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THE GAMMA RADIOLYSIS OF AQUEOUS STANNOUS-BROMIDE SOLUTIONS

STEPHEN JOSEPH STEPENUCK JR.

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THE GAMMA RADIOLYSIS OF AQUEOUS STANNOUS-BROMIDE SOLUTIONS

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THE GAMMA RADIOLYSIS OF
AQUEOUS STANNOUS BROMIDE SOLUTIONS

by

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B.S., Merrimack College, 1959
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[Signatures]

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Stephen J. Steppenick
TABLE OF CONTENTS

LIST OF TABLES ............................................. v
LIST OF ILLUSTRATIONS ...................................... v
ABSTRACT .................................................... vi
I. INTRODUCTION ............................................... 1
II. EXPERIMENTAL ............................................... 5
   1. Materials ................................................................ 5
   2. Apparatus ................................................................ 6
   3. Solutions ................................................................ 9
   4. Instrumentation .................................................. 9
   5. Analytical Procedures ........................................... 10
   6. Calibrations and Standardizations ......................... 17
III. RESULTS AND DISCUSSION .................................... 22
   1. Stannous Chloride ............................................. 22
   2. Stannous Bromide—Results ..................................... 27
   3. Stannous Bromide—Discussion ................................... 32
      A. Primary Yields ................................................... 32
      B. Hydrogen Yields ............................................... 34
         a. Initial yields ................................................... 34
         b. Descent to limiting yields ................................... 36
         c. Effect of added hydronium or bromide ion ........... 37
      C. Tin Yields ..................................................... 37
         a. Basic mechanism .............................................. 37
         b. Participation by bromide .................................... 38
         c. Initial yields .................................................. 39
         d. Limiting yields ............................................... 40
         e. Descent to limiting yields ................................... 43
         f. Added bromide vs. added HBr ............................. 51
   D. Other Experiments ............................................. 54
      a. Experiment 1. Radiolysis with added Sn(IV) .......... 55
      b. Experiment 2. Pre-oxidation ............................... 56
   4. Comparison with Other Investigators ..................... 59
IV. BIBLIOGRAPHY ......................................'........... 662
V. APPENDIX ........................................................... 666
List of Illustrations

<table>
<thead>
<tr>
<th>Number</th>
<th>Illustration Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Recorder Response Units vs. Micromoles of Hydrogen</td>
<td>21</td>
</tr>
<tr>
<td>2.</td>
<td>G(-Sn(II)) vs. Irradiation Time for Stannous Chloride</td>
<td>23</td>
</tr>
<tr>
<td>3.</td>
<td>G(-Sn(II)) vs. Irradiation Time for Stannous Bromide with Added Sodium Bromide</td>
<td>28</td>
</tr>
<tr>
<td>4.</td>
<td>G(-Sn(II)) vs. Irradiation Time for Stannous Bromide with Added Hydrobromic Acid</td>
<td>29</td>
</tr>
<tr>
<td>5.</td>
<td>G(H₂) vs. Irradiation Time for Stannous Bromide with Added Sodium Bromide</td>
<td>30</td>
</tr>
<tr>
<td>6.</td>
<td>G(H₂) vs. Irradiation Time for Stannous Bromide with Added Hydrobromic Acid</td>
<td>31</td>
</tr>
</tbody>
</table>

Tables

I. Primary Radical and Molecular Product Yields in Gamma-Irradiated Aqueous Solutions | 33   |
II. Mean Ionic Activity Coefficients at 25°C                                       | 52   |
ABSTRACT

THE GAMMA RADIOLYSIS OF
AQUEOUS STANNOUS BROMIDE SOLUTIONS

by

STEPHEN JOSEPH STEPENUCK, JR.
Cobalt-60 gamma radiolyses were carried out on dilute, aqueous solutions of SnBr₂. Bromide, then HBr, concentration was varied in the general range of 1–3M. \( G(\text{Sn(II)}) \) and \( G(H₂) \) were determined after irradiations of 0.25–72 hr, at dose rates from 2.45–3.33 \( \times \) \( 10^{16} \) e.v. g⁻¹ min⁻¹.

\( G(H₂) \) descended from 2.0 for a 0.25–hr irradiation to a limiting value of 0.50 for irradiations 4–5 hr or longer. \( G(\text{Sn(II)}) \) descended slowly from 2.50 at 4 hr irradiation to 0.49 for very long irradiations. \( G(\text{Sn(II)}) \) was also determined for \( 10^{-2} M \) SnCl₂ in 1M HCl, and varied essentially the same as that for SnBr₂. These results disagree with previously reported values for SnCl₂. \( G(\text{Sn(II)}) \) for \( 10^{-3} M \) SnSO₄ in 0.8M H₂SO₄ was determined to be 0.51, in agreement with results of other investigators.

High initial yields for the SnBr₂ system are postulated to be the result of oxidation of Br⁻ by H, with reductive reactions of H predominating on longer irradiation. It is believed that \( G(\text{Sn(II)}) \) really behaves identically to \( G(H₂) \), i.e., that slow descent of \( G(\text{Sn(II)}) \) to 0.49 was due to lingering effects of a small amount of adventitious air-oxidation of irradiated solutions. Calculated curves based on this hypothesis match the experimental curves well.

\( G(\text{Sn(II)}) \) and \( G(H₂) \) increased slightly with increasing Br⁻ or HBr concentration. A mechanism is proposed.
Studies of the interaction of radiation with matter date back to the discovery of radioactivity itself. However, the rather intense activity now observable in the field has arisen only in the last 25 or 30 years. For an excellent introduction to the field of radiation chemistry in general, the reader is referred to the book by Spinks and Woods. More germane to the topic of this dissertation, and recommended to anyone seeking a fuller background in this specific area, is Allen's work dealing with water and aqueous solutions.

Very briefly, we shall be concerned with the chemical effects on certain solutes in aqueous solutions irradiated by $^{60}$Co gamma radiation, wherein the primary process is Compton scattering, resulting initially in production of water-molecule ions ($H_2O^+$) and Compton electrons. These electrons in turn have sufficient energy to cause further ionizations, as well as excitations, of solvent molecules. If concentrations of solutes are kept low ($10^{-2}$M or less) the probability of their direct interaction with the radiation is considered so small as to be negligible compared with that of the solvent. Thus, we should really be looking at the results of reactions between our solutes and the primary products of the radiolysis of water.

The simplest, and still the most frequently used, representation of the formation of these primary products is

$$H_2O \xrightarrow{\text{action of the radiation, } H^+ \text{ and } \cdot OH} H^+, \cdot OH, H_2, H_2O_2$$

(1)

where $\xrightarrow{\text{action}}$ represents the action of the radiation, $H^+$ and $\cdot OH$ (hereafter H and OH) the so-called radical products, and $H_2$ and $H_2O_2$ the (primary) molecular products. At this writing the exact nature and the mode of formation of these products continue to be
the subject of much controversy.\textsuperscript{4,5,6} For example, the reducing species may be H, the hydrated electron (e\textsubscript{aq}\textsuperscript{-}), some other species, or a combination of these.\textsuperscript{7} The primary yield of molecular hydrogen may be produced by recombination of hydrogen atoms, or be the result of reaction between two hydrated electrons\textsuperscript{8}

\[ \text{e}^{\text{aq}^{-}} + \text{e}^{\text{aq}^{-}} \rightarrow \text{H}_2 + 2\text{OH} \quad (2) \]
a reaction which seemingly is not hindered by the like charges of the reacting species.\textsuperscript{9} It is quite possible that a true mechanistic picture of the radiolysis of water will turn out to be a superset of several of the apparently conflicting theories proffered today.

A final topic requisite to a general introduction is that of yields, customarily expressed in radiation chemistry in terms of G-values. The G-value is the number of molecules (or ions) of a substance produced per 100 electron volts of energy absorbed in a radiolytic process. Negative G-values, e.g. G(-X), are frequently used to show the disappearance of a substance as a result of the radiation, expressed in the same units as above. One may distinguish between the primary yields, \( g(X) \), those produced in the solvent by the primary processes mentioned above, and the observed yields, \( G(X) \), those actually measured for a particular (solute-solvent) system. The two quantities may be identical. For example in pure water one should find that \( G(\text{H}_2) = g(\text{H}_2) = 0.45 \) molecules per 100 e.v.

The proximate background to the problem at hand begins with the work of Amell\textsuperscript{10} in this laboratory, in investigating the gamma radiolysis of aqueous SnCl\textsubscript{2}-HCl solutions. Tin (IV) and H\textsubscript{2} were identified as the products of the radiolytic reaction. \( G(-\text{Sn(II)}) \) was determined to be 1.25 in 0.80M HCl, independent of the total
dose absorbed. (In accord with general practice, we shall omit the units of G-values in this and subsequent statements of them.) For HCl concentrations above 1M, a slight dependence on acid concentrations was found. G(-Sn(II)) = G(Sn(IV)) also appeared to increase slightly with increasing chloride ion concentration.

Just before publication of Amell's paper, Boyle, Weiner, and Hochanadel\(^\text{11}\) published a report of their work with SnSO\(_4\) solutions in 0.8N H\(_2\)SO\(_4\). They found G(-Sn(II)) = 0.49. Amell carried out two radiolyses of analogous SnSO\(_4\) solutions and obtained values for G(-Sn(II)) of 0.52 and 0.79, which evidently confirmed the work of Boyle, et al. This sharp discrepancy between the chloride and sulfate results was quite unexpected, since both Cl\(^-\) and SO\(_4^{2-}\) concentrations remained constant throughout the respective radiolyses.

Hatch\(^\text{12}\) repeated and extended the work of Amell, investigating the possibility that primary yields might change on going from a sulfuric acid to hydrochloric acid system. His values for G(Sn(IV)), obtained with a different analytical method, duplicated those of Amell exactly. Moreover, he found the primary yields unchanged in the HCl systems.

The mechanism proposed by Boyle, Weiner and Hochanadel predicted that G(H\(_2\)) would be found to be equal to g(H\(_2\)) = 0.45, but they did not perform any analyses for hydrogen. Hatch did determine G(H\(_2\)) for his SnCl\(_2\)-HCl solutions, and found values considerably higher than 0.45. For example G(H\(_2\)) for 10\(^{-2}\)-M SnCl\(_2\) in 1M HCl was 1.16.

All the above investigators found G(-Sn(II)) to be independent of the total dose absorbed, ergo independent of the time of
irradiation. However, a necessary consequence of the mechanism of Boyle, et al., was that $G(-\text{Sn(II)})$ should be considerably higher than 0.45 or 0.49 at low absorbed dose (but not greater than 2.25). Several experiments by that group with short irradiations failed to show evidence of the expected increase.

This, then is the problem: explain "the anion effect" -- this large and quite unexpected change in $G(-\text{Sn(II)})$ on going from a sulfate to a chloride system. Although Hochanadel, et al., did not actually measure hydrogen yields, a full solution of the problem would seem to require a resolution of the apparent discrepancy in hydrogen yields as well. Lastly, if a mechanism similar to that already proposed for the sulfate system be adopted, it would be helpful if the high initial yields of tin (IV) could be demonstrated experimentally.

The approach chosen was to extend the work to other anions. Since bromide seemed the logical first choice, experiments were undertaken with solutions of stannous bromide and hydrobromic acid.
SECTI0N II

EXPERIMENTAL

Materials

Water from a Barnstead Demineralizer system (Model MM-3) was distilled from a Barnstead still. This product was in turn distilled from alkaline permanganate through a four-foot Glass Wool-packed column. A final, slow distillation was effected in a smaller still equipped with a Vigreux column. Since an all-silica system was not available, the latter two stills were constructed of all borosilicate glass, which was cleaned periodically with hot chromic acid and/or hot alkaline permanganate. After any cleaning, all glassware was rinsed repeatedly with triply distilled water (TDW) until the resistance of the washings, measured with a conductivity bridge, reached a maximum. The final product was stored under the protection of activated charcoal, sodalime, and calcium chloride traps. Specific resistance of the TDW ranged from 1.08 - 1.41 Megohm-cm. All ground-glass joints and the all-borosilicate stopcocks were lubricated with the water only.

