Hindman[12] for the corresponding neptunium ion, we shall use our value of $\Delta H = +36.9 \pm 1.0$ kcal. for the reaction

$$AmO^+_2(aq) + H^+(aq) = AmO_2^+(aq) + 1/2H_2(g) \quad (14)$$

in combination with the value of -1.60 v. reported by Penneman and Asprey[13] for this couple, to calculate $S_{AmO_2}^{++}(aq) - S_{AmO_2}^+(aq)$. Straight forward manipulation of the data yields -16 ± 4 e. u. for this difference. We then adopt, for the entropy of $AmO_2^{++}(aq)$, -18 e.u., the value given by Connick and McVey[10] for PuO_2^{++}, to obtain -2 for the entropy of $AmO_2^+(aq)$. We also adopt for $Am^{+4}(aq)$ the entropy of -77 e.u., given by Connick and McVey for $Pu^{+4}(aq)$ and take the difference in entropy $S_{Am}^{+4}(aq) - S_{Am}^{+3}(aq)$ to be -47 e.u., the same value as for $S_{Np}^{+4}(aq) - S_{Np}^{+3}(aq)$ found by Cohen and Hindman.[12] Finally the entropy of Am^0 is assumed to be 12 e.u., the same as that of U^0.

These entropy values in combination with the heat data of Table IV yield the following self-consistent potential scheme: The more reliable values are given to the nearest 0.01 v. and the less reliable to 0.1 v. At best, however, the potentials are uncertain by 0.05 v. and those involving $Am^{+4}(aq)$ by 0.2 v.

It is recognized that differences in ground-state multiplicities of analogous actinide ions will lead to variations in entropy of 1 to 2 entropy units, and

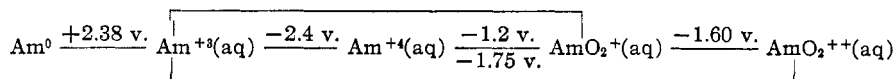(12) D. Cohen and J. C. Hindman, This Journal, 74, 4682 (1952).
(13) R. A. Penneman and L. B. Asprey, American Chemical Society, Chicago, Illinois, 1950.

that the contraction in ionic radius with increasing atomic number will cause the entropies to become more negative along the series. At present, however, it is not possible to evaluate these effects adequately. It does seem most probable, however, that the entropy values assigned by Latimer to the MO_2^+ type of actinide ions are too positive by some 15 to 20 entropy units. The linear structure and high formal charge on the MO_2^+ type of ion should permit close approach and marked ordering of water of hydration, as compared with the large alkali cations, to which Latimer's entropy values correspond.

Use of the longer-lived isotope Am^{243} in studies on the disproportionation of AmO_2^+ in 1 M H^+ may yield equilibrium values that will define the ratio of the potentials of the 3–5 and 3–6 couples more precisely than is possible from the present data. In solutions of Am^{241} of conveniently realizable concentrations the disproportionation in 1 M acid is completely masked by autoreduction.

$$Am^0 \xrightarrow{+2.38\text{ v.}} Am^{+3}(aq) \xrightarrow{-2.4\text{ v.}} Am^{+4}(aq) \xrightarrow[-1.75\text{ v.}]{-1.2\text{ v.}} AmO_2^+(aq) \xrightarrow{-1.60\text{ v.}} AmO_2^{++}(aq)$$

with overall -1.83 v.

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Radiation Chemistry Studies with Cyclotron Beams of Variable Energy: Yields in Aerated Ferrous Sulfate Solution[1]

By Robert H. Schuler[2] and Augustine O. Allen

Yields of ferrous ion oxidation and of hydrogen gas evolution in air- or oxygen-saturated solutions of ferrous sulfate in 0.8 N sulfuric acid have been determined for beams of helium ions and deuterons of various energies. From the results, the yields of total net water decomposed and of hydrogen atoms produced are found. The results are compared with those reported in the literature for various types of radiation, and are discussed in terms of the free radical model of water radiolysis.

