What is likely a more serious uncertainty in the calculation of surface area arises from the assumptions regarding $\sigma_{Kr}$. The conventional device for assigning a cross-section to an adsorbed molecule, X, is to compare the value of $N_m$ obtained with X to the value obtained with nitrogen on the sample, obtaining the ratio $\sigma_X/\sigma_{N_2}$.[24] It is then assumed that $\sigma_{N_2}$ is approximately the same on all adsorbents, the best value—based on both experimental and theoretical grounds—being 15.4 Å.² at 78°K.[24] $\sigma_{Kr}/\sigma_{N_2}$ on a variety of adsorbents have been measured by Beebe, Beckwith and Honig[10] and by Davis, DeWitt and Emmett,[25] the values obtained varying from 1.09 to 1.33 depending on the adsorbent. To obtain a more definitive value for our work, an experiment was performed in which germanium was ground with mortar and pestle to give a specific area of 14,000 cm.² per gram. Both krypton and nitrogen isotherms were derived for a 30-gram sample by employing the adaptor illustrated in Fig. 1-III. The mercury manometer, constructed of 4 mm. tubing and backed with a mirrored meter stick, was employed for metering the gases in both cases, and for measuring equilibrium nitrogen pressures; the thermistor was used for equilibrium krypton pressures.

The results are given in Table III. It will be noted first that the value of the B.E.T. constant, $C$, obtained on the air-treated surfaces is less than half the value observed in the previous experiment when oxygen was sorbed from an atmosphere containing low pressures of pure oxygen, the sorption being deliberately limited to a monolayer. There is evidence however, that not much more than a monolayer of oxygen is chemisorbed from air in the 8 hours required to prepare the sample.[2] The change in $C$ is apparently due to a more subtle transformation of the surfaces which will be studied further. It will be assumed here, as above, that $\sigma_{Kr}$ is unaffected.

TABLE III

COMPARISON OF KRYPTON AND NITROGEN ADSORPTION ON AIR-OXIDIZED GERMANIUM SURFACES; 43.2 m.², 77.8°K.

| A. | Slope (mol.⁻¹ × 10²³) | Intercept (mol.⁻¹ × 10²³) | $N_m$ (mol. × 10⁻¹⁸) | $C$ |
|---|---|---|---|---|
| Nitrogen | 348.8 ± 1.2 | 8.03 ± 0.19 | 280.5 ± 1.2 | 44.4 ± 1.5 |
| Krypton | 438.9 ± 3.3 | 10.67 ± 0.45 | 222.5 ± 1.7 | 41.1 ± 2.0 |

$$\frac{\sigma_{Kr}}{\sigma_{N_2}} = \frac{(N_m)_{N_2}}{(N_m)_{Kr}} = 1.261 \pm 0.009$$

| B. Source | Sample | $\sigma_{Kr}/\sigma_{N_2}$ |
|---|---|---|
| This work | Surface-oxidized germanium | 1.261 ± 0.009 |
| Beebe, Beckwith and Honig[10] | $CaCO_3$ | 1.09–1.20 |
| | $TiO_2$ | 1.20 |
| | Porous glass | 1.33 |
| Davis, DeWitt and Emmett[25] | 6 Metals and oxides | 1.28 |

Using our value of $\sigma_{Kr}/\sigma_{N_2}$, one obtains $\sigma_{Kr}$ = 19.4 ± 0.2 Å.² This value is subject to an uncertainty—probably less than a few per cent.—in the value used for $\sigma_{N_2}$. It is hoped that a yet more significant value of $\sigma_{Kr}$ will be obtained by an absolute method on which work is now in progress.

**Acknowledgments.**—The technical assistance of Miss Alice L. Carney and the many helpful suggestions of Mr. James A. Kafalas are gratefully acknowledged.

LEXINGTON, MASS.

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[24] H. K. Livingston, *J. Colloid Sci.*, **4**, 447 (1949).

[25] R. T. Davis, J. W. DeWitt and P. H. Emmett, *J. Phys. Colloid Chem.*, **51**, 1232 (1947).