As a check on the presence of organic impurities, a fluorescence spectrum of the TDW was determined from 250-550 nm. At the highest sensitivity of the instrument (Range: 0.01; 1 microamp full scale) a very faint fluorescence peak was noted, with an intensity of 1 chart unit (70 chart units = full scale). Without further information, it is impossible to say to what concentration this corresponds. Depending on what the fluorescing compound is, its concentration may be from $10^{-7}$ - $10^{-14}$ M. Because the concen-
tration was so low, no attempt at a more quantitative estimation with an internal standard was made. It would seem safe to say that the amount of fluorescent organic compounds, at least, in the TDW is negligibly small.

Stannous chloride used was Fisher A.C.S. certified crystal $\text{SnCl}_2\cdot2\text{H}_2\text{O}$. Stannous bromide was obtained from K+K Laboratories and was used without further purification (but vide infra).

Santomerse S was obtained courtesy of Monsanto Corp., and Mr. William Farrington. Hexadecyltrimethylammonium bromide was Eastman practical grade. Electrolytic grade hydrogen was used in calibrations for that element. Prepurified nitrogen was used for all deaeration procedures. All other chemicals employed were reagent grade and were used as received.

**Apparatus**

Selection and care of the glassware used for distillation and storage of the solvent water have been described above.

Two types of radiation vessels were used: 100-ml "rabbit-eared" vessels, which have been previously described, were employed in determinations of tin yields. 5-ml ampoules (Kimble 12012-U) with ring break seals were used for irradiation of samples to be analyzed for hydrogen gas. The rabbit-eared vessels were cleaned with hot chromic acid and carried through the rinsing procedure described above. These vessels were stored either upside down or filled with TDW. Although the latter procedure is recommended, the former was used more often. There was no detectable difference in the results obtained on replicate samples with the two different methods of storage. Since the 5-ml ampoules
gave the theoretical yield for an acid-bromide system (vide infra) and since thorough cleaning caused no change in measured yields, those vessels were used as received. Any ampoules showing specks of dust or other visible contamination were used in practice or preliminary runs.

The round-bottomed rabbit-eared vessels were supported during irradiation in an ordinary 12-oz. beverage can. The ampoules were irradiated four at a time in a specially fabricated polyethylene holder, designed to effect more reproducible positioning of the ampoules with respect to the cobalt source than was possible with the cork rings used in previous investigations.

The Cobalt-60 source and its ancillary equipment have been described elsewhere. 13

Collection of the hydrogen gas from the sealed ampoules, and its transfer to the gas sampler for the gas chromatograph, were accomplished with a vacuum system equipped with a manually operated Toepler pump. In our experiments with "known" systems, we found that we could not achieve reproducible and quantitative transfer of the hydrogen by using tubes with capillary break seals as described by previous investigators. 12, 15

Accordingly, a new ampoule holder-breaker assembly was designed and constructed. This consists of a round-bottomed glass tube fitted with a standard taper joint for attachment to the vacuum system. A glass sidearm serves as a guide sleeve for a chisel-pointed brass striker rod. The assembly is made vacuum-tight by addition of a tight-fitting gum rubber outer sleeve, sealed to the sidearm and the striker rod with vacuum wax and wire clamps. The striker rod was amalgamated, and under the conditions
of our experiments showed no reaction with the acid solutions employed, and no spuriously high results for known systems (see \textit{Calibrations and Standardizations}).

In practice, an ampoule is placed in the tube in an inverted position and is supported at its shoulder by the breaker rod. The latter has been adjusted so that tension in the rubber sleeve holds the chisel point firmly against the break seal. After evacuation of this assembly, the Toepler cylinder, gas sampler, and connecting tubing to 0.001 torr or less, a light tap on the breaker rod suffices to smash the ampoule into small pieces and discharge its (liquid) contents to the bottom of the tube. Gentle heating of the tube at its base is sufficient to cause boiling, driving out the last traces of gas. An electro-mechanical vibrator is used to release trapped bubbles and to reduce the probability of bumping.

Although the solubility of hydrogen gas in most liquids is low,\textsuperscript{16} in our experience, procedures which left the body of the ampoule intact and containing the liquid sample did not allow quantitative detection of hydrogen generated radiolytically in a liquid. Because of the low pressure in the system even after rupture of the break seal, heating of liquid remaining in an ampoule which was in turn standing in the outer tube of the ampoule holder-breaker assembly, was so slow as to be quite impractical -- hence the inverted-ampoule technique. Going to such lengths to remove every trace of hydrogen gas dissolved or caged in the liquid may be more understandable if one considers the total quantity of hydrogen involved: \textit{e.g.}, a fifteen-minute irradiation of solution B-II yielded 0.05 micromole of hydrogen.
**Solutions**

Solutions of stannous chloride were prepared by dissolving the calculated amount of the salt in 12M HCl and adding that solution to the required volume of TDW, which had been previously deaerated with a nitrogen purge for two to three hours. The resultant solution was further deaerated for a minimum of one hour.

Attempts at solution of stannous bromide in HBr yielded a colloidal suspension of a white solid, which could not be removed by filtration. Centrifugation for 15-20 minutes separated the solid effectively, and careful decantation into the TDW gave a clear final solution, deaerated as above. Since the white solid contained tin (IV) and dissolved in base but not in acid, presumably it was simply hydrated stannic oxide.17

These solutions were stored in a modified 2-liter Pyrex flask kept under a positive pressure of nitrogen, and equipped with a (nitrogen) gas-dispersion tube for deaeration and mixing. A two-way stopcock attached to a delivery tube at the base of this flask enabled nitrogen flushing of, and direct transfer of solution to, the radiation vessels. Stopcocks coming in contact with the solution or the nitrogen flushed through it, were lubricated only with solution or water respectively. During preparation, storage and transfer, the solution came in contact with Pyrex glass and nitrogen only.

**Instrumentation**

Gas analyses were performed on a Perkin-Elmer Model 154B Vapor Fractometer with gas-sampling attachment. A 2-m glass column packed with 20-60 mesh Molecular Sieve 5A was used at approximately
25°C. Nitrogen carrier gas was used at a flow rate of 30 ml/min. Readout was on a Photovolt Microcord recorder with 10-in chart and 1 mv full scale sensitivity.

Spectrophotometric measurements during the investigation of various complexing agents for tin were performed on a Bausch and Lomb Spectronic 505 uv-visible spectrophotometer.

Colorimetric work in the visible region was done with a B&L Spectronic 20.

Ultraviolet "colorimetry," including that for the ferric ion produced in the Fricke dosimeter, was done on a Beckman DU with regulated power supply.

Conductivity measurements on the distilled water were performed on a Model RC16B2 conductivity bridge, manufactured by Industrial Instruments, Inc.

Fluorescence spectra were obtained on a Farrand Optical Mark I Spectrofluorometer.

**Analytical Procedures**

If $G(\text{Sn(IV)})$ is to be determined, analyses must obviously be made at less than 100% conversion to tin (IV). This necessitates an analytical method capable of detecting either very small changes in tin (II) concentration or very low concentrations of tin (IV) in the presence of large excesses of tin (II). Preliminary investigations indicated that solutions of stannous bromide were extremely sensitive to air oxidation -- much more so than those of stannous chloride, for example. In order to reduce air oxidation as much as possible, an analytical method requiring a minimal amount of time was desired.
Boyle, Weiner, and Hochanadel reacted stannous sulfate solutions with an excess of cerium (IV), which was determined spectrophotometrically. Attempts at using this method on our stannous bromide solutions yielded steadily drifting absorbance measurements, due presumably to a slow oxidation of the bromide ion by the cerium (IV) species. Addition of sodium bromide to solutions of Ce(IV) confirmed this hypothesis. The rate of oxidation was too fast to be avoided by working quickly, yet so slow that waiting for complete reaction was impracticable. Both accurate corrections for this problem and removal of bromide ions by ion exchange were deemed to complicate this method unnecessarily, and so it was discarded.

Amell, working with 10^{-2} M solutions of stannous chloride, had used an iodine titration to determine G-(Sn(II)). In order essentially to eliminate the possibility of "direct hits" of the radiation on stannous ions, as discussed in the introduction, we wished to work with concentrations of 10^{-3}--10^{-4} M. Accordingly, a solution of stannous bromide of this concentration was prepared and added to a solution of iodine (triiodide) whose absorbance was measured at 450 nm before and after the addition of the tin (II). After correction for dilution no change in the concentration of iodine was observed. Apparently, at these concentrations thermal reaction of I_{2} with tin (II) is very slow or does not occur at all.

The simultaneous presence of bromide ion at high concentrations (--at least 1M--from the HBr), and tin (II) at very low concentrations (ca. 10^{-3} M) continued to plague our efforts to find a suitable oxidizing agent for the stannous ion. Iodate converted that ion very quickly to stannic but, like Ce(IV), oxidized the
bromide. Iron (III) is a well-known oxidant for tin (II) and does not oxidize bromide. However, with our tin (II) concentrations, no Fe(III)--Sn(II) reaction occurred. Boyle, et al. reported the same lack of reaction in their work with stannous sulfate solutions. Even heating the Fe(III)-Sn(II) solution to 100°C. in an inert atmosphere failed to induce reaction. Concentration-dilution techniques were deemed to increase handling time (i.e. probable error) too much, and were not tried. Lastly, neither silver (I) nor mercury (II) proved usable. This exhausted our list of promising oxidizing agents, and attention was turned to a number of reagents reported to form complexes specific for stannous or stannic ions.

A blue tin(II)-silicomolybdate complex has been reported, and formed nicely with SnCl₂ solutions, but would not form with SnBr₂ in our experiments. A thiocyanate-molybdate reagent formed a complex specifically with Sn(II) at sufficiently low tin concentrations, but spectral interference (200-350 nm) between the absorption bands of the reagent and the complex was too serious for quantitative work. A Sn(II)-cacoetheline complex gave similar problems, as did haematoxylin. Dithiol, with Santomerse S dispersant, is reported to be a reagent specific for Sn(II) but was also found to form a complex with Sn(IV), whose spectrum overlapped too much with that for the Sn(II) complex. The directions for use of most of these reagents assumed an analysis for total tin, and specified that thioglycolic acid be added to ensure that all tin present existed in the stannous form. Naturally the thioglycolic acid was omitted in our experiments. Apparently it was this which led to the claims that they were specific for Sn(II). They are specific for Sn(II) with respect to most other elements but not with
respect to Sn(IV). The possibility of using thioglycolic acid itself as a reagent for tin(IV) was considered, but feasibility studies were discouraging (no usable absorption maxima in the visible or ultraviolet; insufficient change in acidity on reaction with our tin solutions).