A key phenomenon in the radiolysis of water and aqueous solutions is the variation of yields with the type of radiation. Ferrous sulfate solution is advantageously used for such studies, since the reaction mechanism is believed to be well understood[3-5] and precise measurements of the yield are made with relative ease. A considerable number

of reports have appeared on yields found on irradiation of ferrous sulfate solutions with a wide variety of types of radiation. The cyclotron is one of the most useful radiation sources for studies of this kind, in that it provides beams of charged particles of precisely known initial speed which can be varied at will over a considerable range. Preliminary data on the effect of deuteron and helium ion beams on ferrous sulfate solutions have been published by the present authors[6] and further work has been performed with proton and deuteron beams by Hart, Ramler and Rocklin.[7] This paper

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.
(2) Department of Radiation Research, Mellon Institute, Pittsburgh 13, Pa.
(3) T. Rigg, G. Stein and J. Weiss, Proc. Roy. Soc. (London), A211, 375 (1952).
(4) F. S. Dainton and H. C. Sutton, Trans. Faraday Soc., 49, 1011 (1953).
(5) A. O. Allen, Proc. Intern. Conf. Peaceful Uses Atomic Energy (United Nations, N. Y.), 7, 513 (1956).

(6) R. H. Schuler and A. O. Allen, This Journal, 77, 507 (1955).
(7) E. J. Hart, W. J. Ramler and S. R. Rocklin, Radiation Research, 4, 378 (1956).

presents more extensive and more accurate data than our previous publication.

Experimental

Materials and Analytical Methods.—Chemicals were C.P. grade. Solutions were 1 or 10 mM in ferrous ammonium sulfate and were always 1 mM in NaCl and 0.4 M in H$_2$SO$_4$. Ferric iron was determined directly by measurement of the optical absorption at 305 mμ in a Beckman DU spectrophotometer thermostated at 23.7°; the extinction coefficient was taken as 2174. The hydrogen evolved in the air-saturated solutions was determined by a method suggested by Ghormley and Hochanadel.[8] The solution was sealed in a completely filled stirred cell, and after irradiation connected to a vacuum line through a break-seal. The sample was degassed at Dry Ice temperature and the gas collected on activated charcoal at liquid nitrogen temperature. The hydrogen was then separated quantitatively from the charcoal along with small amounts of nitrogen and oxygen by raising the trap to −130° (ethyl bromide–butyl bromide mush temperature). The resulting mixture was analyzed by combination of the oxygen present with the hydrogen on a hot platinum filament followed by combustion of the remaining hydrogen on hot copper oxide.

Cyclotron Irradiation.—Most of the present work was done with deuterium or helium ion beams. The cyclotron also accelerates the hydrogen molecule ion; but the resulting protons are easily distinguished from deuterons as they have only half the range. Precautions were taken to ensure that the deuteron beams used here were free of proton contamination. Helium ions, which have a slightly different ratio of charge to mass than deuterons, are accelerated under somewhat different operating conditions, so that the helium ion beams are always clean.

Exposures were made at the end of an evacuated pipe 10 meters long through which the deflected beam from the cyclotron passed. Only about 0.1% of the total deflected beam of 10 μa. passed through a $^1/_4$-inch diameter hole and was received by the irradiation cells. Since the beam is spread out by the fringing magnetic field of the cyclotron according to the energy of the particles, the small fraction of the beam reaching our cell was extremely homogeneous in energy. Focusing magnets on the tube are available to increase the fraction of the beam being received by the cell, but ordinarily there was little occasion to use much focusing because low currents were desired. Solutions were contained in magnetically stirred cells of the Saldick type.[9] Both mica and glass windows were used for entrance of the beam into the solution. Solutions could be run either sealed or left open to the air. In some runs the solution was saturated with pure oxygen by bubbling while stirring; the cell was then stoppered during irradiation. Mica window thicknesses (in mg./cm.²) were determined from the weight of known areas. The thicknesses of the glass windows, which were blown to the cell, were determined by focusing a microscope successively on the two surfaces; the thickness was then given by the length of travel of the microscope multiplied by the refractive index of the glass.

Determination of Current.—The beam current absorbed in the solution was read from a wire sealed into the solution and connected to ground through a Higinbotham–Rankowitz integrator.[10] The currents, as read, were corrected for the electric charge displaced from the insulating window into the solution, as discussed in detail elsewhere.[11] The present current integrator gives results reproducible to better than 0.1%. The instrument was recalibrated every day on which runs were made. An earlier model of the current integrator gave poor results at lower currents due to zero drift, and some of the low current determinations presented in Fig. 1 were monitored by activation and counting of appropriate weighed metal foils; copper was used for helium ion bombardments and titanium for deuteron bombardments.