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

# Effects of $\gamma$-Radiation on Ice[1]

BY J. A. GHORMLEY AND A. C. STEWART

RECEIVED FEBRUARY 1, 1956

The $\gamma$-ray induced formation and disappearance of hydrogen peroxide in ice was investigated as a function of total dose, temperature, dissolved gas and thermal cycling with intermittent irradiation. When oxygen saturated water was frozen rapidly and irradiated with cobalt-60 $\gamma$-rays, analysis of the melted samples gave the following results. The initial 100 e.v. yield of hydrogen peroxide increased from 0.2 below −200° to 0.7 at −15°. The hydrogen yield increased from 0.1 below −100° to 0.25 at −15°. Long irradiations at −196° resulted in continued build up of hydrogen peroxide and hydrogen to at least $10^{-3}$ $M$ while at higher temperatures steady states were reached at much lower concentrations of products. The initial presence of oxygen or hydrogen had little effect on hydrogen peroxide observed after irradiations at −196° but had considerable effect on hydrogen peroxide production at higher temperatures. When samples prepared by freezing hydrogen-saturated 50 $\mu M$ hydrogen peroxide solution were irradiated for short times at temperatures from −220 to −5°, the hydrogen peroxide concentration was observed to decrease at all irradiation temperatures. The initial 100 e.v. yield for peroxide disappearance increased from 0.6 at −100° to 4.0 at −60°. When a sample initially containing hydrogen and hydrogen peroxide was subjected to two short irradiations at −196° and was allowed to warm to −180° or above between irradiations, the observed final concentration of hydrogen peroxide was less than that for an equivalent irradiation with the sample held at −196°. The greater disappearance of hydrogen peroxide with intermittent warming is attributed to reaction induced by release of some reactive species trapped during irradiation at the low temperature. Ice irradiated at −196° exhibited an absorption peak at 2800 Å. which on warming at a rate of 10° per min. disappeared below −143°.

## Introduction

Chemical effects of ionizing radiation on ice reported in the literature are difficult to interpret. Gunther and Holzapfel[1] were unable to detect hydrogen in ice irradiated with X-rays at −180°. On the other hand Ghormley and Allen[2] found gas yields up to 0.27 molecules per 100 e.v. produced by self irradiation of tritium ice at −196°. Bonet-Maury and Lefort[3] irradiated ice containing titanium sulfate and sulfuric acid[4] and observed hydrogen peroxide production with a yield of 0.3 molecules per 100 e.v. in the frozen solution sub-

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[1] P. Gunther and L. Holzapfel, *Z. physik. Chem.*, **B44**, 374 (1939).

[2] J. A. Ghormley and A. O. Allen, A. E. C. Document ORNL-128, paper presented at 115th American Chemical Society Meeting, San Francisco, California, March, 1949.

[3] P. Bonet-Maury and M. Lefort, *Compt. rend.*, **226**, 1445 (1948); *Nature*, **162**, 381 (1948).

[4] P. Bonet-Maury and M. Frilley, *Compt. rend.*, **218**, 400 (1944) and Bonet-Maury and Lefort, *J. chim. phys.*, **47**, 179 (1950).

jected to α-particles at −4° or −190° but with X-ray irradiations found hydrogen peroxide only at irradiation temperatures above −116°. Duane and Scheuer[5] observed production of hydrogen and oxygen in equivalent amounts with a yield of 0.14 hydrogen molecule per 100 e.v. in ice at −183° bombarded with α-particles. Lefort[6] has observed in ice irradiated with α-particles at −80° and at −196° a hydrogen yield of 0.7 and hydrogen peroxide yield of 0.4 molecules per 100 e.v.

The production of hydrogen, hydrogen peroxide and oxygen in water and aqueous solutions subjected to ionizing radiation has been studied extensively in recent years.[7] The postulated reaction mechanisms involve ions and free radicals whose lifetimes are too short to permit their observation in liquid systems. However, in ice at sufficiently low temperatures some of these same entities may reach high enough concentrations to permit their detection either through the manner in which chemical effects are altered by intermittent irradiation and thermal cycling, or by physical methods.

In the work to be described here the γ-ray induced formation of hydrogen and oxygen and the formation and disappearance of hydrogen peroxide in ice have been investigated. The conditions varied were concentration of hydrogen peroxide and dissolved gases present during freezing, total dose, temperature and temperature cycle with intermittent irradiations at low temperature. The absorption spectra following irradiations at low temperature and the annealing of the absorption have also been measured.

## Techniques

The ice was prepared from distilled water that was further purified by distillation from acid permanganate followed by distillation from alkaline permanganate; the water was then transferred to a silica apparatus and after an additional distillation was stored in a silica flask. Hydrogen peroxide solutions were prepared using stabilizer-free 30% "Baker Analyzed" reagent. About 10-g. samples were irradiated in unsealed ampoules made from Pyrex test-tubes drawn down at the top to small diameter. Sealing the ampoules had no measurable effect on the results.