Catechol violet (pyrocatecholsulfonephthalein) has been reported to be a selective reagent for Sn(IV), with the color reaction greatly sensitized by cetyl trimethylammonium bromide. This reaction appeared quite promising: a $10^{-4}\text{M}$ solution of Sn(IV) gave a green complex with $\varepsilon(554\text{nm}) = 92200 \text{ mole}^{-1}\text{cm}^{-1}$ and a $10^{-3}\text{M}$ solution of Sn(II) yielded a blue complex (vis max 660 nm, $\varepsilon(554\text{ nm}) = 2120$). Very careful pH control is essential to reproducible results. The above values were obtained with solutions stabilized by McIlvaine's buffers at pH 2.2. After some work with this system, an observation that a $10^{-4}\text{M}$ solution of Sn(II) gave the characteristic Sn(IV) color led to an investigation which concluded ultimately, that the reagent was indeed specific for Sn(IV) but formed two different complexes, a 1:2 Sn:reagent complex and a 2:1 moiety. Apparently the reagent itself had oxidized Sn(II) in the stannous solution to Sn (IV), which then reacted with unreduced catechol violet to produce a complex whose stoichiometry depended on the relative concentrations of the two reactants. Addition of color reagent to a solution of Sn(II) plus reducing agent produced no color, thus confirming the stannous-oxidation hypothesis. It will be remembered that the concentrations of the stannous and stannic solutions used in the preliminary experiments were $10^{-3}$ and $10^{-4}\text{M}$ respectively, these being approximately the values we expected to encounter in our radiolysis experiments. It would seem
that the crossover point between the 1:2 and the 2:1 complex occurs between $10^{-3}$ and $10^{-4}$M Sn(IV) concentration. Calculation of the molarity of the prepared-as-directed catechol violet solution showed it to be $7 \times 10^{-4}$M (assuming 100% purity) which is consistent with our explanation.

Use of an excess of catechol violet reagent would yield only an analysis for total tin, but use of a limiting amount of the dye offered some hope as an agent for following the course of a radioinduced oxidation of Sn(II) to Sn(IV). However, following the total absorbance (as a function of time) at several selected wavelengths for radiolyses of up to 2 hours showed that the absorbance change occurring was too small to be of value.

Polarography would seem to be an obvious analytical method for tin (IV) and was used by Hatch\textsuperscript{12} in earlier investigations in this laboratory. Especially with Sn(IV) halides, however, the reduction potential and the shape of the wave depend markedly on which polyhalide complex (or which combination in a series of such complexes) obtains in the solution at hand. The results are also a sensitive function of the supporting electrolyte and the pH.\textsuperscript{25} The polarographic reduction wave illustrated by Hatch (p 13) was obtained after some little experimentation, yet was still rather ill-defined. Further library work on our part failed to reveal a more promising polarographic system. So, although Hatch was able to obtain good precision and accuracy with his method, we opted not to use it.

At this point, it was decided to return to an iodine-titration technique as used by Amell, but to work with as low concentrations of Sn(II) as could be reliably detected. It will be remembered
that, in our early spectrophotometric experiments, we found no evidence of reaction between $I_2$ and Sn(II) when both were present at $10^{-3}$-$10^{-4}$ M, whereas Amell experienced no difficulties with $10^{-2}$ M solutions. Reproducibility problems became severe with Sn(II) solutions much below $5 \times 10^{-3}$ M, so that concentration was chosen for our stannous bromide solutions. $2.5 \times 10^{-3}$ M Iodine (triiodide) was used in order that the 25.00-ml aliquots of the stannous solutions would require a reasonable volume of titrant. Iodine solutions were standardized against arsenious acid, with titrations reproducible to 1 ppt.

Yields of Sn(IV) from the radiolysis of a series of stannous chloride solutions were determined as follows: 100-ml radiation vessels pre-flushed with nitrogen were filled with solution to a predetermined mark, which allowed some space (approximately 5 ml) beneath the stoppers for accumulation of gaseous radiolysis products. The space above the solutions was further flushed with nitrogen and the vessels stoppered. After irradiation the solution was transferred to a pipetting-holding (p/h) flask, from which 25.00-ml aliquots were taken for titration under nitrogen with the iodine solution. The transfer to the p/h flask was found necessary to ensure homogeneity of the sample from which aliquots were taken. This procedure was repeated immediately afterward with the non-irradiated or "stock" solution, in order to cancel as much as possible the effects of any adventitious air oxidation. The difference between the two titration values provided a measure of the amount of Sn(II) which had disappeared — presumably the amount of Sn(IV) produced by the radiolysis.

Densities of the solutions, necessary for calculation of
the G-values, were measured with a 25-ml pyknometer. Concentrations of HCl and HBr solutions were determined by titration against primary standard sodium carbonate. A sample G-value calculation is included in the Appendix.

Solutions of stannous bromide, in contrast to those of the chloride, posed such serious problems with respect to the reproducibility of the results that some modification of the procedure above was required. Successive titrations of the same solution seemed to show a rough trend toward lower Sn(II) concentrations, possibly indicating air-oxidation. Pre-flushing the pH flask with nitrogen and maintaining a nitrogen flow over the solution there reversed this trend (too much!). This time the solution became more concentrated with successive titrations -- a phenomenon attributed to pickup of solvent by the stream of dry nitrogen passing along the surface of the solution and on out of the pH flask. Presaturation of the nitrogen with solution or water allowed good precision to be obtained most of the time, but the nitrogen flow rate was critical. Analyses (and radiations) had to be repeated in a distressing percentage of cases. Apparently, the correct flow rate represented a precarious balance between diffusion of oxygen into the pH flask and incomplete saturation of the nitrogen. The small total amount of tin present and the smaller difference between titration values (irradiated vs. non-irradiated) for the shorter irradiations were probably contributing factors.

Perhaps, with hindsight, the extreme sensitivity of these stannous bromide solutions to air-oxidation should not have been unexpected. Air-oxidation of acidic solutions of iodide is known to occur very quickly. A similar reaction involving bromide would
lead to immediate oxidation of stannous ion by the bromine produced. The ease-of-oxidation heirarchy in the halide series could explain why the tin(II) chloride solutions did not show this susceptibility. It might be mentioned here that use of this same heirarchy was made in testing our deaeration procedures, viz. flow rates, flushing times, etc. were adjusted so that addition of an acidified solution of KI + starch showed no production of iodine.

The analysis for gaseous products of the radiolysis was a much easier task. A 5-minute nitrogen flush of an ampoule was followed by addition of 5.00 ml of stock solution, held under nitrogen in the pH flask. A 30-second nitrogen post-flush was continued while the ampoule was sealed with a torch. Treatment of the sample after irradiation has been described above under the use of the gas-analysis apparatus. Hydrogen, the only gaseous product found, was transferred to a gas sampler by means of the Toepler pump, the sampler attached to the fractometer, and the gas chromatogram recorded.

Since the gas chromatographic peaks were very symmetrical, the peak height times the half-width (width at half-height) was used as an estimation of the area. Conversion of these data to micromoles of hydrogen and finally to \( G(H_2) \) values was rather tedious, so a computer program was written to do the job, and was used in all \( G(H_2) \) calculations.

**Calibrations and Standardizations**

The \(^{60}\text{Co} \) source was calibrated with the Fricke dosimeter, using \( G(\text{Fe(III)}) = 15.5 \text{ ion/100 e.v.} \). The absorbance due to the ferric ion was measured at 304 nm, using a measured \( \epsilon = 2272 \text{ liter} \).
mol\(^{-1}\) cm\(^{-1}\) at 23°C. The molar absorptivity was corrected by 0.7% per \(^\circ\)C for all calculations.\(^{29}\) Providing that the absorption cells were kept scrupulously clean, no cell correction was necessary. Several calibrations with the rabbit-eared vessels gave a dose rate as of 15 January 1969 of 3.33\(\pm\)0.11 \(\times\) \(10^{16}\) e.v. \(g^{-1}\) \(\text{min}^{-1}\). Separate calibrations were performed for each position in the four-place polyethylene holder used for gas-analysis ampoules, but there was no statistically significant (95%) difference between them. The average dose rate for this sample holder was 2.52 \(\times\) \(10^{16}\) e.v. \(g^{-1}\) \(\text{min}^{-1}\) as of 1 December 1969. Dose rates used in calculations of G-values were corrected for decay.

Standardization of the iodine (triiodide) titrant was against \(H_2\text{AsO}_3^-\), prepared from 99.98% \(\text{As}_4\text{O}_6(s)\)\(^{30}\) which was acidified, then buffered at pH8. \(^{26}\) 3 ml of 1% soluble starch solution, stabilized with boric acid, was used as indicator. Precision of the titrations was 1 ppt. Since neither freshly prepared \(\text{SnBr}_2\) nor \(\text{SnCl}_2\) solutions are stable for approximately 24 hr (due probably to oxidation by traces of dissolved oxygen not removed by nitrogen-flushing of the solvent) no attempt was made to prepare primary "known" solutions from tin metal.

Calibration of the gas chromatographic system for hydrogen gas was accomplished by direct injection of various volumes of ultra-pure hydrogen with a gas-tight syringe. Samples were taken from a 500-ml bulb, fitted with a vacuum stopcock on one end and a syringe stopper on the other. Repeated evacuation and filling of the bulb with hydrogen, in our judgment, provided a pure, usable source of the gas. Results of the calibration for hydrogen are shown in Fig. 1.
Statistical analysis of these data, performed with the aid of a computer program kindly loaned to us by Mr. Robert M. Murphy, showed an excellent (better than 99%) correlation with a straight line for quantities of hydrogen greater than 0.04 micromole. Amounts less than 0.04 micromole initially gave low values, which increased gradually to coincide with the least-squares line at the above-mentioned value. Such anomalous behavior at very low concentrations of hydrogen was also observed by Hatch, and has been reported elsewhere. It is of little or no consequence here, since even our shortest irradiations proved to produce more than this critical minimum quantity of hydrogen, so that part of the calibration curve never had to be used.

As a check on the accuracy of the gas-tight syringe technique, one determination with an independent sampling method was performed. The gas sampler, filled with hydrogen, was connected to the (evacuated) vacuum system, and the hydrogen expanded into the whole system. After waiting several minutes for equilibrium to be attained, the pressure was read with a McLeod gauge, the temperature recorded, and the stopcock of the gas sampler closed. Following removal of the gas sampler from the vacuum system, its necks were flushed with nitrogen, the sampler attached to the gas chromatograph, and the chromatogram recorded. Since the volume of the gas sampler had been determined previously (by filling with mercury) the molar quantity of hydrogen used could be calculated from the ideal gas law. Our results with this method were slightly above the corresponding point on our least-squares calibration line, due probably to failure to wait a sufficient time for entropic equilibrium to be attained. (The gas sampler was constructed of very
small bore glass tubing, and had the added disadvantage of an approximately 330-degree bend -- required by the geometry of the fittings on the gas chromatograph.) Hatch,\textsuperscript{12} using a similar gas-sampler technique, and the identical gas chromatographic system, obtained a value which -- after conversion to our "response units"-- falls exactly on our line. This would seem to support the validity of the gas-tight syringe sampling technique. The estimated (random) error of this sampling technique was 2%.

As a final test of this calibration -- and of our analytical method for hydrogen -- two samples of a deaerated solution 10^{-3} M in NaBr and 0.8 N in H_{2}SO_{4} were irradiated and analyzed for hydrogen. This system is well-known to yield G(H_{2}) = g(H_{2}). Our determined values were 0.41 and 0.45, in good agreement with the accepted value, reported variously as 0.40\textsuperscript{32} and 0.45\textsuperscript{33}. 
Fig. 1 Gas chromatographic calibration curve for hydrogen gas. $\Theta$, with gas-tight syringe; $\Box$, with gas sampler technique described in text; $\bigcirc$, Hatch$^{12}$ with sampler.

$^a$Please see Appendix for explanation of recorder response units.
RESULTS AND DISCUSSION

Stannous Chloride

As a matter of good practice, and in order to establish a
firm foundation for the work with the SnBr₂ system, we first de-
termined G(-Sn(II)) for several solutions of 10⁻²M SnCl₂ in 1M
HCl. It will be recalled that both Amell and Hatch found G(-Sn(II))
= 1.26 for this system. Further, this G-value was independent of
irradiation time or, more properly, of total dose absorbed.