Determination of Beam Energies.—The energy was determined from the mean range of particles in aluminum

(8) J. A. Ghormley and C. J. Hochanadel, This Journal, **76**, 3351 (1954), and personal communications.

(9) J. Saldick and A. O. Allen, *J. Chem. Phys.*, **22**, 438 (1954).

(10) W. Higinbotham and S. Rankowitz, *Rev. Sci. Instr.*, **22**, 688 (1951).

(11) R. H. Schuler and A. O. Allen, *ibid.*, **26**, 1128 (1955).

using standard range–energy relationships.[12] The range was determined by placing increasing amounts of aluminum absorber before the cell and noting the fall in current as the end of the range was reached. Absolute determinations of the energy were made with a mica window of thickness 5.4 mg./cm.². It was assumed that the current divided midway within the window; *i.e.*, that charges brought to rest within the outer half of the window had passed to ground through the outside, those stopped in the inner half of the window had passed to ground through the solution and the measuring instrument. The error resulting from this assumption should be less than 1 mg./cm.² in the mean range. Subsequently range measurements were made by putting in enough absorber to bring the beam nearly to the end of the range, and estimating the residual energy from the amount of oxidation of ferrous sulfate. Since in such measurements only a very small fraction of the range was expended in the solution, a large error in the assumed value of the ferrous sulfate oxidation yield for the low energy particles will produce a negligible error in the total range. The beam energy is subject to appreciable day-to-day variations, and will even vary slightly within a series of runs if the conditions of operation of the cyclotron are changed. In the Brookhaven cyclotron the initial beam energy is 40.4 ± 0.8 Mev. for helium ions, and 20.2 ± 0.4 Mev. for deuterons.

For helium ions, the probable error in range determination was about 1 mg./cm.², which at full range of about 38 Mev. (after passing through the windows) corresponds to an energy change of 0.14 Mev. or only 0.4% of the beam energy. We are however interested in cutting down the energy over as great a range as possible by the use of absorbers. When the energy is reduced to 10 Mev., with a residual range of 15 mg./cm.², an error of 1 mg./cm.² will affect the energy by 0.4 Mev. or 4% of the total. For deuteron beams the probable error in the range is about 3 mg./cm.². At full beam energy of 20 Mev. a 3 mg./cm.² error will affect the energy by 0.1 Mev. or 0.5%, but when the energy is reduced to 6 Mev. the error becomes 0.26 Mev. or 4%. The percentage uncertainty in the energy increases rapidly as the energy is further decreased, and we place little reliance on data taken at helium ion energies below 10 Mev. or deuteron energies below 6 Mev.

The inherent range straggling appeared to be about ±2 mg./cm.² for helium ions and ±5 mg./cm.² for deuterons, as expected theoretically for monoenergetic beams. Except for measurements made near the extreme end of the range, variations in energy due to straggling average out and introduce no appreciable error in the yield determinations.

Results and Discussion

Effect of Beam Current and Stirring Speed.— Apparent yields of iron oxidized in air-saturated solutions at various beam currents are shown in Fig. 1 for full-range deuterons and helium ions. Small adjustments have been made to the data obtained in different cells to allow for the slight changes in beam energy. The yield is seen to be constant at currents below 10^{-8} amp. and an apparent drop occurs at higher currents (similar to that observed with electron beams). The drop is believed to result from depletion of oxygen in regions of high energy release near the end of the beam. The stirring was unable to supply material to these regions fast enough to maintain the oxygen concentration when the rate of energy supply was too great. The data in Fig. 2 confirm this explanation by showing that a drop in stirring speed lowered the yields appreciably at currents near 10^{-8} amp. but had a much smaller effect at currents near 10^{-9} amp. We believe the constancy of the results at currents below 10^{-8} amp. indicates than the yields obtained are not significantly below the true values. All data presented later in this paper were obtained at currents less than 10^{-8} amp.

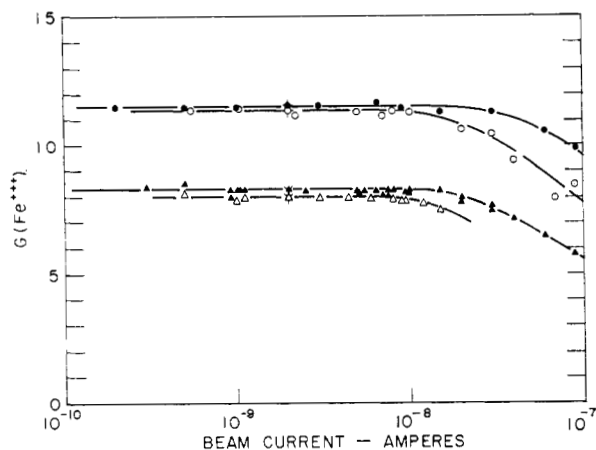(12) W. A. Aron, B. G. Hoffman and F. C. Williams, Document AECU-663 (1951).

