

787. *The Chemical Action of Ionising Radiations in Solution. Part XXIII.* The Action of ^{60}Co -Gamma-rays on Aqueous Solutions of Ethanol in the Liquid and the Frozen State.*

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The action of ^{60}Co -gamma-rays on deaerated aqueous solutions of ethanol at different concentrations (from 10^{-3} — 5M) was studied in the liquid and in the frozen state from 20° to -196° . The products were acetaldehyde, butane-2,3-diol, hydrogen peroxide, and molecular hydrogen. The dependence of the yields of these products on solute concentration, physical state, and temperature has been investigated in detail. A mechanism is put forward to account for the experimental results, with particular reference to the reactions in the frozen solutions.

THE chemical effects of ionising radiations in dilute aqueous solutions yield reactive species such as H and OH¹ and, to a smaller extent, so-called "molecular" products H₂ and H₂O₂ from water.² The effect of gamma-radiation on ice, in the presence and in the absence of oxygen, was recently investigated by Ghormley and Stewart.³ They found the yields of H₂ and H₂O₂ in oxygenated systems to increase with increase in temperature, e.g., $G(\text{H}_2\text{O}_2)$ increased from 0.2 to 0.7 and $G(\text{H}_2)$ from 0.1 to 0.25 between -200 and -15° . In earlier work on the effect of X-rays, γ -rays, and α -particles, the yields of H₂ and H₂O₂ at different temperatures of irradiation^{4a} were found in all cases to decrease appreciably on going from water to ice, and generally to decrease with a decrease in temperature. Recent work^{4b} on the tritium β -ray irradiation of water vapour has shown that the total yield from its decomposition is considerably greater than from the liquid.

It was thought, therefore, that irradiation of frozen aqueous solutions of an organic solute which is a good acceptor for the radiation-produced reactive species formed from the water, might be of interest particularly with regard to the extent of the total decomposition of water at various low temperatures. Ethanol was chosen as solute, as the radiation chemistry of its aqueous solutions has been investigated previously.⁵

At room temperature in absence of oxygen it gives mainly acetaldehyde and butane-2,3-diol; in presence of oxygen, glycol was not formed. We investigated the yields of the radiolysis products from -196° to 20° , and the dependence on the ethanol concentration.

RESULTS

Unless otherwise stated, the irradiations of aqueous ethanol were carried out in 0.1N-sulphuric acid *in vacuo*. The products from deaerated ethanol solutions were acetaldehyde, butane-2,3-diol, hydrogen peroxide and hydrogen. The diol, previously found in the liquid systems,

* Part XXII, *J.*, 1958, 2467.

¹ Weiss, *Nature*, 1944, **153**, 748.

² Allen, *Ann. Rev. Phys. Chem.*, 1952, **3**, 57.

³ Ghormley and Stewart, *J. Amer. Chem. Soc.*, 1956, **78**, 2934.

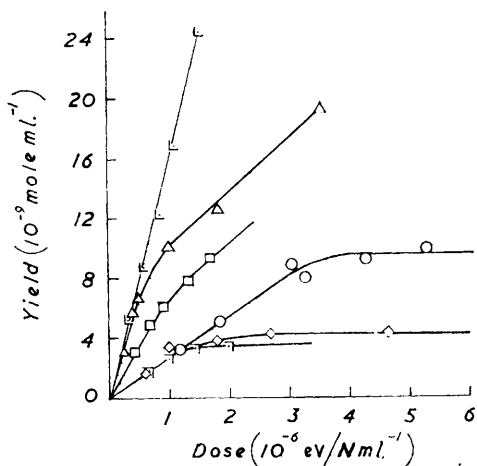
⁴ (a) Bonet-Maury and Lefort, *J. chim. Phys.*, 1950, **47**, 179; Lefort, in "Actions Chimiques et Biologiques des Radiations," Part II, Ed. M. Haissinsky, Masson et Cie, Paris, 1955, p. 203; (b) Firestone, *J. Amer. Chem. Soc.*, 1957, **79**, 5593.

⁵ Jayson, Scholes, and Weiss, *J.*, 1957, 1358.

is also formed in the frozen solutions, but no quantitative measurements were made on the latter.