To our great surprise (and consternation) we were quite
unable to reproduce their results. Scrupulous re-cleaning of glass-
ware, taking extreme care with respect to exclusion of atmospheric
oxygen, preparing fresh solutions made with SnCl₂·2H₂O reagent
crystals from a new bottle, and using a new source of HCl, all
failed to solve the problem. Our own results consistently showed
G-values which varied with the time of irradiation. G(-Sn(II))
decreased rather rapidly at first, then more slowly, from a high
of 2.08 for a 5- hr irradiation to approximately 0.55 for radia-
tions longer than 45 hr or so. These results are plotted in
Fig. 2.

Since we had from the beginning taken what we thought were
extensive precautions to ensure the absolute purity of our water,
we were loathe to suspect it as the cause of the discrepancy in
results. Both Amell and Hatch had done their work in the old
chemistry building, James Hall, and had used distilled water from
that building's system in making up their solutions. Preventing a
too-quick condemnation of the James Hall distilled water, is the
Fig. 2 Dependence of $G(\text{-Sn(II)})$ on irradiation time for $1 \times 10^{-2} \text{ M SnCl}_2$ in $1 \text{ M HCl}$. Dose rate = $3.23 \times 10^{16}$ e.v. g$^{-1}$ min$^{-1}$. 

- Triply distilled water solvent
- James Hall distilled water solvent
work of Amell\textsuperscript{10} with SnSO\textsubscript{4}--H\textsubscript{2}SO\textsubscript{4} solutions. Although he was working hastily due to circumstances mentioned in the introduction, his two determinations of $G(-\text{Sn(II)})$ for this system were 0.52 and 0.79, "... in satisfactory agreement with the value of 0.49" obtained by Boyle, Weiner, and Hochanadel.\textsuperscript{11} The rub is that Boyle, et al. used triply distilled water (TDW).

Suspecting our own results again, we made up a solution of SnSO\textsubscript{4} in 0.8N H\textsubscript{2}SO\textsubscript{4} equivalent to those used above, but naturally using our own TDW as solvent. Several analyses of two samples irradiated for different times gave $G(-\text{Sn(II)})$ values ranging from 0.44--0.59, with an average of 0.51. The average value for each sample was also 0.51. Since Amell only had time for two determinations, the question of which of those values to believe would seem to be legitimate. It is perhaps fortuitous, but nonetheless interesting, that the ratio of Amell's higher $G(-\text{Sn(II)})$ value for SnSO\textsubscript{4} to the value reported by Boyle, et al. is $0.79/0.49 = 1.61$; and the ratio of $G(-\text{Sn(II)})$ for SnCl\textsubscript{2} as obtained by Amell and by Hatch to our 68-hr value for the same system is $1.26/0.78 = 1.61$. That is, each ratio represents results obtained for a given tin compound. The higher value in each case was obtained with solutions made with James Hall distilled water. The lower value in the first case was obtained with solution made at Oak Ridge National Laboratory with TDW prepared there, and in the latter case with solutions made with our TDW.

In the hope that the composition of the James Hall distilled water had not changed substantially in the 6 or 8 years since Hatch did his work, we next made up a solution of $10^{-2}$M SnCl\textsubscript{2} in 1M HCl with that water. Two determinations of $G(-\text{Sn(II)})$ yielded values
of 1.29 and 1.17, respectively, in good agreement with the quoted value found by Amell and Hatch.

At the time our water sample was taken, the James Hall still had very recently been cleaned. According to the technician most closely connected with the still, after approximately two weeks of steady operation the product water would give a strong test for Cl\(^-\). (This was the only contaminant for which a test was made.) Further conversation with the technician and the janitor for that area revealed that the cleaning crew had removed "some large brown chunks" from the holding tank. We suspect that they meant the distillation pot itself, but they were quite insistent that a brown sludge had been removed from the bottom of the holding tank. The technician also recalled having "sometimes" noticed brown particulate matter in the distilled water product. The specific resistance of our sample of this water, measured with a commercial conductivity bridge, was 0.465 Megohm-cm (cf. values for our TDW of 1.08--1.41 Megohm-cm).

Finally, out of curiosity, we titrated with I\(_2\): first, 10.00 ml of our SnSO\(_4\) solution, to which 10 ml of our TDW had been added, and secondly, 10.00 ml of the same SnSO\(_4\) solution, to which 10 ml of James Hall distilled water had been added. In two separate trials, the sample with the James Hall water required 0.28 and 0.39 ml less of the 3.62 x 10\(^{-3}\)M I\(_2\). This suggests strongly the presence in the James Hall water of an agent capable of oxidizing tin(II). The most likely explanation is simply that the James Hall water may have been distilled earlier than our TDW, and contained some dissolved O\(_2\). However, the reaction of such dissolved O\(_2\) with SnCl\(_2\) has been reported\(^{10}\) to be slow. A rough estimation of the concen-
tration of this species, assuming a 1:1 molar equivalence upon reaction with tin(II), places its concentration at $1 \times 10^{-4} \text{M}$, not an unreasonable value. Whatever one's judgment of this evidence, it should be noted that the presence of an oxidizing agent in the solvent water is not a strict requirement in order than abnormally high radiolysis yields be obtained. For instance, one mole of an otherwise innocuous contaminant could, under the influence of the radiation, produce one or more moles of an oxidizing species.

The situation is by no means simple. For example, even if there be an oxidizing agent in the James Hall water, according to the experiment above, its reaction with tin(II) would surely be over before the start of an irradiation. Since both the irradiated and non-irradiated solutions are analyzed after the irradiation, any (thermal) oxidation of Sn(II) caused by this species would not appear in the results. However, this does not preclude interaction of oxidized or reduced form of this agent with the radiation so as to cause higher-than-normal radiolysis yields. The antithetic behavior noted for solutions prepared from TDW vs. James Hall distilled water, with respect to dependence of $G(-\text{Sn(II)})$ on the irradiation time, is still unexplained, as is the difference between our observations and those of Amell in regard to the effect of added Sn(IV) on $G(-\text{Sn(II)})$.

All things considered, we are forced to conclude, however sadly, that the discrepancies between our results and those of Amell and Hatch are due to something in the James Hall distilled water, and stand by our own results. It is, of course, entirely possible that the lower of Amell's values of $G(-\text{Sn(II)})$ for the SnSO$_4$ system is the correct one. If this be the case, and if our
supposition is correct, then that "something" in the James Hall water -- once tentatively identified -- must be shown to affect the tin chloride system but not the sulfate. We shall return to a discussion of the discrepancies in results for the stannous chloride solutions after presentation of our results for the stannous bromide system and the development of our proposed mechanism for the radiosynthesis.

**Stannous Bromide—Results**

Both $G(-Sn(II))$ and $G(H_2)$ were determined for two series of deaerated stannous bromide solutions. The first such series consisted of solutions approximately $5 \times 10^{-3}M$ in $SnBr_2$ and $1M$ in HBr, with total Br$^-$ concentration varied from 1 to 3M by addition of NaBr. In the second set of solutions, the concentration of HBr was varied from 1 to 3M. The reducing titer of the solutions decreased on irradiation, indicating a net oxidation of tin(II). Hydrogen gas was produced and was identified by gas chromatography. No other gaseous products were found. The results are summarized in Figs. 3--6, where the respective G-values are plotted against the time of irradiation. The estimated error in the values for $G(-Sn(II))$ is 12%; for $G(H_2)$, 5%.

The behavior observed for the stannous bromide solutions was quite similar to that found (in this investigation) for stannous chloride. $G(-Sn(II))$ for $SnBr_2$ in 1M HBr was very high for shorter irradiation times, being approximately 2.5 for a 5-hr irradiation. Extrapolation to "zero time" yielded a G-value of approximately 4. The apparent limiting value for $G(-Sn(II))$ in this system was 0.49, and was attained only after irradiation for about 70 hr. Increasing
Fig. 3 Dependence of $G(-\text{Sn(II)})$ on irradiation time for $5 \times 10^{-3}$ M SnBr$_2$, with added NaBr. Dose rate = $3.15 \times 10^{16}$ e.v. g$^{-1}$ min$^{-1}$.
Fig. 4 Dependence of $G(-\text{Sn(II)})$ on irradiation time for $5 \times 10^{-3}$ M SnBr$_2$, with added HBr. Dose rate = $3.1 \times 10^{16}$ e.v. g$^{-1}$ min$^{-1}$. 

- 1 M HBr
- 2 M HBr
- 3 M HBr
Fig. 5 Dependence of $G(H_2)$ on irradiation time for $5 \times 10^{-3}$ M SnBr$_2$, with added NaBr. Dose rate = $2.6 \times 10^{16}$ e.v. g$^{-1}$ min$^{-1}$.
Fig. 6 Dependence of G(H₂) on irradiation time for 5 x 10⁻³ M SnBr₂, with added HBr. Dose rate = 2.5 x 10¹⁶ e.v. g⁻¹ min⁻¹.
the Br⁻ concentration seemed to cause a more rapid decrease of
$G(\text{Sn}^{II})$ at shorter irradiation times, but the limiting value
became higher at the same time, rising to 0.81 for a 72-hr irra-
diation of a solution 3M in Br⁻. Increases in the concentration of
HBr showed similar G-values at 72 hr, but the rate of descent
appeared to be different, as will be discussed later.

The hydrogen yields behaved somewhat differently, showing
similar high initial and low limiting values, but exhibiting a
nearly vertical rate of descent to the limiting values at very
short irradiation times. The highest $G(H_2)$ observed was 2.0 for a
0.25-hr irradiation. All observed hydrogen yields dropped to their
limiting values for 4- or 5-hr irradiations, in sharp contrast to
the 72-hr irradiation required for most of the tin yields to attain
their steady-state values. Although the limiting hydrogen yields,
like those for tin, increased with increasing concentration of
sodium bromide or hydrobromic acid, the increments appeared to be
smaller. Thus, the limiting $G(H_2)$ rose from 0.50 to 0.68 in going
from 1 to 3M bromide ion concentration.

**Stannous Bromide--Discussion**

Primary Yields

Any quantitative test of a proposed mechanism requires a
knowledge of the primary yields (G-values) for the particular
solvent system used. For convenient reference and comparison, some
of the generally accepted values for the pertinent parameters are
printed in Table I.

It will be noted that the radical yields, as opposed to the
molecular yields, increase markedly with a decrease in pH. This
effect, as shown by continuous curves of similar data published elsewhere, begins below about pH 3, and apparently continues to higher acid concentrations than the 0.8N listed below. Data for solutions of higher acidities are very scarce.

Table I. Primary Radical and Molecular Product Yields in Gamma-Irradiated Aqueous Solutions

<table>
<thead>
<tr>
<th>Hydronium Ion Concentration (M)</th>
<th>$g(H_2)$</th>
<th>$g(H_2O_2)$</th>
<th>$g(H)$</th>
<th>$g(OH)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-7}$</td>
<td>0.42</td>
<td>0.71</td>
<td>2.80</td>
<td>2.22</td>
<td>32</td>
</tr>
<tr>
<td>0.8</td>
<td>0.45</td>
<td>0.80</td>
<td>3.65</td>
<td>2.95</td>
<td>33</td>
</tr>
<tr>
<td>1.0</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>2.0</td>
<td>0.47</td>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>3.0</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
</tbody>
</table>

Probable error for all values is about 3%.

It is interesting that Hatch (Ref. 12) found a steady increase in $g(H_2)$ with increasing HCl concentrations of the same molarities as used in our HBr systems. Noting that $g(H_2)$ is the parameter least sensitive to changes in pH, Hatch's results would seem to indicate that primary (especially radical) yields do continue to increase at hydronium ion concentrations greater than the 0.8N listed above. It has been argued that the (truly) primary yield of radicals is not itself affected by decreases in pH, but the number of available radicals is increased through inhibition of recombination of radicals produced in pairs. This seems quite
plausible, but does not change the net results.