Fig. 1.—Dependence of apparent iron oxidation yield on beam current in air-saturated solutions: circles, D^+; triangles, He^{++}; solid symbols, 10 mM FeSO$_4$; open symbols, 1 mM FeSO$_4$; flagged points (at 2×10^{-9} amp.) represent slopes of lines in Fig. 3. Values normalized to energies of 20.2 Mev. for D^+ and 33.4 Mev. for He^{++} by use of the curves in Figs. 4 and 5.

Constancy of Yield with Increasing Dose.—

Figure 3 shows that the yield remains constant as ferric iron builds up in the solution to concentrations of at least 2.7×10^{-4} M. At much higher doses the yield begins to fall because of general depletion of oxygen throughout the solution, as has been shown also to occur with X-rays and γ-rays.[13]

Effect of Ferrous Sulfate Concentrations.—

Figures 1 and 3 show that the yield in 10 mM ferrous sulfate solution is higher than that in 1 mM solutions by about 3.5% for helium ions and about 1.5% for deuterons. According to Fig. 1, the effect is independent of current at low currents and therefore presumably is not due to insufficient stirring and resultant ferrous ion depletion in the more dilute solutions. This effect also has been found for less energetic particles[14] under conditions where no local depletion of iron or oxygen was possible.

Effect of Oxygen Concentration.—

Table I shows the results of comparison runs made at the same time between solutions saturated with oxygen and companion solutions saturated with air. Although the reproducibility is not as good as might be hoped, a real difference is found of the order of 6%.

TABLE I
EFFECT OF OXYGEN CONCENTRATION

Particle	Energy (Mev.)	FeSO$_4$ concn. (mM)	G_{O_2}/G $_{ir}$[a]
D^+	18	10	1.06
D^+	10	10	1.04
He^{++}	34	10	1.08
He^{++}	34	10	1.07
He^{++}	34	10	1.04
He^{++}	34	1	1.07

[a] Ratio between ferrous oxidation yields in solutions saturated with pure oxygen and with air, found in successive runs in the same cell under otherwise identical conditions.

(13) J. Weiss, A. O. Allen and H. A. Schwarz, *Proc. Intern. Conf. Peaceful Uses Atomic Energy* (*United Nations, N. Y.*), **14**, 179 (1956).
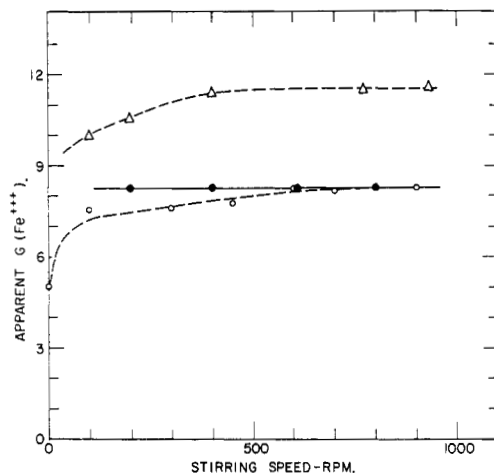(14) N. Barr and R. H. Schuler, This Journal, **78**, 5756 (1956).

Fig. 2.—Dependence of apparent iron oxidation yield on stirring speed in air-saturated solutions: $\triangle$, 19.4 Mev. deuterons, 1 mM FeSO$_4$, beam current 8×10^{-9} amp.; O, 34-Mev. helium ions, 10 mM FeSO$_4$, 5×10^{-9} amp.; ●, 34-Mev. helium ions, 10 mM FeSO$_4$, 1×10^{-9} amp.