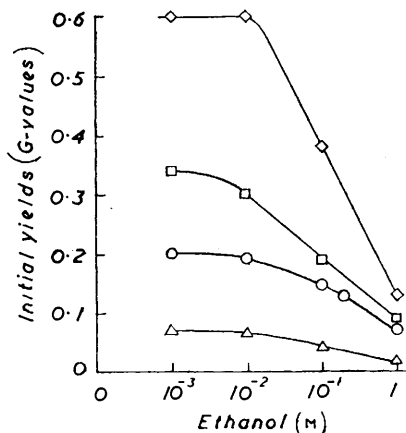
The lowest practicable doses were used to determine the *initial* yields. Fig. 1 shows several yield-dose plots for the formation of acetaldehyde from frozen ethanol solutions at -78° in

FIG. 1. Yield-dose curves for the formation of acetaldehyde in the irradiation of deaerated aqueous solutions of ethanol (pH = 1.2) with ^{60}Co -gamma-rays at -78° , at different solute concentrations.



□, 10^{-3}M ; ◇, 10^{-2}M ; ○, 10^{-1}M ; □, $5 \times 10^{-1}\text{M}$; △, 1M; ⊠, 5M-ethanol.

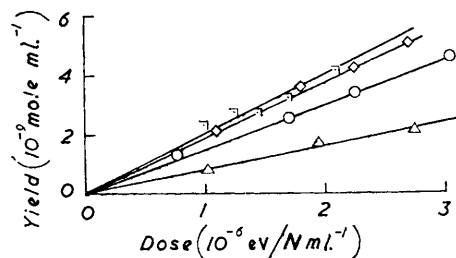
FIG. 3. Dependence of the initial yields of hydrogen peroxide on the concentration of ethanol in deaerated aqueous solutions irradiated with ^{60}Co -gamma-rays at different temperatures (pH = 1.2).



◇, 18° and 2° ; □, -10° ; ○, -78° ; △, -196° .

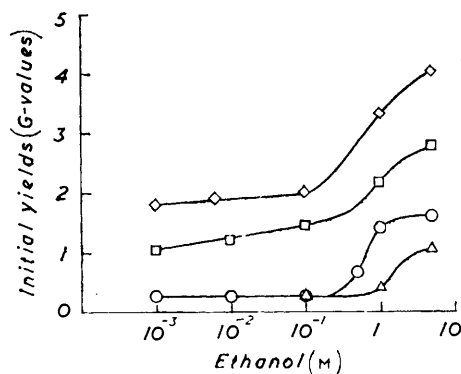
10^{-3}M — 5.0M -ethanol. Fig. 2 shows similar yield-dose plots for the simultaneous formation of hydrogen peroxide. Fig. 1 shows that the *initial* yields of acetaldehyde are the same from 10^{-3} to 10^{-1}M -ethanol. Above 10^{-1}M -ethanol the yield of acetaldehyde increases with increasing solute concentration. On the other hand, the yields of H_2O_2 decrease with increase in solute concentration in the range of 10^{-3} — 1.0M -ethanol (Fig. 2).

FIG. 2. Yield-dose curves for the formation of hydrogen peroxide in the irradiation of deaerated aqueous solutions of ethanol (pH = 1.2) with ^{60}Co -gamma-rays at -78° at different solute concentrations.



□, 10^{-3}M ; ◇, 10^{-2}M ; ○, 10^{-1}M ; △, 1M-ethanol.

FIG. 4. Dependence of the initial yields of acetaldehyde on the concentration of ethanol in deaerated aqueous solutions irradiated with ^{60}Co -gamma-rays at different temperatures (pH = 1.2).



◇, 18° and 2° ; □, -10° ; ○, -78° ; △, -196° .

FIG. 5. Temperature-dependence of the initial yields of hydrogen peroxide in deaerated aqueous solutions of ethanol irradiated with ^{60}Co -gamma-rays (pH = 1.2).

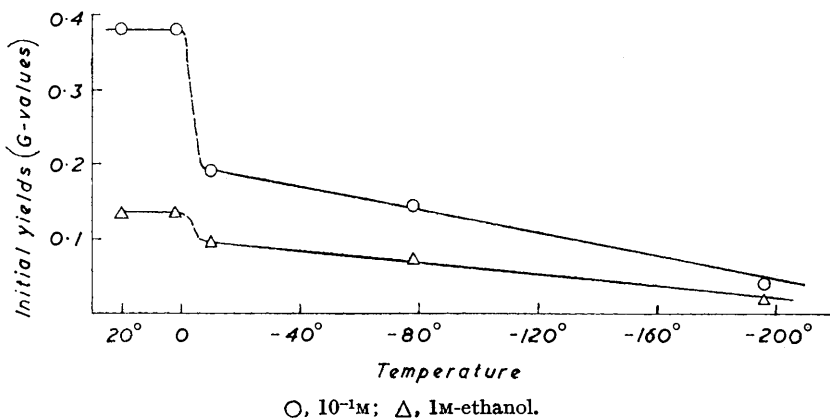


FIG. 6. Temperature-dependence of the initial yields of acetaldehyde in deaerated aqueous solutions of ethanol irradiated with ^{60}Co -gamma-rays (pH = 1.2).