Ice samples containing hydrogen, oxygen or helium, were prepared from water or solutions saturated with commercial grade gas by means of glass tubing pulled down to a slender capillary and inserted through the neck to near the bottom of each ampoule. After gas was bubbled through the water about 15 minutes, the capillary was withdrawn to above the surface of the liquid and the ampoule was immersed in liquid nitrogen to freeze the water rapidly. Analysis of frozen unirradiated samples indicated that the gas retained was approximately the amount present in water saturated with the gas at room temperature. Degassed samples were prepared by alternate freezing and thawing while the ampoules were connected with a vacuum system.

Irradiation temperatures of −269, −196, −78 and −5° were maintained by means of liquid helium, liquid nitrogen, solid carbon dioxide and ice–salt mixtures, respectively. Samples were held at about −220° by placing them in a Dewar vessel with liquid nitrogen and reducing the nitrogen pressure with a vacuum pump.

For irradiations of about 5 minutes or less at temperatures above −196°, samples with thermocouple junctions attached were cooled in liquid nitrogen, allowed to warm in air to just below the desired temperature, placed in the irradiation Dewar vessel, and allowed to warm to the selected temperature. In a test sample containing a thermocouple junction frozen into the ice the rate of warming at −100° was 0.3°/min. The difference in temperature indicated by the thermocouple junction frozen into the center of this sample and a junction fastened to the outside of the sample, where the temperature was normally measured, was 2°.

In the apparatus used to maintain intermediate temperatures for longer times, cold nitrogen gas from a Dewar flask of liquid nitrogen was blown over the sample ampoule in a copper tube in an inverted Dewar vessel. A heater in the liquid nitrogen was controlled by means of a thermocouple junction within the copper tube. Another thermocouple junction, soldered to the copper tube, was used for recording the sample temperature. This temperature agreed to within one degree with the temperature indicated by a thermocouple junction frozen into a test sample.

Irradiation intensities between $0.5 \times 10^{17}$ and $1.9 \times 10^{17}$ e.v./g. min. were obtained with a 300 curie $Co^{60}$ γ-ray source which has been described.[8] Two other $Co^{60}$ sources of 1000 and 1500 curies were used for higher intensities. A 2 Mev. Van de Graaff generator was used to produce high energy X-rays for a few irradiations when it was more convenient to set up the temperature controller in front of the X-ray target than in the $Co^{60}$ shield. Current, voltage and sample position were adjusted to duplicate as nearly as possible the radiation conditions in the center of the 300 curie $Co^{60}$ source.

Hydrogen peroxide was determined in melted samples by its oxidation of iodide in the presence of molybdate catalyst followed by spectrophotometric determination of triiodide ion formed with excess iodide. In order to eliminate drift in the reagent blank due to air oxidation of iodide the method was altered from that described previously.[9] Measured volumes of the two reagent solutions were mixed in a small volumetric flask immediately before addition of the sample. A direct spectrophotometric method for the determination of hydrogen peroxide in ice at −196° would have been desirable, but ultraviolet absorption was detectable only when the hydrogen peroxide concentration was somewhat greater than 0.001 molar.

Hydrogen and oxygen evolved from samples after melting were determined in a micro gas analysis system.[9] In irradiated samples initially degassed, oxygen and an equivalent amount of hydrogen were converted to water by means of a platinum filament and the excess hydrogen was determined by addition of oxygen followed by a second combustion. In order to accurately determine small quantities of hydrogen in oxygen saturated samples, the gas from the sample was first admitted to a charcoal trap at −78° to remove the oxygen. For example, one gram of coconut charcoal, previously outgassed at about 500°, and then cooled to −78°, was found to remove all of the 0.2 cc. of oxygen from an oxygen–hydrogen mixture while removing less than 2% of the 0.002 cc. of hydrogen in the mixture.

The large, clear samples necessary for absorption spectrum measurements were prepared in a large test-tube. The tube was half-filled with purified water and was immersed in liquid nitrogen just long enough to form a film of ice on the surface of the tube thus preventing subsequent supercooling of the water. The tube was then placed in a cooling bath consisting of an ice–salt mixture at the bottom and ice at the top. In order to prevent freezing-in of gas bubbles the water was continuously stirred with a motor-driven glass stirring rod until sufficient clear ice was obtained at the bottom of the tube. The ice was then removed from the test-tube and shaped by means of a warm bar of copper to a size about 1 × 2 × 3 cm. Small holes were made by means of a copper wire for freezing thermocouple junctions into the ice. Samples were suspended over boiling liquid nitrogen to cool slowly before they were immersed in liquid nitrogen.

Absorption spectra were measured by means of a Cary recording spectrophotometer with the samples suspended in a silica Dewar vessel having an unsilvered band through which the light could pass. Measurements at −196° were made with the sample immersed in relatively pure liquid nitrogen. Ultraviolet absorption by oxygen was observed

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(5) W. Duane and O. Scheuer, *Compt. rend.*, **156**, 466 (1913).