Effect of Particle Energy.—

The data as obtained give the total amount of product formed by a measured amount of charge input, and the yields are therefore most realistically reported as the number of molecules oxidized per particle entering the solution. Figures 4 and 5, for the deuteron and helium ion beams, respectively, show this quantity as a function of E_0, the energy of the beam entering the solution. The data are for air-saturated solutions 10 mM in ferrous ion. In terms of the usual notation, the number of molecules oxidized per particle may be called 10^4 G_0E_0, where G_0 is the average yield over the entire range of the particle in molecules oxidized per 100 e.v., and E_0 is the initial energy in Mev. The curvature of the plots shows that the yield decreases as the particles are slowed down. The slope of the curves at any point in Figs. 4 and 5 shows the amount of chemical change produced per unit energy loss by the particles during the instant in which they actually have the given energy.[15] This instantaneous or "thin-target" yield, $G_i = d(G_0E_0)/dE_0$, is the quantity called G_l by Hart.[7] The more usual yield, G_0, is given simply by the quotient of ordinate to abscissa in the curves of Figs. 4 and 5, or the slope of the line connecting any point to the origin.

Comparison of Proton and Deuteron Yields.—

A number of experiments were also performed with the 10-Mev. proton beam; its energy was measured by determining the total range in aluminum absorbers as with the other beams. The current displacement correction factor was determined separately for the proton beams by the method used previously for the deuteron beams[11] and was found to have the same value, 0.932, as for the full range deuterons. For 8.4-Mev. protons the total yield for oxidation of ferrous sulfate in 10 mM air-saturated solution was $G_0 = 11.23 \pm 0.07$ (standard deviation of four determinations). This quantity is identical with the yield found for 16.8-Mev. deuterons (see Fig. 6) which have the same energy loss parameter as the protons used.

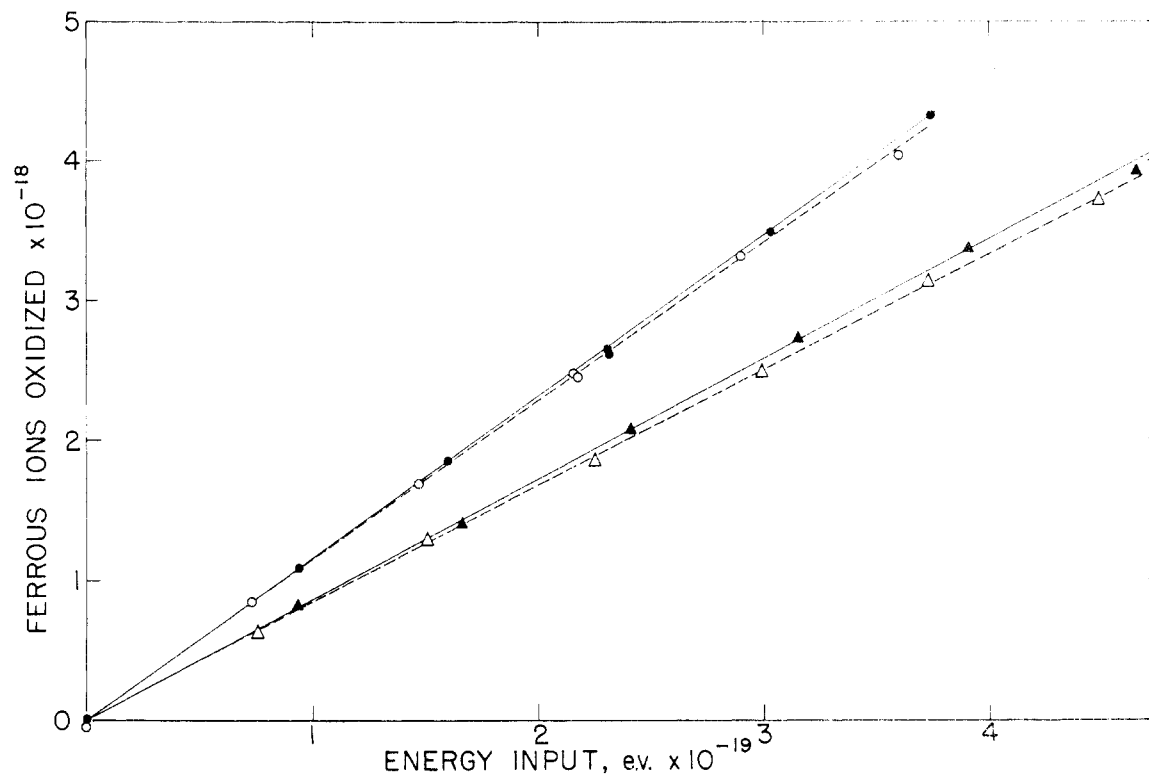(15) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