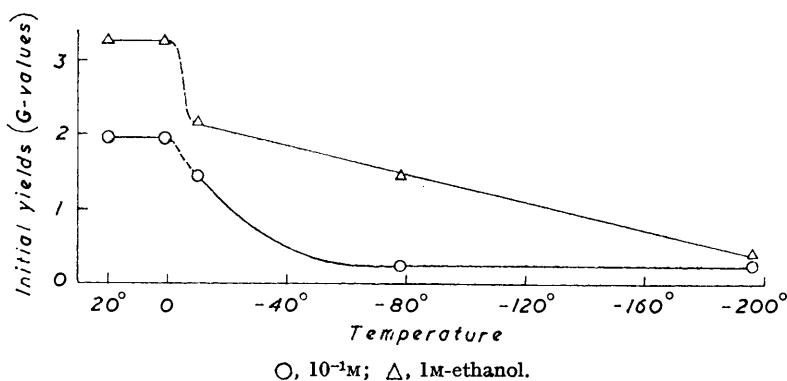


FIG. 7. Temperature-dependence of the initial yields of hydrogen in deaerated solutions of ethanol irradiated with ^{60}Co -gamma-rays (pH = 1.2).

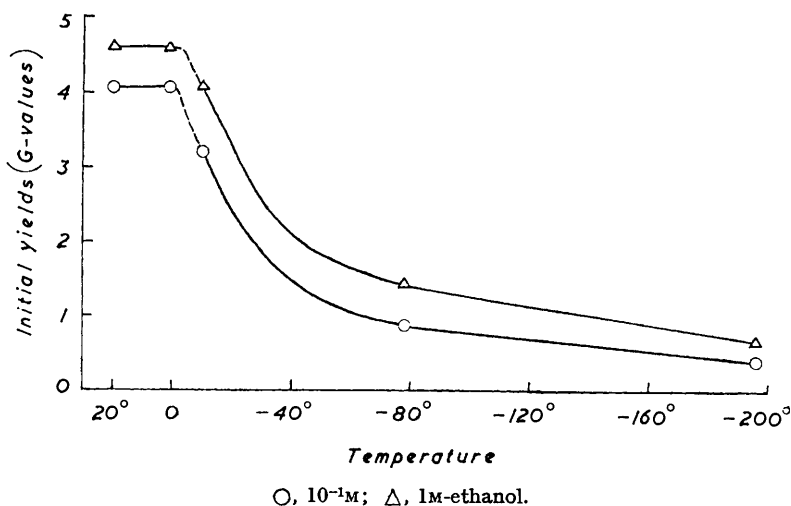


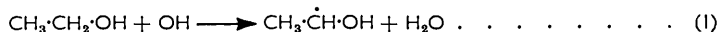
Fig. 3 shows the variation of the *initial* yields of hydrogen peroxide with solute concentration in 10^{-3} – $1.0M$ -ethanol and their dependence on temperature. Measurements were carried out at 20° and 2° and in the frozen state at -10° , -78° , and -196° . The yields of H_2O_2 decrease (i) with increase in solute concentration, (ii) in going from the liquid to the solid phase, and (iii) with decrease in temperature. Initial yields were all derived from yield-dose curves. The yield of hydrogen peroxide obtained on irradiation of deaerated dilute ethanol solutions at room temperature (20°) was $G = 0.6$.

