1.15
6.0	10.1	1.54	10.5	9.3	1.09
9.6	12.8	1.97	13.0	12.0	1.07
13.0	16.4	2.75	18.0	16.8	0.98
17.8	19.0	3.25	21.1	19.7	0.96

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At 25 w-hr/g., about 21% of the barium nitrate has been converted to nitrite. The conversion increases uniformly with time of exposure, and shows no sign of approach to saturation. The oxygen produced on solution is roughly equivalent to the nitrite, showing that the gas largely remains trapped in the crystal, either as O_2 molecules or as O atoms, and emerges only on solution. We have no explanation at present for the slight but definite decrease in the ratio of gas formed to nitrite produced as the exposure time is increased.

Qualitative experiments showed that heating the crystal did not greatly reduce the evolution of gas on subsequent solution in water. When the crystals were fused, however, the gas was apparently released, as no bubbling occurred on solution of the fused material. The melting point of the salt was considerably lowered by irradiation, presumably because of the admixture of nitrite.

The salt initially becomes pale yellow on irradiation, but later the crystals become milky or turbid, obscuring the yellow color. The salt never turned dark.

The mechanism of the decomposition of nitrate under bombardment is somewhat obscure. Clearly the chief overall result is a decomposition of NO_3^- to $NO_2^- + O$. This process may occur in the initial act, but more likely the primary process is to form the radical NO_2 and a trapped electron. The radical may later pick up an electron, with a certain probability of forming $NO_2^- + O$ rather than NO_3^- ; or it may decompose thermally to $NO_2 + O$, the NO_2 later picking up an electron to give the nitrite ion.

The entire subject of reaction of irradiated salts with water is an unexplored field, with highly interesting possibilities.

313 MEC 2501: Instruments - F. J. Safford

The 1.25 Mv generator has been operating satisfactorily throughout the month.

314 MEC 2502: Scattering - F. J. Safford, R. T. Schenk

Measurements have been made of the magnetic field in the beam bendier. Several pieces of apparatus are under construction in the machine shop.

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