Fig. 3.—Iron oxidized as a function of total energy input in air-saturated solutions: circles, 19.75-Mev. D$^+$; triangles, 38.2-Mev. He^{++}; solid symbols, 10 mM FeSO$_4$; open symbols, 1 mM FeSO$_4$.
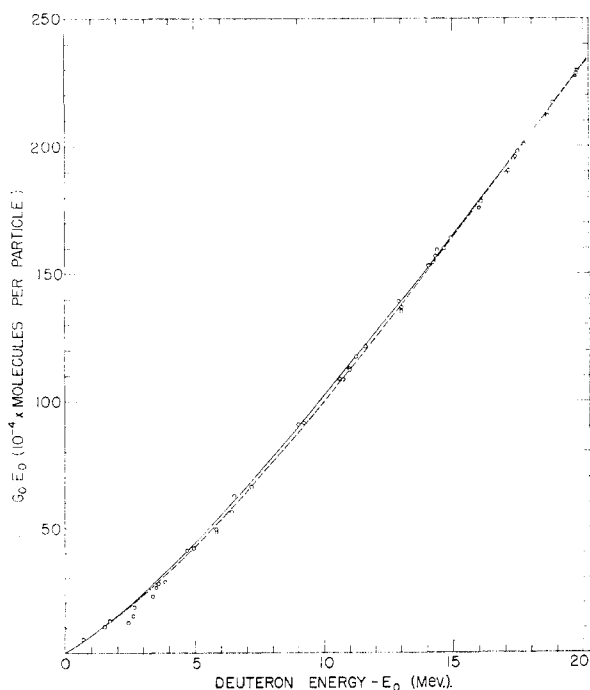

Fig. 4.—Iron oxidized per deuteron in 10 mM, air-saturated solutions. Upper point is mean of 13 determinations; length of bar shows standard deviation. Solid curve obtained by integration of eq. A, broken curve from eq. B.

Hydrogen Yields.—Measured hydrogen yields are assembled in Table II. They are less reproducible than the iron oxidation yield, presumably because of analytical difficulty. The hydrogen
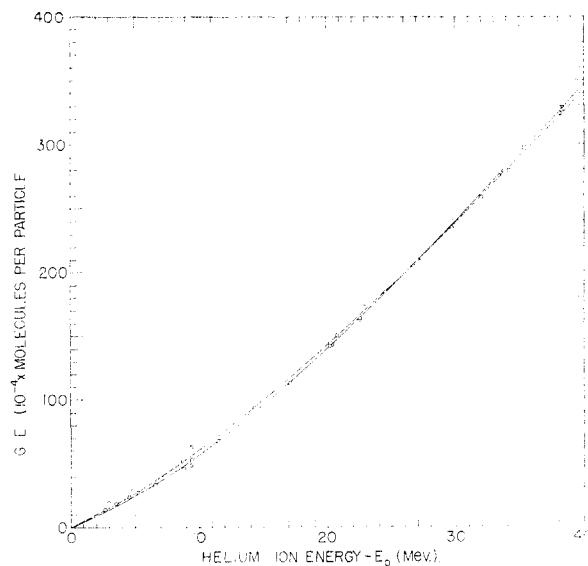

Fig. 5.—Iron oxidized per helium ion in 10 mM, air-saturated solutions. Upper limit is mean of 15 determinations; length of bar shows standard deviation. Broken curve from integration of eq. C; solid curve from eq. E. Integration of eq. D leads to a curve which lies very close to the broken curve below the crossing point and to the solid curve above this point.

yield generally increases as the particle speed and the iron oxidation yield decrease.

Yields as a Function of Rate of Energy Loss (LET).—A convenient parameter to use in characterizing various kinds of radiation is the amount

Table II

Hydrogen Formation and Net Water Decomposition

Particle	Energy (Mev.)	$G_0(H_2)$[a]	G_{H_2}[b]	G_{-H_2O}[c]	G_H[d]
D$^+$	18.2	0.81	0.72	3.98	2.53
	18.5	.89	.81	4.11	2.50
	18.8	.82	.73	4.00	2.53
He^{++}	34.5	1.06	1.01	3.61	1.60
	31.3	1.06	1.01	3.55	1.53
	21.8	1.18	1.14	3.55	1.27