The point of all this is twofold. First, with respect to our hydrogen yields, for solutions more acid than 0.8N, there is a reasonable expectation that the primary yield of hydrogen gas will be greater than the generally accepted value of 0.45. Secondly, since the molecular hydrogen produced is generally unreactive toward solutes (ours included) there will be, in such solutions of increasing acidity, a net increase in the yield of oxidizing species relative to that of reducing species. (By material balance, this proportionate increase (in equivalents per 100 e.v.) would be equal to twice the increase in \( g(H_2) \).) The latter expectation has implications for our observed yields of tin(IV) at various HBr concentrations.

Despite these considerations, in our discussions of possible mechanisms we shall use the primary yield values quoted above for 0.8M hydronium ion concentration, since they constitute the only complete and self-consistent set available.

**Hydrogen Yields**

The behavior of the observed yields of hydrogen, \( G(H_2) \), as a function of the irradiation time is notably simpler than that of the corresponding yields of tin. For this reason, and because the yields of hydrogen and tin are interdependent, we have chosen to discuss the hydrogen yields first.

**Initial Yields.** Probably the most distinctive feature of these results is the high initial value of \( G(H_2) \) observed for each solution investigated. Two factors discussed above, viz. the usually low reactivity of molecular hydrogen, plus the relative constancy
of \( g(H_2) \) over wide ranges of acidity, combine to make observed hydrogen yields different from 0.45 rather unusual occurrences.

Also as mentioned above, our results are in sharp contrast to Hatch's (irradiation) time-independent values of \( G(H_2) \).

The reaction
\[
H + H^+ + I^- \rightarrow H_2 + I
\]
(3)
has recently been well established.\(^{36}\) Postulation of an analogous reaction with \( Br^- \) will explain the unexpectedly high yields at very short irradiation times:
\[
H + H^+ + Br^- \rightarrow H_2 + Br
\]
(4)
That is, reaction (4) represents an additional source of \( H_2 \) beyond those primary processes which produce the yield \( g(H_2) \). If all \( H \) atoms produced in the solution were scavenged by reaction (4), one would expect \( G(H_2) = g(H_2) + g(H) = 0.45 + 3.65 = 4.10 \). As can be seen from Figs. 5 and 6, our initial yields are not at all inconsistent with this. Unfortunately, the experimental difficulty of detecting the micro-amounts of hydrogen involved prevented a determination of the exact initial yield. Extrapolations of our curves to "zero time" produce estimates of the initial yield equal to or less than 4.1. One can not only explain, but would in fact predict, yields less than 4.1 by invoking reaction (10) (p. 38) as there is certainly tin(II) present at the beginning of the irradiation to offer some effective competition for the \( H \) atoms consumed in reaction (4). Although the concentrations of both \( H^+ \) and \( Br^- \) are admittedly much greater than that of Sn(II) in all of our experiments, reaction of the latter with \( H \) atoms has been estimated\(^{11}\) to be essentially diffusion-controlled, whereas a recent\(^{36}\) measurement of \( k \) for the termolecular reaction (4) gives the value
5.3 \times 10^6 \text{m}^{-2}\text{sec}^{-1}. \text{ It is indeed unfortunate that the steepness of our plots of } G(H_2) \text{ vs. irradiation time at short times, and the relatively large error associated with those points on the curve, prohibit any attempt at accurate extrapolation to initial values, since such intercepts could provide an independent estimate of the ratio of these two rate constants.}

**Descent to Limiting Yields.** We have next to explain the rapid decrease in \( G(H_2) \) to the limiting value of about 0.55. This drop can be attributed to an increasing competition for \( H \), with \( \text{Sn(III)}, \text{Sn(IV)} \) and \( H_2O_2 \) vying with \( \text{Br}^- \) (reaction (4)) for the hydrogen atoms. \( H_2O_2 \) is included, since its reaction with \( \text{Sn(II)} \) has been reported to be slow. If they have sufficiently long lifetimes, species such as \( \text{Br} \) and \( \text{Br}_2^- \), formed as a consequence of reaction (4), would also compete with reaction (4) for available \( H \) atoms.

Hentz and Johnson, studying the radiolysis of deaerated acidic solutions of iodides, found results very analogous to ours, with high initial yields of both \( H_2 \) and \( I_2 \) (determined from the slopes of their curves to be 4.1 \pm 0.2) dropping to a limiting value of \( G(I_2) = G(H_2) = g(H_2) = 0.45 \). Their concentrations of \( X^- \) and \( H^+ \) were lower than ours, which may explain their lower limiting value. In their case, the drop to the limiting yield was ascribed to the back reaction

\[
H + I_2 \text{ (or } I_3^- \text{)} \rightarrow H^+ + I^- + I \text{ (or } I_2^- \text{)} \quad (5)
\]

which is diffusion-controlled. Attainment of the limiting yield was found to be a function of the total dose absorbed, and required about 1 hr for their system. Since our dose rate was about one-third theirs, a strict analogy would predict that our yields would reach
the minimum value in approximately 3 hr. Actually, 4-5 hr were required for our system's $g(H_2)$ values to reach their level, which is not at all surprising considering the greater difficulty of oxidizing $Br^-$ vs. $I^-$. Also, at least some of our "back reactions" are apparently not diffusion-controlled (see discussion of tin yields, below). Buildup of higher concentrations of our oxidized products would then be necessary in order for them to attain an $H$-scavenging effectiveness equivalent to reaction (5). In any event, the agreement between the two systems is certainly encouraging.

The fact that our limiting yield is slightly greater than $g(H_2)$ we would interpret to mean simply that in the steady state, even though the various tin species dominate the competition for $H$ atoms, the preponderant concentrations of $H^+$ and $Br^-$ still give them (via reaction (4)) a chance, so to speak, in the competition. Also, our previous discussion of primary yields as a function of hydronium ion concentration offers a partial explanation, as does a probable error of $\pm 0.03$ G-value unit.

**Effect of Added Hydronium or Bromide Ion.** One may notice a slight increase in $g(H_2)$ with increasing $H^+$ or $Br^-$ concentration. This, accompanied by increased $I_2$ yields for the $I^-$ analogy, has been observed before by several investigators,\textsuperscript{36,37,38} and is easily explained by looking at the effect of the concentrations of these species ($H^+$ and $Br^-$) on reaction (4). Incidentally, this further supports our primary explanation in the paragraph above.

**Tin Yields**

**Basic Mechanism.** In order to explain our results with respect to tin, the following reactions seem reasonable, where $Sn(II)$
will be used to represent whatever halo-complex of Sn(II) actually takes part in the particular reaction, Sn(III) for the appropriate Sn(III) species, etc.

\[ \text{Br}^- + \text{OH} \rightarrow \text{Br} + \text{OH}^- \]  \hspace{1cm} (6)

or

\[ \text{Br}^- + \text{H}^+ + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O} \]  \hspace{1cm} (6a)

\[ \text{Sn(II)} + \text{Br} \rightarrow \text{Sn(III)} + \text{Br}^- \]  \hspace{1cm} (7)

\[ \text{Sn(II)} + \text{OH} \rightarrow \text{Sn(III)} + \text{OH}^- \]  \hspace{1cm} (8)

\[ \text{Sn(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Sn(III)} + \text{OH} + \text{OH}^- \]  \hspace{1cm} (9)

\[ \text{Sn(II)} + \text{H} \rightarrow \text{Sn(I)} + \text{H}^+ \]  \hspace{1cm} (10)

\[ \text{Sn(I)} + \text{Sn(III)} \rightarrow 2\text{Sn(II)} \]  \hspace{1cm} (11)

\[ \text{Sn(I)} + \text{Sn(IV)} \rightarrow \text{Sn(II)} + \text{Sn(III)} \]  \hspace{1cm} (12)

Sn(I) can react analogously to (7), (8), and (9). Sn(III) can undergo reactions analogous to (7), (8), (9), and (10), and Sn(IV) can react in the same fashion as Sn(II) in reaction (10). The OH produced in reaction (9) can, of course, undergo reactions (6) or (8). In discussions of our results for SnCl\(_2\), one may substitute Cl and Cl\(^-\) for Br and Br\(^-\) in reactions (6), (6a), and (7). Reactions (8)--(12) and their analogs have been proposed for tin systems before.\(^{10,11,12}\)

**Participation by Bromide.** The presence of the complexes Cl\(_2^\cdot\) and Br\(_2^\cdot\) during the radiolysis of acidic solutions of the corresponding halides appears to have been established.\(^{39,40}\) It is recognized that these species will almost certainly react at rates different from the respective halogen atoms, and that a full mechanistic picture of our radiolysis requires consideration of the reactions of these complexes -- reactions probably similar to (7) and its Sn(I) and Sn(III) analogs. Very little is known about the
concentrations or reactivities of these halogen molecule-ions, which helps to make a quantitative kinetic analysis of our system a formidable task. However, it has been reported$^{41}$ that, with respect to some organic compounds at least, rate constants for $\text{Cl}_2^-$ reactions are 20 to 200 times smaller than for the corresponding $\text{OH}$ reactions.

Reaction (6) is believed to be diffusion-controlled, with $k$ estimated$^{42}$ to be $3.6 \times 10^{10}\text{M}^{-1}\text{sec}^{-1}$. Competitive kinetics experiments indicate$^{11}$ that reaction (8) is about ten times slower. With this in mind, and considering the high concentrations of both hydronium ions and bromide ions in our experiments, it would seem that a sequence of reactions (6) and (7) would greatly predominate over reaction (8). Our own observations in regard to the much greater susceptibility of stannous bromide vs. stannous chloride toward air-oxidation offer strong evidence, we think, of active participation by some bromide species. For simplicity's sake, we shall leave reactions (6) and (7) as written, with the understanding that some unknown fraction of the oxidized bromine species exists -- and reacts -- as $\text{Br}_2^-$, and proceed to a discussion of our results.

**Initial Yields.** Very early in the radiolysis, with such negligible amounts of $\text{Sn(III)}$ and $\text{Sn(IV)}$ present that back reactions involving those species may be ignored, one would expect a maximum, i.e. initial, value of $G(-\text{Sn(II)}) = G(\text{Sn(IV)}) = g(\text{H}_2\text{O}_2) + g(\text{OH})/2 = 0.80 + 1.48 = 2.28$. For $\text{SnBr}_2$ in 1M $\text{HBr}$, as we found for $\text{SnCl}_2$, our initial values are evidently much higher than this. Also as for $\text{SnCl}_2$, extrapolation gives an initial value of $G(-\text{Sn(II)})$ of about 4. Once again, we make recourse to reaction (4)

$$\text{H} + \text{H}^+ + \text{Br}^- \rightarrow \text{H}_2 + \text{Br}$$

(4)
noting that its production of bromine atoms represents an additional source of Sn(IV) from reaction (7). Assuming all H to be scavenged by reaction (4), the enhanced Br yield would be equal to \( g(H) = 3.65 \), corresponding to an increased yield of Sn(IV) of \( 3.65/2 = 1.83 \). The maximum initial yield of Sn(IV) would now be predicted to be \( 2.28 + 1.83 = 4.11 \), which is consistent with our results. Unfortunately, the extreme difficulty of accurate determination of G-values at these small percentages of reaction precluded a decisive extrapolation of our curves. Hentz has succeeded in measuring the initial yield of \( I_2 \) from gamma-irradiated acidic solutions of \( I^- \) as 4.3. Since \( I_2 \) is well known to oxidize Sn(II) quantitatively, this system would seem to be a rather good supportive analog for our estimation of our initial yields.