(6) M. Lefort, Part II of "Actions Chimiques et Biologiques des Radiations," Edited by M. Haissinsky, Masson et Cie, Paris, 1955, p. 203.

(7) See, for example, A. O. Allen, *Radiation Research*, **1**, 85 (1954).

(8) J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instr.*, **22**, 473 (1951).

(9) A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).

in liquid nitrogen in which oxygen had been allowed to concentrate by evaporation of nitrogen, and strong ultraviolet absorption attributed to ozone was observed in irradiated liquid nitrogen, therefore, samples of ice irradiated in liquid nitrogen were washed in fresh liquid nitrogen before transfer to the Dewar vessel used as an absorption cell.

## Results

**A. Product Formation.**—In a series of preliminary experiments samples either degassed or containing one of the possible decomposition products, hydrogen or oxygen, were irradiated at −5, −78 and −196°. The results shown in Table I, indicate two general trends. The yield of hydrogen peroxide was consistently greater at −196° than at −78°. The presence of added hydrogen or oxygen had little effect at −196° but became more important at higher temperatures.

TABLE I

HYDROGEN PEROXIDE PRODUCED IN WATER AND ICE $\gamma$-IRRADIATED 16 HOURS AT 0.5 × $10^{17}$ E.V./G. MIN. AT THE TEMPERATURES INDICATED

| Sample | $H_2O_2$ in melted sample ($\mu$moles/l.)<br>−196° | <br>−78° | <br>−5° |
|---|---|---|---|
| Degassed | 74 | 9 | 6 |
| $O_2$-saturated | 74 | 32 | 84 |
| $H_2$-saturated | 54 | 3 | 4 |

Figure 1 shows the build-up of hydrogen peroxide in samples prepared from oxygen-saturated water irradiated at several different temperatures. The initial yield increased with increasing temperature and was appreciably greater in liquid water at 0° than in ice at −5°. At −78° a steady-state concentration of hydrogen peroxide was reached in less than two hours while at −196° there was no indication of a steady state.

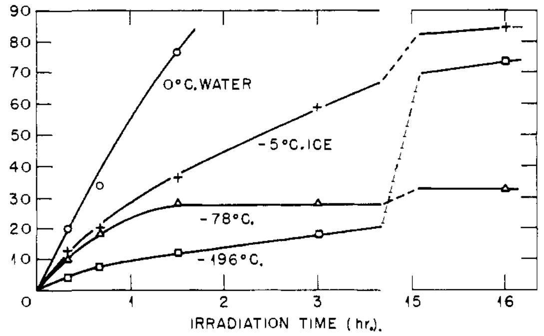

Fig. 1.—Hydrogen peroxide production in rapidly frozen oxygen saturated water irradiated with cobalt-60 $\gamma$-rays at 0.5 × $10^{17}$ e.v./g. min. (1000 r./min.).

Results obtained with higher radiation intensity and longer exposures at −196° are shown in Fig. 2. In these experiments, hydrogen and hydrogen peroxide were determined in all samples and oxygen also was determined in samples initially degassed. Hydrogen peroxide continued to increase up to 2850 min., the longest irradiation time used in the degassed sample, at which time the concentration had reached $10^{-3}$ *M*. Oxygen present initially in the ice had little effect on hydrogen peroxide production during long irradiations. In the initially degassed samples, the total number of equivalents of oxidants formed (oxygen and hydrogen peroxide) were roughly equal to equivalents of reductant (hydrogen).

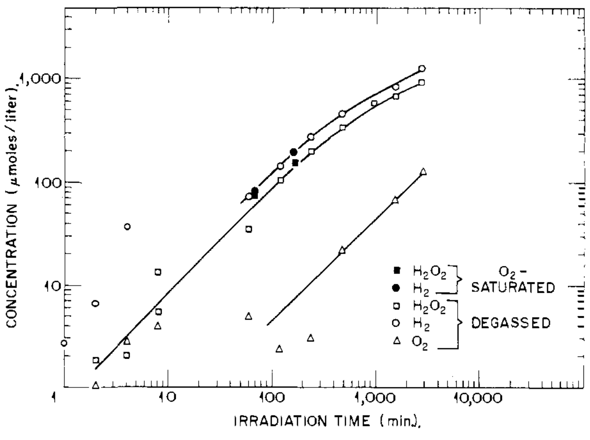

Fig. 2.—Products found in oxygen-saturated and degassed water after irradiation as ice at −196° with cobalt-60 $\gamma$-rays at an intensity of 7.0 × $10^{17}$ e.v./g. min.