The dependence of the initial yields of acetaldehyde in the range 10^{-3} – $5.0M$ -ethanol is given in Fig. 4, which also shows their dependence on temperature and state between 20° and -196° . It is noteworthy that at any one temperature there is only a slight concentration-dependence of the yield of acetaldehyde in the region 10^{-3} – $10^{-1}M$ -ethanol: above $10^{-1}M$ the yields of acetaldehyde increase rapidly with increase in solute concentration, this increase taking place in the liquid as well as in the frozen solutions down to -196° . Fig. 5 shows the temperature-dependence of the yields of hydrogen peroxide in the irradiation of deaerated $0.1N$ -sulphuric acid solutions of $10^{-1}M$ - and $1.0M$ -ethanol. The abrupt decrease in the yields between the liquid and the frozen state, and particularly the almost linear decrease of hydrogen peroxide with decrease in temperature from -10° to -196° , is notable. Figs. 6 and 7 show the temperature-dependence of the yields of acetaldehyde and hydrogen, respectively, from irradiations of 10^{-1} and $1.0M$ -ethanol solutions.

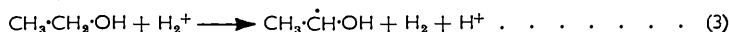
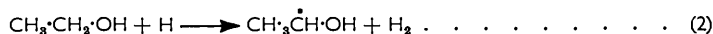
DISCUSSION

The physical processes following absorption of ionising radiation consist of excitations and ionisations. The formation of the "molecular" products H_2 and H_2O_2 is probably due to molecular interactions in the regions of dense energy release within the "clusters." Outside the "clusters" the excitations and ionisations will lead to H atoms and OH radicals which may react with any solute present. For present purposes, the various suggested species allied to H or OH radicals will be ignored. At sufficiently high solute concentrations, it is to be expected that the solute will compete with the interaction of the active species within the "clusters." The results in Fig. 3 indicate that the yields of "molecular" hydrogen peroxide obtained from irradiation of deaerated solutions of ethanol decrease with increase in solute concentration. The same effect was observed over the range from 2° to -196° .

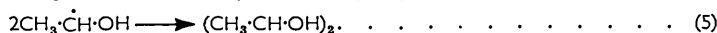
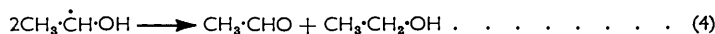
The reaction of OH radicals with ethanol in aqueous solution is generally assumed to result in a dehydrogenation at the α -carbon atom:



Hydrogen atoms, in air-free acidified solutions, dehydrogenate organic solutes at the α -carbon atom:



The formation of acetaldehyde and of butane-2,3-diol can be accounted for as follows:



The question now arises as to whether the interpretation of the radiation-induced chemical effects in frozen systems involve the same reactive species and chemical reactions as have been assumed for the liquid phase.

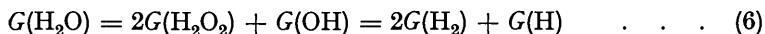
Although lowering of the temperature may not alter very radically the primary radiation processes,⁶ it is bound to affect the subsequent chemical reactions. In general, it may be difficult to give a straightforward interpretation of the radiation-induced reactions when the system is irradiated in the frozen state because, owing to the greatly reduced mobility

⁶ Livingston, Zeldes, and Taylor, *Discuss. Faraday Soc.*, 1955, **19**, 166.

of the reactive intermediates and of all the other reactants in the solid state, most of the reactions subsequent to irradiation probably take place during the "thawing" and not in the frozen state at the lowest temperature during irradiation.

However, in a comparison of the liquid and solid systems, several other factors may also have to be taken into account, *e.g.*, the structure of the frozen solid at different temperatures and excitation and/or electron transfers in the solid state.

The above results show that the primary chemical processes are apparently considerably shortened as seen from a comparison of ice at -10° and water at 2° , and that the radiolysis is further reduced with decrease in temperature between -10° and -196° . The total decomposition of the water molecules can be calculated from the stoichiometric relation:



Taking the yield of "molecular" hydrogen to be the yield of hydrogen found on irradiation of rapidly frozen oxygen-saturated water³ and assuming that the yield of hydrogen found on irradiation of aqueous ethanol solutions (Fig. 7) to be the sum of the "molecular" hydrogen plus that formed by the dehydrogenation process [reactions (2) and (3)], one can calculate $G(-\text{H}_2\text{O})$ from eqn. (6). The result is shown in columns 5 and 6 of Table 1.