In sharp contrast to those of \( G(H_2) \), plots of \( G(-Sn(II)) \) vs. irradiation time decrease only slowly to their limiting values. Moreover, every tin solution examined showed a different rate of descent. This behavior is quite puzzling, and discussion of it will be postponed until after consideration of the respective limiting yields.

**Limiting Yields.** If our proposed mechanism for the radiolysis is correct, one should find that, for the observed yields,

\[
G(-Sn(II)) = G(Sn(IV)) = G(H_2)
\]

This relationship is dictated partly by the requirement for material balance (see below) and partly by our contention -- and observation -- that tin(IV) and hydrogen gas constitute the only (permanent) products of the radiolysis. In regard to material balance, one is saying simply that, if some water molecules are decomposed by the radiation essentially into H and OH, then the radiolytic yields
should be found to contain equal numbers of equivalents of oxidized and reduced products.

In terms of primary yields, the condition of material balance may be stated as

\[ g(H) + 2g(H_2) = g(OH) + 2g(H_2O_2) \]  

For a very simple system of tin(II) in aqueous solution the assumption that tin species are oxidized by \( H_2O_2 \) and \( OH \), and reduced by \( H \), would lead to the prediction that

\[ G(-Sn(II)) = G(Sn(IV)) = g(H_2O_2) + \frac{g(OH) - g(H)}{2} \]

This mechanism assumes that, in a sufficiently dilute solution, the solute(s) will not interfere in whatever process or processes cause formation of the primary yield of \( H_2 \). Therefore, one should find \( G(H_2) = g(H_2) \). Solution of equation [2] for \( g(H_2) \) will show that quantity to be equal to the right-hand side of equation [3], or that

\[ G(-Sn(II)) = G(Sn(IV)) = G(H_2) = g(H_2) = 0.45 \]

with appropriate substitution of numerical values for the various primary yields, or simply for \( g(H_2) \).

Considering limiting yields, our mechanism predicts that the SnBr\(_2\) system is only slightly more complex than that described above, the complication arising from the contribution of reaction (4) to the steady-state yields. Taking reaction (4) into account, one may write

\[ G(H_2) = g(H_2) + g(H)_{(4)} \]

where \( g(H)_{(4)} \) represents the fraction of \( g(H) \) participating in reaction (4) in the steady-state condition. Similarly, one may state that

\[ G(-Sn(II)) = G(Sn(IV)) = g(H_2O_2) + \frac{g(OH) - g(H)_{(4)}}{2} \]

where \( g(H)_{(T-4)} \) signifies the net yield of reducing species i.e. the total yield of reducing species minus the amount taking part in reaction (4), since that amount causes oxidation of \( Br^- \) to \( Br \).

For \( 5 \times 10^{-3} M \) \( SnBr_2 \) in \( 1M HBr \) our experimental value for \( G(H_2) \) is 0.50. Assuming \( g(H_2) = 0.45 \), equation [5] dictates a value of \( g(H)(4) = 0.05 \). Substitution of this and other appropriate numerical equivalents in equation [6] shows it to predict, in accord with the discussion above, that \( G(-Sn(II)) = 0.50 \). Our determined value for this quantity (from Fig. 3) is 0.49, in good agreement. In our judgment, this constitutes a strong argument for the validity of our mechanism. A similar comparison for the results with \( 2M \) total \( Br^- \) concentration also shows good agreement, which augurs well for our proposal that enhancement of reaction (4) is responsible for the higher limiting yields observed with increasing bromide ion concentration. Agreement for the \( 3M \) bromide values is not as good, with tin yields being slightly high, hydrogen yields low, or perhaps a combination of both.

Thus, with respect to

a) initial yields of both hydrogen and tin(IV)

b) limiting yields of both hydrogen and tin(IV) as a function of bromide ion concentration, and

c) limiting yields of hydrogen as a function of hydrobromic acid concentration, one can consider our system to be simply a case of tin(II)'s being caught in the middle of a bromine-bromide-hydronium ion analogy to the iodine-iodide-hydronium ion system investigated by Hentz and Johnson. That is, rather than observing a buildup of molecular bromine, we find accumulation of an exactly equivalent amount of tin(IV).
This apparently logical picture of the behavior of our system fades on inspection of the $G(Sn(IV))$ values for 72-hr irradiations of $SnBr_2$ solutions which are 2- and 3M in HBr. In both instances, the 72-hr tin yields are higher by up to 0.3 G-value unit than the corresponding values of $G(H_2)$. However, for either the 2- or 3M HBr solutions, $G(Sn(IV))$ at 72 hr is evidently not a limiting yield, as can be seen from Fig. 4. It seems that $G(-Sn(II))$ values for these solutions of high HBr concentration are heading toward some lower limiting value -- a value we would presume is equal to $G(H_2)$ for the respective solutions.

We are loathe to believe that our determined values for $G(H_2)$ are seriously low, since both the accuracy and precision of our hydrogen analysis technique appear to have been very good. A slight leak in the gas sampling valve for the vapor fractometer did develop while the work with 2- and 3M HBr solutions was being done, and might have contributed to slightly low values, but so far as we could determine, our correction technique was effective. On the other hand, sources of Sn(IV) formation extraneous to our mechanism are possible. So, if only because of the ease of oxidation of tin(II) we expect larger possible errors for $G(-Sn(II))$ than for $G(H_2)$.

**Descent to Limiting Yield.** As explained above, our mechanism requires that $G(-Sn(II)) = G(H_2)$. We believe that this situation obtains for virtually all of our limiting yields. However, as Figs. 3--6 show, with decreasing time of irradiation, it is painfully obvious that agreement of tin yields with the corresponding hydrogen yields becomes progressively worse. Indeed, with reference to the values from approximately 5--25 hr, use of the word "agreement"
would seem to qualify as one of rhetoric's higher order euphemisms.

Continuing with the premise that it is the tin yields which are in error, rather than those of hydrogen, one may conceive of several possible causes of high tin yields, viz. a) reaction (4), which converts an ordinarily reducing species to an oxidizing one, is occurring; b) \( \text{H}_2\text{O}_2 \) and/or \( \text{OH} \) are oxidizing more than their usual number of equivalents of \( \text{Sn(II)} \); c) something is reacting with the reducing species before that can react with any tin species; d) something presumed not to be in the solution is present and oxidizing \( \text{Sn(II)} \) more or less directly.

With respect to possibility a), if we are to believe our hydrogen yields, we cannot invoke reaction (4) as a cause of high yields of tin for radiolyses any longer than 1 or 2 hr, since each \( \text{Br} \) produced must be accompanied by one molecule of \( \text{H}_2 \), or \( G(\text{Sn(IV)}) \) must equal \( G(\text{H}_2) \), as usual.

Possibility b) could be caused by the existence of a chain reaction, which would produce extremely high \( G(\text{-Sn(II)}) \) values (not observed) or, by analogy with the \( \text{Fe(II)} - \text{Fe(III)} \) system, by the simultaneous presence of oxygen and an organic contaminant. Considering the care taken with deaeration and water purification, this seems unlikely, but remains a possibility.

Possibility c): in our tables of rate constants, the reactant boasting the highest \( k \) \( (\text{m}^{-1}\text{sec}^{-1}) \) for reaction with \( \text{H} \) atoms is \( \text{Sn(II)} \). Its closest competitor is \( \text{O}_2 \), with a \( k \) three times smaller. Assuming both \( \text{O}_2 \) and \( \text{Sn(II)} \) to undergo bimolecular reaction with a more or less constant concentration of \( \text{H} \) atoms, a first approximation would predict a requirement for an \( \text{O}_2 \) concentration three times that of \( \text{Sn(II)} \) for equally effective competi-
tion. However, each \( O_2 \) can ultimately react with more than one \( H \) atom or other equivalent reducing species, as can Sn(III) or Sn(IV), which makes evaluation of probable reaction paths very difficult. In any case, with respect to reaction with \( H \) atoms, \( O_2 \) and Sn(II) are probably Tweedledum and Tweedledee, since the probable reaction sequence for \( O_2 \) with \( H \) is

\[
H + O_2 \rightarrow HO_2
\]

and the \( H_2O_2 \) produced is known to oxidize Sn(II). Thus, if oxygen can compete successfully with Sn(II) for \( H \) atoms, the result will be a high yield of tin, partly as a consequence of reaction (14) and partly since \( H \) atoms which would have caused reduction of tin will have been scavenged by something else, whereas if oxygen cannot so compete successfully, it will oxidize Sn(II) directly anyway, causing equivalent high tin yields. This last alternative, of course, represents possibility (d).

Looking at the discrepancy between the yields of tin (IV) and hydrogen from a slightly different angle: if the tin yields are higher than those for hydrogen gas, in order to satisfy the condition of material balance, there must exist in the solution (or at least in the radiation vessel) a reduced form of something, equivalent in amount to the difference between the observed yields of tin(IV) and hydrogen gas. If hydronium ions or water were reduced, one would expect the product to be hydrogen atoms or hydrogen gas. Either eventuality would produce a situation where \( G(Sn(IV)) = G(H_2) \); the former product would lower \( G(Sn(IV)) \) to meet \( G(H_2) \), and the latter would raise \( G(H_2) \) to the observed value for the tin yield. Obviously, this is not in agreement with our re-
suits. Proposing reduction of any of the valence states of tin would seem absurd, since that should result in reduction of tin yields to meet \( G(\text{H}_2) \). The only tin species conceivable would be a vastly greater stability for \( \text{Sn(I)} \) than seems possible, or production of \( \text{Sn}^0 \). Ten per cent reaction would produce 6 mg of tin metal, which should be visible. We did look carefully a few times, but saw nothing. Reduction of \( \text{Br}^- \) to some exotic (and stable!) species seems equally absurd. Active impurities on or in the glass of the radiation vessel characteristically decrease with continued use of the vessel. Since our irradiations of a given solution were run in random order, this cause seems unlikely.

**Added Bromide vs. Added HBr.** If the considerations discussed above are accepted as being essentially a correct, or at least acceptable, interpretation of our observed values of \( G(\text{-Sn(II)}) \) for solutions 1--3 M in \( \text{HBr} \), further contemplation of all of our results with respect to tin raises the question of why the solutions with 2- and 3 M bromide ion concentration, but 1 M in hydronium ion, did not behave in the same manner. It will be recalled that those solutions with increasing amounts of \( \text{Br}^- \) at constant \( \text{pH} \) showed tin yields which dropped rather quickly to their limiting values. As can be seen from Fig. 3, the extent of pre-oxidation (or whatever) appears to have been rather small.

The simplest explanation is that some determinate error occurred when the work with solutions of increasing \( \text{HBr} \) concentration was done, but that that error was absent in the experiments with 2 M and 3 M bromide ion concentrations. However, neither examination of our laboratory notebooks nor careful reflection has provided us with any clues in regard to what that determinate error might have been.
Assuming our technique and our materials to have been consistent, one has little choice but to treat these differences (cf. Figs. 3 and 4) as being real.

Since both the $Br^-$ concentration and the ionic strength of a $2M$ NaBr solution are presumably identical to those for a solution $2M$ in HBr, one would suspect immediately that the hydrogen ion concentration is the critical factor in the differences in behavior noted between Figs. 3 and 4. Table II shows some interesting differences in the mean ionic activity coefficients for solutions of HCl and NaCl, which should provide a good analogy with our HBr and NaBr systems.

Table II. Mean Ionic Activity Coefficients at $25^\circ C$.