Figure 3 shows yields of hydrogen peroxide and hydrogen observed after five-minute irradiations of ice prepared from oxygen saturated water, plotted as a function of irradiation temperature. The observed yield of peroxide was about the same at −269° (not shown) as it was at −220°, but it increased continuously from about −200° up to −16°. The hydrogen yield was nearly constant from −220° to about −100° and then increased between −100° and −16°. The actual product concentrations were so low (for example, 1.5 micromoles/liter of hydrogen produced at −196°) that the yields may be considered as initial yields. Corresponding 100 e.v. yields in oxygen saturated water at 25° are 0.20 for hydrogen and 1.31 for hydrogen peroxide.[10]

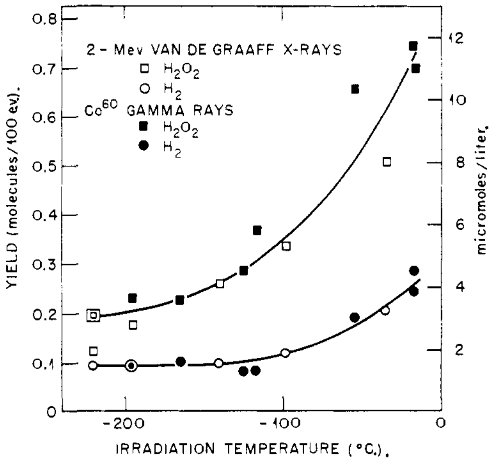

Fig. 3.—Hydrogen and hydrogen peroxide found after melting irradiated ice prepared by rapid freezing of oxygen saturated water. Irradiated 5 minutes at 1.9 × $10^{17}$ e.v./g. min.

**B. Back Reaction.**—It has been shown (Fig. 1) that at −78° the concentration of hydrogen peroxide builds up to a steady state with relatively small doses. If peroxide is produced continuously

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(10) J. A. Ghormley and C. J. Hochanadel, THIS JOURNAL, **76**, 3351 (1954).

during irradiation, then when the steady state is reached hydrogen peroxide must undergo radiation-induced decomposition or reaction with hydrogen at a rate equal to the rate of its formation. The following experiments have been carried out to determine this rate of radiation induced decomposition and reaction with hydrogen.

Yields for peroxide decrease were obtained by freezing 50 $\mu M$ hydrogen peroxide solutions saturated either with hydrogen or helium gas and irradiating with doses from $4 \times 10^{17}$ e.v./g. to $2 \times 10^{18}$ e.v./g. These doses were assumed to be sufficiently brief to give the initial yield. The results are shown in Fig. 4. The yield for peroxide disappearance in the presence of hydrogen went through a maximum between −220 and −175°. Above −175° the yield increased continuously with temperature, with a seven-fold increase between −100 and −50°. At −196° the yield for peroxide disappearance was approximately the same in ice made from hydrogen saturated or helium saturated hydrogen peroxide solution. Above this temperature the presence of hydrogen greatly increased the rate of hydrogen peroxide disappearance. For comparison, at 25° the initial 100 e.v. yield for hydrogen peroxide disappearance in hydrogen saturated 50 $\mu M$ hydrogen peroxide solution is about 18.[11]

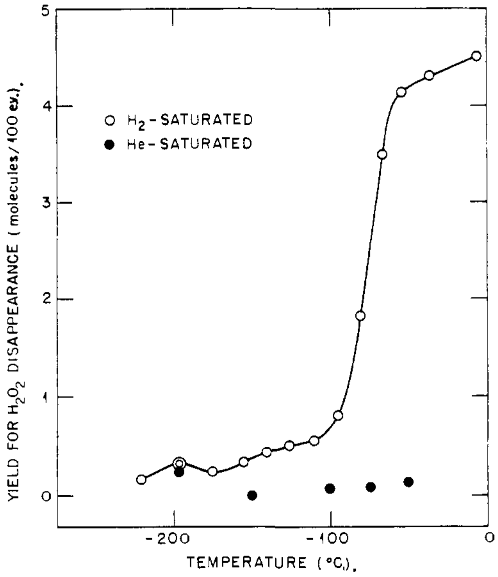

Fig. 4.—Initial yields for γ-ray-induced disappearance of hydrogen peroxide in frozen solution containing 50 micromoles of hydrogen peroxide per liter and saturated with hydrogen or helium.