TABLE 1. *G-Values for hydrogen and total water decomposition in frozen and liquid ethanol-water solutions and comparison with water.*

Temp.	Aqueous ethanol				Water $G(\text{H}_2)$
	EtOH = 0.1M		EtOH = 1.0M		
	$G(\text{H}_2)$	$G(-\text{H}_2\text{O})$	$G(\text{H}_2)$	$G(-\text{H}_2\text{O})$	
-200°	0.40	0.50	0.68	0.78	0.10 ^a
-78	0.88	1.03	1.68	1.83	0.15 ^a
-10	3.10	3.35	4.08	4.33	0.25 ^a
20	4.05	4.50	4.60	5.05	0.45 ^b

^a According to Ghormley and Stewart (ref. 3). ^b Schwarz, Losee, and Allen, *J. Amer. Chem. Soc.*, 1954, **76**, 4693.

This assumes further that for this purpose one can treat ice in the same way as water, ignoring the changes in crystalline structure and composition due to changes in temperature and solute concentration.

The yield of acetaldehyde obtained on irradiation of deaerated ethanol solutions decreases with decrease in temperature from 0° to -196° (Fig. 4). It is, however, almost independent of solute concentration in the range 10^{-3} – 10^{-1} M-ethanol. This contrasts with the results obtained on the yield of acetaldehyde in the irradiation of oxygenated aqueous solutions of ethanol with X-rays at room temperature.⁵

At any one concentration of ethanol the yield of "molecular" H_2O_2 decreases with decrease in temperature below 0° (Fig. 3). Fig. 5 shows the "sudden" decrease in the yield of "molecular" hydrogen peroxide at about 0° in the irradiation of deaerated solutions of 10^{-1} – 1.0 M-ethanol. In addition, it indicates the almost linear decrease in the yield of hydrogen peroxide between -10° and -196° . The above data suggest that (i) the formation of "molecular" hydrogen peroxide dependent upon the diffusion and/or mobility of some reactive intermediates and (ii) the chemical reaction between these reactive species may require some activation energy. However, in the liquid phase, the yields of acetaldehyde and of hydrogen peroxide obtained on irradiation of nitrogen-saturated solutions of ethanol at 90° were the same as those obtained at 20° and at 2° .⁷

Above 10^{-1} M-ethanol the yield of acetaldehyde increases sharply with increase in the solute concentration. This increase takes place in liquid solutions irradiated at room temperature, as well as in the frozen solutions down to -196° . Table 2 gives data on the concentration-dependence of the initial yields of acetaldehyde formed on irradiation of

⁷ Nixon and Weiss, unpublished results.

deaerated ethanol solutions at different temperatures. No correction has been made for the absorption of radiation by the solute at the higher ethanol concentration. The relative increase in the yields of acetaldehyde with increasing solute concentration in 1–15M-ethanol is greater for the frozen solutions at or below -78° than at room temperature (see Table 2, where yields for pure alcohol are also given).

TABLE 2. *Irradiation of aqueous ethanol with ^{60}Co -gamma-rays in the liquid and the frozen state. Dependence of the initial yields of acetaldehyde (G ; molecules/100 ev) on the concentration of ethanol at different temperatures in the presence of 0.1N- H_2SO_4 . Dose rate 5×10^{-8} (ev/N) ml. $^{-1}$ min. $^{-1}$.*

Ethanol (M)...		10^{-3}	10^{-2}	10^{-1}	1.0	5.0	7.5	15.0	pure
Liquid	2° and 20°	1.79	1.90	1.95	3.27	4.00	11.50	21.60	3.14
Frozen	-10°	1.10	1.20	1.45	2.16	2.75	—	—	—
	-78°	0.26	0.25	0.26	1.43	1.60	—	9.50	—
	-196°	0.27	0.27	0.27	0.40	1.05	—	6.00	3.60

The yields of acetaldehyde formed in the irradiation of ethanol solutions above 10^1M at room temperature, cannot be explained on the basis of the number of free radicals known to be formed is the ^{60}Co -gamma-ray radiolysis of acidified aqueous solutions, *viz.*, $G_{\text{H}} = 3.7$; $G_{\text{OH}} = 2.84$. Table 1 shows that in 1.0M-ethanol $G(-\text{H}_2\text{O}) = 5.05$, compared with $G(-\text{H}_2\text{O}) = 4.5$ in 10^{-1}M -ethanol.

The observed increase in the yields of the products with increasing solute concentration could be explained if one assumes (i) a further increase in the number of reactive species that become available at the higher solute concentrations, *e.g.*, by an inhibition of the back reaction $\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$, or (ii) that propagation reactions of a chain type are initiated by unstable reactive organic intermediates formed on irradiation. Thus in the irradiation of solutions above 5.0M-ethanol at room temperature (Table 2) the yields of acetaldehyde can no longer be explained on the basis of assumption (i) and one must assume a chain reaction to take place. It was also found that the yields of oxidation product at higher solute concentrations were inversely proportional to the dose rate of the radiation. However, the suggested propagation reactions initiated by the radiation-induced species at high ethanol concentrations occur in aqueous systems only, since the yields of the oxidation products formed in the gamma-ray irradiation of pure air-free ethanol are much smaller (Table 2).