<table>
<thead>
<tr>
<th>Molality</th>
<th>HCl</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.811</td>
<td>0.656</td>
</tr>
<tr>
<td>2.00</td>
<td>1.011</td>
<td>0.670</td>
</tr>
<tr>
<td>3.00</td>
<td>1.31</td>
<td>0.719</td>
</tr>
</tbody>
</table>

The pH-dependent sign and magnitude of the potential of the electrochemical cell formed by $O_2$ and $Br^-$ has been mentioned above, i.e. $Br^-$ is oxidized more easily (thermodynamically speaking) at higher acid concentrations. The greater tendency toward spuriously high tin yields observed for solutions of increasing HBr concentration would, as discussed above, correlate well with these increasingly favorable energetics for air-oxidation of bromide ions.
If oxygen or some other oxidizing contaminant was present in all (irradiated) solutions, and if techniques, etc., were consistent, why was there not air-oxidation of some Sn(II) in the solutions with 2- and 3M Br⁻ concentration? First of all, there was some "extra" oxidation of Sn(II) for those solutions, as can be seen from Fig. 3. Secondly, a hydronium-ion dependent, radio-induced (i.e., not thermal) reaction may be responsible for the small amount of Sn(IV) produced in excess of that expected on the basis of our mechanism. Thirdly, it has been reported⁴⁵ that the ease of oxidation of tin(II) decreases with increasing halide ion concentration. Indeed, increasing the chloride ion concentration to 2M is sufficient to inhibit completely the well-known oxidation of SnCl₂ by HgCl₂, supposedly because of the effect of the higher Cl⁻ concentration on the oxidation potential of the Sn(II).⁴⁵ With the usual proviso that a chloride analogy is valid for our bromide system, a decreasing reactivity of Sn(II) toward an oxidizing contaminant, with increasing bromide ion concentration would agree with our results, so long as that retarding effect could somehow be nullified by a suitable increase in hydronium ion concentration.

With respect to our second suggestion above, namely that radioinduced reactions may account for the differences in behavior under discussion here, if one assumes only a slight contamination with oxygen, the following sequence of reactions may be postulated, all of which have been proposed before:⁴³
\[ \text{Br}^- + \text{OH} \rightarrow \text{Br} + \text{OH}^- \quad (6) \]

\[ \text{H}^+ + \text{Br}^- + \text{O}_2 \rightarrow \text{Br} + \text{HO}_2 \quad (15) \]

\[ \text{H} + \text{Br} \rightarrow \text{H}^+ + \text{Br}^- \quad (16) \]

\[ \text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 \quad (17) \]

\[ \text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH} \quad (18) \]

\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad (13) \]

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (14) \]

\[ \text{Br} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{HO}_2 \quad (19) \]

These reactions may be considered to represent the competition for those reactions involving the various tin species (reactions (7--11)). The sum of reactions (6) and 13--19 above is

\[ 4\text{H} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \quad (20) \]

Thus, the \( \text{O}_2 \) consumes an equivalent amount of the reducing species \( \text{H} \), leading to higher tin yields.

Since, as discussed above, the hydronium ion concentration seems to be more critical than the bromide ion concentration, it is interesting to note the effect of changes in acidity on the above sequence. It can be seen that an increase in hydronium ion concentration will favor reactions (6) and (15) and have the reverse effect on reactions (16) and (19). Every one of these eventualities would tend to increase the formation or longevity of \( \text{Br} \) atoms, giving them more time -- or a higher probability -- of reacting with a (reduced) tin species. This would seem to lead to higher tin yields with increasing acid concentration. As soon as the small amount of oxygen contaminant was consumed, this sequence would
cease to be of importance. Although we do not profess to know what causes the difference in our results as summarized in Figs. 3 and 4, and recognize that many other reactions are probably occurring in the solution, the above explanations seem as reasonable as any to us.

**Other Experiments**

Two final experiments remain to be described and discussed. In the first of these, Sn(IV) in the form of SnBr₄ was added to a SnBr₂ solution prior to irradiation, and in the second, the stock solution of SnBr₂ was partially oxidized with bromine water before the radiolysis, so as to have a Sn(IV):Sn(II) ratio equal to that for a SnBr₂ solution which had been irradiated for 72 hr.
Experiment 1. Radiolysis with Added Sn(IV). An amount of Sn(IV) equivalent to that present after a 72-hr irradiation was added, and a 25-hr radiolysis executed on a solution of SnBr$_2$ in 1M HBr. $G(-\text{Sn(II)})$ was slightly below the value expected from Fig. 3. The experiment was repeated for a 5-hr irradiation, and this time $G(-\text{Sn(II)})$ was determined to be 1.1 — considerably below the "expected" value of 2.5. The latter result is in sharp contrast to the lack of effect of added Sn(IV) on $G(-\text{Sn(II)})$ as noted by Ansell.° Taken together, the results are puzzling to say the least. We would consider the following possible explanations.

(a) Increasing the concentration of Sn(IV) should exert a repressive effect on all reactions forming Sn(IV), and increase the rate of any reactions with Sn(IV) as a reactant. The result of these effects would be a decrease in $G(-\text{Sn(II)})$ as observed. The slightly lower-than-expected value of $G(-\text{Sn(II)})$ observed for the 25-hr irradiation could indicate that the amount of Sn(IV) produced radiolytically had apparently not changed the competitive kinetics situation set up by the already added Sn(IV).

(b) It would seem that, since we have attributed $G$-values higher than 0.50 to the presence of some (presumably oxidizing) contaminant, a full explanation of the drop in $G(-\text{Sn(II)})$ for the 5-hr irradiation should include explicit consideration of the contaminant. In line with our hypothesis that $O_2$ is the foreign species in our solutions, one could consider the effect of added Sn(IV) on the equilibrium of a thermal reaction producing Sn(IV), e.g.

$$\text{Sn(II)} + \frac{1}{2}O_2 + H^+ \rightarrow \text{Sn(IV)} + OH^- \quad (21)$$
Naturally, increasing the concentration of Sn(IV) would not change the equilibrium constant for the equation of such a reaction, but it would increase the absolute amount of Sn(II) — the only quantity measured in these experiments — and so cause lower determined values of $G(-\text{Sn(II)})$.

c) Since $G(H_2)$ was not measured in these cases, it is possible that the added Sn(IV) reacted with H atoms which would ordinarily have recombined to form $H_2$. The stable tin species produced by such reaction would be Sn(II), which could account for part of the observed decrease in $G(-\text{Sn(II)})$.

Experiment 2. Pre-Oxidation with Bromine Water. Although addition of the correct amount of Sn(IV) duplicates the Sn(IV) concentration present after a 72-hr irradiation, it does not achieve an identical situation, since the amount of Sn(II) present after a 5-hr irradiation with added Sn(IV), for example, is considerably greater than that obtaining after a 72-hr irradiation of a solution with the same initial Sn(II) concentration. That is to say, the Sn(IV):Sn(II) ratio in our solutions with the 72-hr amount of Sn(IV) added, was less than that ratio for a Sn(II) solution which had been irradiated for 72 hr, since the Sn(IV) in the latter case had been produced from Sn(II). Also, the total tin concentration was necessarily different for the two situations. For this reason, in accord with the suggestion of Amell, a solution of SnBr$_2$ was pre-oxidized with standardized bromine water, so as to have the 72-hr Sn(IV):Sn(II) ratio before irradiation commenced. This approach also provided a total tin concentration comparable to that present in our other irradiations.

Radiolysis of this solution was allowed to continue for
only 3.75 hr -- an irradiation time which would ordinarily lead to a very high value of \( G(-\text{Sn(II)}) \). Three determinations each of the concentrations of the irradiated and non-irradiated solutions gave a value of \( G(-\text{Sn(II)}) = 0.32 \pm 0.22 \). The low absorbed dose, plus our old reproducibility problems, perhaps combined to cause the large probable error. As an indication of the former source of error, with this short irradiation time, the difference in Sn(II) concentration between the irradiated and the non-irradiated solutions was equivalent to about 0.30 ml of iodine titrant. At any rate, \( G(-\text{Sn(II)}) \) was emphatically not 1.0, 1.5, 2.0, or whatever, but some value considerably lower.

For shorter irradiations at least, the effects of reducing the concentration of Sn(II) would act so as to reinforce the effects of a relatively high Sn(IV) concentration, as discussed above.

Looking at the effect of a decreased Sn(II) concentration from a broader viewpoint, the smaller number of Sn(II) ions in solution would correlate with a lower probability of reaction of Sn(II) with the other species in solution. As a result of this, one would expect recombination reactions to be more frequent. For example

\[
\begin{align*}
\text{H}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{H} \\
\text{Br} + \text{H} & \rightarrow \text{Br}^- + \text{H}^+ \\
\text{H}_2\text{O}_2 + \text{H} & \rightarrow \text{H}_2\text{O} + \text{OH} \\
\text{OH} + \text{H} & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

would be expected to occur with relatively greater frequency, leading to lower observed values of \( G(-\text{Sn(II)}) \).

Neither of these considerations, however, explains the fate of the oxidizing contaminant, which is supposedly the primary cause
of the spuriously high yields. We can only surmise that either the oxidizing contaminant was not present during this experiment because

a) techniques used in this experiment excluded oxygen completely, as they were supposed to have done for all experiments, or

b) since the solution used in this final experiment had been stored for several weeks, perhaps the oxidizing contaminant was light-sensitive or otherwise unstable, and had disappeared by some slow reaction whose effect was not seen in the other experiments --- performed with fairly fresh solution, or

c) the pre-irradiation treatment with bromine water destroyed the contaminant, leaving it in a form which would not react so as to cause high tin yields under the influence of the radiation; or that the contaminant was present during this experiment, but that it or its derivative(s) or successor(s) had been causing the "extra" oxidation of Sn(II) (or Sn(I) or Sn(III)) by some reaction which would not occur at the very low initial Sn(II) concentration used in this experiment.

In this regard, it is interesting to note that Hatch\textsuperscript{12} reported a sudden, sharp decrease in G(SnIV)) for solutions with initial Sn(II) concentrations below about $5 \times 10^{-3}$M. The drop became more severe with decreasing initial tin concentrations, down to about $6 \times 10^{-4}$M, the lower limit dictated by his analytical technique. This is the identical range of initial Sn(II) concentration obtaining in our pre-oxidation experiment. Hatch had postulated a rather large amount of oxidation by H atoms, in order to explain his high tin yields, and proposed more reducing action by the H atoms at low Sn(II) concentrations to explain the lower
oxidative yield observed with those solutions. For irradiations longer than 3 hr or so, we assume that virtually all H atoms cause reduction, so his explanation is of no use in clarifying our results. To us at least, the fate of the oxidizing contaminant -- if there be such a substance -- upon pre-irradiation treatment with bromine water, remains a mystery.

Comparison of Results with Those of Other Investigators

We believe that Boyle, Weiner, and Hochanadel's value of 0.49 for $G(-Sn(II))$ for the SnSO$_4$--H$_2$SO$_4$ system is correct, and have been able essentially to duplicate it in this laboratory. Although neither they nor we have hydrogen yields to support it, we would attribute the excess yield: 0.49 vs. 0.45 to oxidation of Sn(II) by a small fraction of the H atoms acting in conjunction with hydronium ions from the acid solution. Our hydrogen yields for the SnBr$_2$ system indicate very high initial yields of Sn(IV), as predicted by those investigators, but we believe those high yields to be due to oxidation by H atoms, not simply to a lack of back reactions or reducing reactions involving tin, as suggested by them.

Our initial tin yields are high -- extrapolating to 4.0 -- and decrease very slowly to a limiting value of 0.49 after 72 hr of irradiation at a dose rate of about $0.33 \times 10^{17}$ e.v.$^{-1}$ min$^{-1}$. Our results for SnCl$_2$ are similar, and presumably drop to a $G(-Sn(II)) = 0.49$, though after a longer irradiation than is necessary for the bromine system. So, we suggest that the apparent discrepancy between $G(-Sn(II))$ for the sulfate system and the chloride system was not real, and suspect contamination of solvent
water as the cause of the previously reported higher value of $G(-\text{Sn(II)})$ for $\text{SnCl}_2$.