Figure 5 shows change in peroxide concentration with dose in frozen hydrogen saturated hydrogen peroxide solutions at three different temperatures. At −53° the peroxide decreased rapidly and presumably would continue to decrease to a low steady state. At −175° the initial rate of peroxide disappearance was lower than at −53°. At −196° hydrogen peroxide decreased when samples were subjected to continuous 10, 20 or 30 minute irradiations, but after continuous irradiations longer than one hour the final peroxide concentration showed a net increase. When a sample was subjected to two or more ten minute irradiations at −196° and allowed to warm to a temperature of −180° or higher between irradiations, the observed final concentration of peroxide was less than for an equivalent continuous irradiation at −196°.

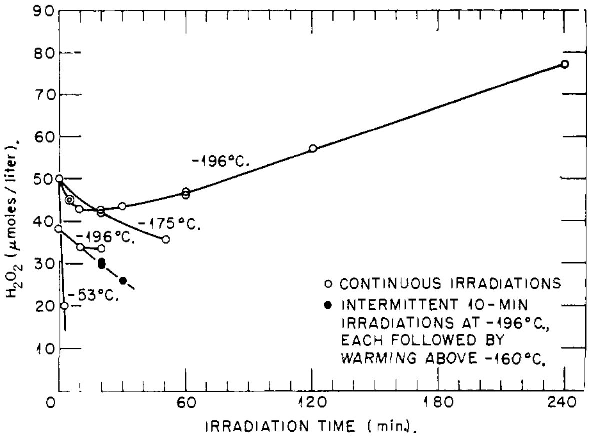

Fig. 5.—Effect of gamma radiation ($1.90 \times 10^{17}$ e.v./g. min.) on frozen hydrogen peroxide solution saturated with hydrogen.

In order to study the temperature dependence of the process which leads to disappearance of hydrogen peroxide following irradiations at −196°, samples prepared by freezing hydrogen saturated 50 $\mu M$ hydrogen peroxide solution were irradiated 10 minutes ($1.9 \times 10^{17}$ e.v./g. min.), warmed to various temperatures, then cooled to −196°, irradiated an additional 10 minutes and then melted and analyzed. The results indicate that most of the reaction on warming occurred within the relatively small temperature range of −183° to −160°.

**C. Absorption Measurements.**—A typical absorption spectrum for ice irradiated at −196° is shown in Fig. 6. The shoulder on the short wave length side of the peak builds up and anneals out simultaneously with the 2800 Å. peak, suggesting

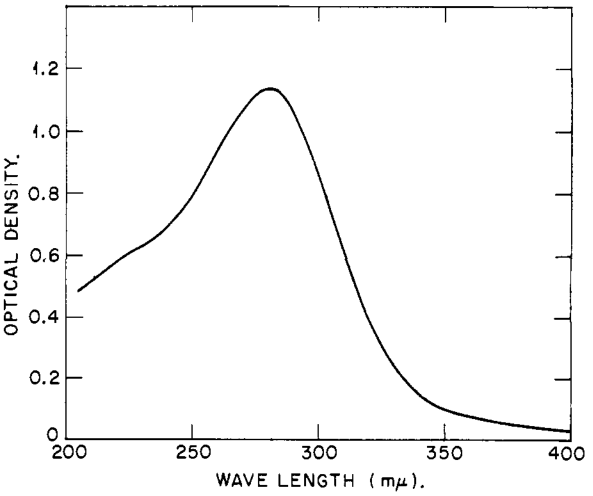

Fig. 6.—Absorption spectrum at −196° of 1.5-cm. thick ice sample irradiated at −196° with cobalt-60 γ-rays for 28 hours at approximately $1.6 \times 10^{17}$ e.v./g. min.

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(11) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

that all of the absorption is by a single species of absorber.

On warming ice irradiated at −196° at a rate of 10° per minute, the absorption peak at 2800 Å. anneals out completely below −143° as shown in Fig. 7. To obtain this curve, the transmission at 2800 Å. was recorded continuously as the sample warmed, and the measured slope of the curve was plotted as a function of time. The shape of the curve was interpreted as indicating that one process, which reached a maximum rate at −152°, predominated, but that at least one other process occurred at lower temperatures. This has been verified by another experiment in which an irradiated sample was allowed to warm to −165°, then was cooled to −196° and was allowed to warm again. When heated the first time the rate of change of absorption was similar to that shown in Fig. 7. However, when the sample was heated the second time the shoulder on the low temperature side of the −152° peak was absent, leaving only the peak at −152°, indicating that processes with more than one activation energy are involved, but suggesting that the predominant process involves only one activation energy.