A similar effect was observed on X -irradiation of 2-chloroethanol;⁸ the yields of hydrogen produced on irradiation of deaerated aqueous solutions at pH 1.2 increased in solute concentration over the whole range from 10^{-3}M to 3.0M-chloroethanol. Above 1.0M, in particular, the yield of hydrogen increased sharply to $G(\text{H}_2) = 6.2$ at a solute concentration of 3.0M, but the yields of product obtained on irradiation of pure deaerated 2-chloroethanol were considerably less.

The relative increase in the yields of acetaldehyde at above 1M-ethanol is greater at -196° than at -78° or room temperature. Up to 5.0M-ethanol the increase in the products could be accounted for on the basis of a decrease in the back reaction. However, above 5.0M-ethanol the yields are so great that they cannot be a result of simple radical-solute reactions.

EXPERIMENTAL

Technique.—Solutions were irradiated with gamma-rays from a 500-Curie ^{60}Co source. The apparatus was similar to that described by Ghormley and Hochanadel.⁹ About 40 ml. of solution in a cylindrical Pyrex vessel was placed inside a wide-neck Dewar flask, and fixed into position in the Co-source.

Doses were measured by means of the ferrous sulphate dosimeter, with a G -value of 15.5 (molecules of Fe^{2+} oxidised by 100 ev). The dose rate, measured in 0.1N-sulphuric acid solutions, was 5×10^{-8} ev/N ml. $^{-1}$ min. $^{-1}$.

⁸ Hayon and Weiss, unpublished results.

⁹ Ghormley and Hochanadel, *Rev. Sci. Instr.*, 1951, **22**, 473.

Solutions were prepared in triply-distilled water, *i.e.*, ordinary distilled water redistilled from alkaline permanganate and then from sulphuric acid. "AnalaR" ethanol was used. The irradiation vessels were cleaned with "Teepol," rinsed several times, and then washed with nitric-sulphuric acid cleaning mixture. The vessels were subsequently rinsed several times with distilled water followed by triply-distilled water.

Evacuation down to 10^{-3} mm. was by a mercury diffusion pump backed by a two-stage oil-pump.

The temperatures of 2° , -10° , -78° , and -196° were obtained by using ice, ammonium nitrate freezing mixture, Drikold-methanol freezing mixture, and liquid nitrogen respectively. After irradiation the frozen solutions were brought to room temperature by immersing the vessels in a bath through which passed a continuous flow of tap water.

Determination of Acetaldehyde.—This was based on Friedman and Haugen's method as modified by Johnson and Scholes¹⁰ using 2,4-dinitrophenylhydrazine.

Determination of Hydrogen Peroxide.—Eisenburg's method,¹¹ using the titanium sulphate reagent, was here not sensitive enough to measure the small yields of hydrogen peroxide formed on irradiation. Instead, that of Egerton *et al.*¹² was used which is based on the oxidation of ferrous thiocyanate which was about ten times more sensitive. The red ferric thiocyanate formed was measured colorimetrically at $450\text{ m}\mu$ on a "Unicam" spectrophotometer (SP.500). Calibration was carried out simultaneously by use of a hydrogen peroxide solution standardised with titanium sulphate reagent. At ethanol concentrations above 10^{-1}M , the thiocyanate method gave high values and a correction was applied.

Gas Analysis.—The gas formed on irradiation was pumped from the vessel, by means of a Töpler pump, through a trap containing liquid oxygen. The volume of gas was measured on a semimicro-burette, and collected for analysis by mass spectrometry.

We thank the North of England Council of the British Empire Cancer Campaign and the Rockefeller Foundation for financial support.

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[Received, June 9th, 1959.]

¹⁰ Johnson and Scholes, *Analyst*, 1954, **79**, 217.

¹¹ Eisenberg, *Ind. Eng. Chem. Anal.*, 1943, **15**, 327.

¹² Egerton, Everett, Minkoff, Rudrakanchana, and Salooja, *Analyt. Chim. Acta*, 1954, **10**, 422.