With respect to our work vs. that of Amell and of Hatch with $\text{SnCl}_2$, it should be emphasized that the mechanisms deduced by both Amell and Hatch are substantially correct. That is to say, not only do those mechanisms explain their results satisfactorily but, with some important exceptions, turn out to be basically the same as our explanation.

It is interesting that Hatch's $G$-values for $\text{Sn(IV)}$ and $\text{H}_2$ are self-consistently higher than our limiting ones. Hatch postulated a reaction analogous to (4) to account for the excess of $G(\text{Sn(IV)})$ over 0.45, the difference being that he proposed a direct oxidation of $\text{Sn(II)}$ by $\text{H}$ and $\text{H}_2^+$, i.e., with no participation by $\text{Cl}^-$. This assumption necessitates an exactly equivalent increase in $G(\text{H}_2)$ which, in most cases, was observed within a few percent. In fact, although it was not so stated, all Hatch was saying in developing his calculations of "theoretical" tin yields, is that $G(\text{Sn(IV)}) = G(\text{H}_2)$, an observation which we have shown also to be true for our (limiting) results. Thus, his comparisons of $G(\text{Sn(IV)})$ observed vs. $G(\text{Sn(IV)})$ calculated are really tabulations of $G(\text{Sn(IV)})$ observed vs. $G(\text{H}_2)$ observed. The agreement between his tin and hydrogen yields leads us to believe that Hatch's higher $G$-values really were the result of a constant radiolinduced oxidation of $\text{Sn(II)}$ or $\text{Cl}^-$ by $\text{H}$ atoms. This contrasts with our experiments, which correlate well with a very high initial yield of $\text{Sn(IV)}$, whose effects linger for many hours of irradiation, causing apparent high tin yields until swamped out by the large amounts of $\text{Sn(IV)}$ produced by the "ordinary" radiolytic processes.
(with $G = 0.45$) at high absorbed doses. Why both Hatch and Amell continued to find $G(-\text{Sn(II)}) = 1.26$ at doses where we, Hentz and Johnson, and Boyle, Weiner and Hochanadel observed oxidative yields within 0.05 $G$-value unit of the theoretically expected 0.45, we are at a loss to explain. We can only guess that the presence of some — presumably trace — contaminant favored oxidative over reductive reactions by a certain fraction of the $H$ atoms produced by the radiolytic processes.

Recent experiments indicate that -- even considering only primary processes -- there is very likely more than one precursor of molecular hydrogen. This implies the existence of more than one kind of "$H$ atom." Differing reactivities of a trace contaminant toward the different "$H$ atoms" could explain why some of Hatch's "$H$ atoms" underwent oxidation and others reduction.

Note: Considerations similar to these can be used to provide a purely speculative -- but intriguing -- alternative explanation of our own results, viz. that the "extra" $H_2$ produced in reaction (4) is, in fact, different from that produced by the primary processes, whatever they may be. If the "extra $H_2$" were extremely reactive toward the oxidizing species in the solution, it would very soon disappear, leaving one to observe only the results of the primary processes producing $H_2$, which had been occurring all the while. This would interfere with the ordinary processes producing $\text{Sn(IV)}$ at a rate equal to $G = 0.45$, resulting in a lowering of $G(-\text{Sn(II)})$, but the extra $\text{Sn(IV)}$ would act to support $G(-\text{Sn(II)})$ at some value higher than 0.45. Once the "extra $H_2$" had all reacted, $H_2$ and $\text{Sn(IV)}$ would be produced at a rate equal to $G = 0.45$ and the "extra $\text{Sn(IV)}$" would cause high observed values of $G(-\text{Sn(II)})$, but be of
decreasing importance with longer and longer irradiations, as has been discussed before.

The difference between Hatch's results and ours becomes all the more mysterious if one makes the logical (?) presumption that his (higher) results were caused by the presence of organic impurities in his solvent water supply. We trust that this will not be construed as simply personal prejudice since we did use triply distilled water, whereas he makes no mention of any special precautions taken with water purification. Organic impurities in aqueous solvents have caused trouble with radiolyses before,\textsuperscript{14} and are the chief reason for insistence that such water be distilled at least once from a strong oxidizing agent. What is strange is this: these contaminants have been found to cause lowered (oxidized) product yields in deaerated solutions, and higher yields in aerated solutions!

Probably the most thoroughly studied system in this class is Fe(II) in 0.8M H\textsubscript{2}SO\textsubscript{4}.\textsuperscript{47} It is generally assumed that decreased (oxidative) yields in such solutions result from reaction of OH radicals with organic molecules

\[ \text{OH} + \text{R} \rightarrow \text{H}_2\text{O} + \text{R} \quad (25) \]

Apparently, the species R will reduce Fe(III) rather than oxidize Fe(II). Thus, an oxidizing species has been converted to a reducing one. In the presence of O\textsubscript{2}, however

\[ \text{R} + \text{O}_2 \rightarrow \text{RO}_2 \rightarrow \text{HO}_2 \text{ or } \text{H}_2\text{O}_2. \quad (26) \]

Here, an OH which could oxidize only one Fe(II) has been converted to a species which can oxidize more than one, leading to spuriously high yields.

If this analogy were valid, it would be our yields which
would be suspect, since we are concerned with deaerated solutions. Yet we agree closely with Hochanadel on values for the SnSO₄ radiolysis, and he used water distilled from both acid dichromate and alkaline permanganate (followed by a third distillation) in an all-silica system. Hatch does not mention having done any radiolyses of SnSO₄. Our H₂ yields for an acid-bromide system matched the accepted literature G-value closely. Hatch did not perform such an experiment, so no comparison can be made.

If an organic compound (or compounds) is the culprit, then species R must be capable of causing oxidation of Sn(II) but not Fe(II) -- this since Hatch obtained accepted values for radiolyses of Fe(II) solutions made with the same water as used for his SnCl₂ solutions. As a first approximation (neglecting concentration corrections introduced by the Nernst equation) species R would be expected to have an oxidation potential between those of iron(II) and tin(II). To add to the fun, all H atoms apparently cause oxidation of Fe(II), as evidenced by G(Fe(III))= 8.2 in deaerated solution. But Fe(II) has a higher oxidation potential than Sn(II)!

With respect to such suspected contamination of water or solutions by organic matter, we concede readily that the atmosphere in the now chemistry building where our work was done is almost certainly dirtier than that in James Hall, where Hatch performed his experiments. We have never before experienced such extreme difficulty in keeping glassware clean. In our judgment, a forced-air circulation system, combined with more or less constant heavy construction activity in the immediate vicinity of the new chemistry building, is the chief cause of this problem. Let us
hasten to add that all glassware was subjected to the cleaning procedure described in the experimental section as soon as water or an aqueous solution was observed to have any difficulty wetting the glass, however frequent or onerous that task might have been (and it was both). Significantly, we think, there was no detectable difference in results observed before and after one of these cleanings.

On the other hand, one can make a case for disregarding any explanation based on the effect of traces of organic matter. In the FeSO$_4$ system at least, the presence of small concentrations (1m$^4$) of Cl$^-$ is sufficient essentially to eliminate the effects of small amounts of organic molecules. Here, presumably

$$\text{OH} + \text{Cl}^- \rightarrow \text{Cl} + \text{OH}^-$$ (27)

occurs, and the chlorine atom reacts much more quickly with Fe(II) than with organic molecules, thus preserving a "normal" situation with respect to reactions of the OH group. In the Fricke dosimeter as ordinarily used, the solution is made $10^{-3}M$ in chloride ion for this very reason. If extrapolation from the Fe(II) to the Sn(II) system is valid, consideration of 1) the more-than-adequate chloride ion concentration in both Hatch's solutions and ours, and 2) the fairly high specific resistance of the James Hall water when we measured it (cf. SnCl$_2$ results above) would seem to leave one without a curse in his quiver, as someone has said. That is, 1) and 2) would seem to militate against organic and inorganic contamination respectively.

Whose water -- if anyone's -- was contaminated with organic molecules may never be known. Whether that knowledge would be of any consequence, considering the high chloride ion concentrations,
is open to speculation. With respect to possible ionic impurities, on the basis of our conductivity measurements we are confident that our water was the purer. So, oddly enough, we prefer our own (limiting) results for the SnCl$_2$ system, even though we cannot pinpoint the exact cause of the discrepancy between our results and those of other investigators.
BIBLIOGRAPHY


3. Ibid., p 100.


33. Ibid., p 41.


46. R.C. Hatch, op.cit., p 63.

APPENDIX
Sample Calculation of \( G(\text{-Sn(II)}) \)

Data for Sample A-II-8-1

Initial concn of \( \text{SnBr}_2 \) : \( 4.65 \times 10^{-3} \text{ M} \)
Concn of \( I_2 \) titrant : \( 2.76 \times 10^{-3} \text{ M} \)
Concn of \( \text{HBr} \) : \( 1.07 \text{ M} \)
Size of aliquot : \( 25.00 \text{ ml} \)
Density of soln : \( 1.057 \text{ g ml}^{-1} \)
Time of irradiation : \( 66.38 \text{ hr} \)
Dose rate : \( 3.15 \times 10^{16} \text{ e.v. g}^{-1} \text{ min}^{-1} \)

Titrant required for non-irradiated soln: \( 51.87 \text{ ml} \)
Titrant required for irradiated soln : \( 42.02 \text{ ml} \)
Titrant equivalent to \( \text{Sn(II)} \) oxidized : \( 9.85 \text{ ml} \)

\[
\begin{align*}
G(\text{-Sn(II)}) &= \frac{(9.85 \text{ ml})(2.76 \times 10^{-3} \text{ M})(6.023 \times 10^{23} \text{ ion mol}^{-1})}{(66.38 \text{ hr})(60 \text{ min hr}^{-1})(25.00 \text{ ml})(1.057 \text{ g ml}^{-1})} \\
&\times \frac{(10^{-3} \text{ ml}^{-1}) \times 100}{(3.15 \times 10^{16} \text{ e.v. g}^{-1} \text{ min}^{-1})} \\
&= 0.50 \text{ ion/100 e.v.}
\end{align*}
\]
Sample Calculation of \( G(H_2) \)

Data for Sample B-II-1-1:

- Initial concn of SnBr\(_2\) : \( 4.92 \times 10^{-3} \) M
- Concn of HBr : 1.0 M
- Sample size : 5.00 ml
- Density of solution : 1.060 g ml\(^{-1}\)
- Time of irradiation : 23.95 hr
- Dose rate : \( 2.59 \times 10^{16} \) e.v. g\(^{-1}\)min\(^{-1}\)
- Peak height : 52.1 cu\(^a\)
- Half-width : 6.3 mm
- Recorder attenuation (1 mv full scale) : 32

Response Units (RU) = Peak height (mm) x Half-width x Attenuation

\[
= (52.1 \text{ cu})(2.54 \text{ mm cu}\(^{-1}\))(6.3 \text{ mm})(32)
= 26678.
\]

From Fig. 1, 26678 RU \( \equiv \) 1.64 \( \mu \) mole of \( H_2 \)

\[
G(H_2) = \frac{(1.64 \mu \text{ mol})(6.023 \times 10^{23} \text{ mol'les mol}^{-1})}{(23.95 \text{ hr})(60 \text{ min hr}^{-1})(5.00 \text{ ml})} \times \\
\frac{(10^{-6} \text{ mol mol}^{-1}) \times 100}{(1.060 \text{ g ml}^{-1})(2.59 \times 10^{16} \text{ e.v. g}^{-1}\text{min}^{-1})}
= 0.50 \text{ mol'le/100 e.v.}
\]

\(^{a}\) cu = chart units; 100 cu = full scale deflection on recorder.