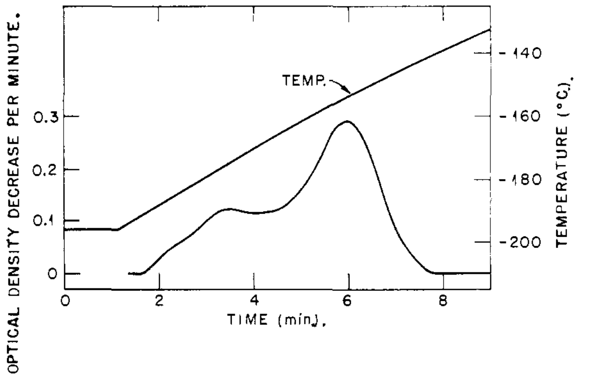

Fig. 7.—Rate of decrease in optical density at 2800 Å. on warming ice irradiated at −196°.

The tan coloration observed by Jones[12] in tritium oxide subjected to its own β-radiation at −197° may possibly be due to the long wave length tail of the 2800 Å. band extending into the visible. His ice received doses which were several hundred times greater than that received by the sample of Fig. 6.

## Discussion

The interpretations of effects produced by ionizing radiations in liquid aqueous systems generally involve the free radicals, H and OH, as intermediates. These free radicals have been observed in gases by various spectroscopic techniques but have never been directly observed in liquids. Recently Livingston, Zeldes and Taylor[13,14] have observed in some frozen acid solutions a paramagnetic resonance absorption with a hyperfine splitting very close to that observed for H atom in the gas phase. Matheson, Smaller and Yasaitis[15,16] have observed in irradiated ice a paramagnetic species whose hyperfine splitting is less by a factor of 16 than that for gaseous H atom. In each case the change from two to three in the number of lines observed when deuterium was substituted for hydrogen indicated that the unpaired electron interacted with the proton or deuteron nuclear spin. Thus the existence in irradiated ice of species having unpaired electrons has been shown experimentally. Such species are chemically very reactive and probably play a role in the chemical effects of γ-radiation in ice and frozen solutions.

In a comparison of liquid and solid systems the relative mobilities of possible intermediates must be taken into consideration. Free radicals are certainly much less mobile in solids than in liquids, but on the other hand electrons and positive "holes" may diffuse rapidly in solids and their effects may be important in reaction mechanisms. Energy transfer by means of excitons may also be important in solids.

In liquid water subjected to ionizing radiation, molecular hydrogen and hydrogen peroxide are thought to be formed in regions of dense energy release such as in the tracks of slow secondary electrons and at the ends of the tracks of primary electrons. The free radicals, H and OH, diffuse out of the tracks from regions of less dense energy release. For water and aqueous solutions it is possible to determine yields for each of the four primary products.[7] These yields depend on the type of radiation and on the nature and concentration of the solute.

It may be assumed that the initial geometrical distribution of energy received from ionizing particles is about the same in ice as in water. In regions of dense energy release the primary chemical entities, whether excited molecules, free radicals, or unstable ions, will be formed close together and their reactions with each other will be influenced very little by their mobilities. On the other hand the reactions of those products which are formed in regions of less dense energy release will depend on their ability to diffuse.

The production of hydrogen and hydrogen peroxide in ice irradiated at low temperatures probably occurs in the regions of high energy density along the tracks of the ionizing particles. The data in Table I indicate that at −196° dissolved hydrogen or oxygen molecules do not enter into reactions which appreciably affect the final concentration of hydrogen peroxide. Also the data in Fig. 2 show that the presence of oxygen does not affect the production of hydrogen at −196°.

At higher temperatures reactions involving solutes present in low concentration are observed. These reactions require transfer of energy from the tracks of the ionizing particles through the solid to the solute molecules. For example, an electron diffusing from a track could be trapped by an oxygen molecule. If the temperature were sufficiently high to permit ionic conductivity, the resulting $O_2^-$

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(12) W. M. Jones, *J. Chem. Phys.*, **20**, 1974 (1952).

(13) R. Livingston, H. Zeldes and E. H. Taylor, *Phys. Rev.*, **94**, 725 (1954).

(14) H. Zeldes and R. Livingston, *ibid.*, **96**, 1702 (1954).

(15) B. Smaller, M. S. Matheson and E. L. Yasaitis, *ibid.*, **94**, 202 (1954).

(16) M. S. Matheson and B. Smaller, *J. Chem. Phys.*, **23**, 521 (1955).

ion could attract a proton to become an $HO_2$ free radical which in turn could enter into subsequent reactions.

The observed radiation induced reaction between hydrogen and hydrogen peroxide (Fig. 4) can occur only at temperatures where the diffusion of atoms, molecules, or ions is possible. The high yields at temperatures above −50° suggest the possibility of a chain reaction such as has been postulated for liquid solution[9,11]

$$H_2O_2 + H \longrightarrow H_2O + OH$$
$$H_2 + OH \longrightarrow H_2O + H$$

This mechanism involves the diffusion of H and OH free radicals and could occur in ice only at temperatures where these free radicals could diffuse.

The yield for the radiation induced reaction between hydrogen and hydrogen peroxide in ice is nearly constant above −50°, indicating that no step in the process is inhibited by lack of the necessary activation energy. On lowering the temperature from −50 to −100° the yield is greatly reduced and it may be assumed that some step in the mechanism which predominates at high temperatures is much less probable at low temperatures. It is possible that a different mechanism is applicable below −100°.

The data plotted in Fig. 5 show that during irradiation of ice at −196° some of the absorbed energy is stored, possibly as trapped electrons or free radicals. When the irradiated sample is warmed, the release of this stored energy leads to disappearance of hydrogen peroxide.

The absorption spectrum measurements confirm the production, during irradiation at −196°, of an entity which disappears on warming.

It is of interest to compare the annealing temperatures observed in these experiments with the temperatures observed by Matheson and Smaller[16] for annealing of paramagnetic species in irradiated ice. The resonance peaks which they attribute to hydrogen atoms disappeared completely at −158 ± 10°. Within experimental error this corresponds with the upper limit of the temperature range in which hydrogen peroxide disappears following irradiations at −196°. The 2800 Å. absorption band anneals out in two temperature ranges which appear to correspond with the annealing temperatures for the paramagnetic resonance absorption which Matheson and Smaller attributed to OH. It seems reasonable that anything which would react with $H_2O_2$ (such as H atoms or trapped electrons) in the temperature range −180 to −160° could also react with OH. Therefore if the 2800 Å. absorption band is due to OH, part of the band should anneal out in the temperature range where $H_2O_2$ has been shown to undergo reaction. The remainder of the OH free radicals should disappear at a temperature where they can diffuse in some manner to react with each other.

Oak Ridge, Tenn.

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[Contribution from the Polymer Research Institute, Polytechnic Institute of Brooklyn and the Brookhaven National Laboratory]

# γ-Ray Initiated Polymerization of Crystalline Monomers[1]

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Acrylamide, methacrylamide, methylene-bis-acrylamide, vinyl carbazole, vinyl stearate, acrylic acid, methacrylic acid and potassium, calcium and barium acrylates have been polymerized in the solid state by irradiation with γ-rays. The molecular weight of polyacrylamide obtained at low conversion was constant over a 270-fold variation of radiation intensity and in the temperature range 20 to 65°, but increased slightly with the energy of the radiation. The polymerization rate, however, was linear with field intensity, independent of the energy of radiation and had an over-all activation energy of 4.7 kcal./mole. Irradiation of acrylamide at −179° produced "frozen-in" radicals in concentrations of the order of $10^{-4}$ molal. In the polymerization of vinyl stearate the temperature dependences of rate and molecular weight exhibit a discontinuity on passing through the melting point of the monomer. With barium acrylate there is no significant variation in polymerization rate between 10 and 65°. Crystalline maleic anhydride, allylamine hydrochloride and picrate, and stilbene did not polymerize on exposure to γ-rays.

In an earlier communication[3] it was reported that acrylamide undergoes rapid polymerization in the solid state upon irradiation with γ-rays. In this paper detailed results are presented on the polymerization of acrylamide and other crystalline monomers in order to ascertain any unique features that may be characteristics of solid state polymerizations.

## Experimental

**Materials.**—Acrylamide monomer (American Cyanamid Co.) was purified by sublimation at 50–60° under reduced pressure to produce a white, crystalline substance of m.p. 84°. Methacrylamide, m.p. 110°, and N,N′-methylene-bis-acrylamide, m.p. 185° dec. (American Cyanamid Co.) were dried over phosphorus pentoxide prior to use.

Acrylic acid (Monomer-Polymer, Inc.) was separated from methylene blue inhibitor by vacuum distillation through a column packed with copper gauze to inhibit polymerization, b.p. 30° (3 mm.) and m.p. 11°. To prepare potassium acrylate, a portion of distilled acrylic acid was added slowly to a solution of potassium hydroxide in methanol maintained at 12–15° to the end-point of phenolphthalein indicator. The methanol solution was then added in small portions to a large volume of diethyl ether and the crystals that precipitated were filtered, dried *in vacuo* at room temperature and stored at Dry Ice temperature. Barium acrylate was prepared in a similar manner

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(2) (a) Portion of thesis submitted to the Chemistry Department of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree. (b) Members of the Brookhaven National Laboratory.

(3) R. B. Mesrobian, P. Ander, D. S. Ballantine and G. J. Dienes, *J. Chem. Phys.*, **22**, 565 (1954).