[a] Measured hydrogen yield; doses about 7×10^{19} e.v. [b] Represents that part of the measured hydrogen arising directly from water decomposition: $G_{H_2} = 1.0175G(H_2) - 0.00871G(Fe^{+3})$. [c] Calculated by $G_{-H_2O} = 0.241G(Fe^{+3}) + 1.52G(H_2)$. [d] $G_H = G_{-H_2O} - 2G_{H_2}$.

of energy lost per unit distance along the tracks of the charged particles which constitute the radiation. This energy loss parameter, perhaps best represented by the symbol $-dE/dx$, has often been called "linear energy transfer" or LET. For ions at non-relativistic velocities, it is given by the formula[16]

$$-dE/dx = (2\pi e^4 z^2 NZ/E)(M/m)\ln(4E/I)(m/M) \quad (1)$$

where m and e are the electron mass and charge, M and E the mass and energy of the moving charged particle, z the number of unit charges carried by the particle, NZ the number of electrons per unit volume of irradiated material, and I the parameter characteristic of each material. We have taken I = 66 e.v. for water.[17] Equation 1 applies to deuterons over the whole range of interest and to helium ions above 3 Mev. For lower energies, values of $-dE/dx$ for helium ions have been given by Bethe.[18] The above formula reduces for water to $-dE/dx = (3.740/E) \log_{10} (E/0.0605)$ for deuterons and $-dE/dx = (29.735/E)\log_{10}(E/0.1203)$ for helium ions, where $-dE/dx$ is in e.v./Å. and the energy E is in Mev.

In Fig. 6 the data of Figs. 4 and 5 are replotted with both G_0 and G_i shown as functions of the reciprocal LET, $-dx/dE$. The present results entirely supersede those of our former publication[6] since in the earlier measurements too high a current was used and the charge transfer effect was not corrected for.

Although the data for the deuterons and alphas do not actually overlap on this plot any reasonable extrapolation indicates that the α-rays give an iron oxidation yield significantly (about 7%) higher than deuterons of the same LET. A similar difference has been shown to exist between the ferrous ion oxidation by the triton component of the $Li(n,\alpha)T$ reaction[14] and cyclotron helium ions. We sought for appropriate empirical equations to express variation of yield with LET over the range studied. The most logical expression would relate G_i and $-dE/dx$. This yield should approach 3.6 for radiations of very high LET[19] and 15.6 for zero

(16) H. A. Bethe and J. Ashkin, in "Experimental Nuclear Physics," E. Segré, Editor, Vol. I, John Wiley and Sons, New York, N. Y., 1953, pp. 167 and 253.

(17) Derived from the values of I for O and H used by J. Weiss and W. Bernstein, Phys. Rev., 98, 1828 (1955).

(18) H. A. Bethe, Rev. Mod. Phys., 22, 213 (1950).

(19) In the limit of high LET the free radical yields will vanish and $G(Fe^{+3})$ will approach G_{-H_2O} or $2G_{H_2}$. For $B(n,\alpha)$ recoils[14] (1.5 Mev. α-particles), $G_{-H_2O} = 3.6$ and $2G_{H_2} = 3.4$. For 5.3 Mev. α-particles, $2G(H_2) = 3.2-3.6$ in a variety of aqueous solutions (M. Cottin and M. Lefort, J. chim. phys., 52, 549 (1955)).

LET. (The value for 1 or 2 mv. electrons[20] should be within 1% of the limiting value.[15]) A form of equation having a single adjustable parameter which fits these limiting conditions is $G_i = 3.6 + 12.0/(1 + C(-dE/dx))$. This equation is found to give a fair fit to the experimental data with C taken as 0.47 for the deuterons and 0.37 for the helium ions. The curves of G_0E_0 vs. E_0 obtained by numerical integration of these equations are shown for comparison with the data in Figs. 4 and 5. An even better fit for the helium ion data over the experimental range is obtained by increasing the second constant to give $G_i = 3.6 + 14.0/(1 + 0.47(-dE/dx))$. This form presumably would fail at very high energies. The form of these expressions resembles that of the competition equations obtained in reaction kinetics on the assumption that an intermediate is being competed for by two materials uniformly distributed throughout the solution. Such kinetics would not be expected theoretically to hold in the present case, in which intermediates are being formed in extremely heterogeneous distribution and the main competition is between recombination and diffusion. A similar form of equation connecting G_0 and E_0 is found to fit the data almost as well for both helium ions and deuterons, although there is no theoretical reason to expect a simple relationship between these quantities. The G_0–E_0 equation for the deuteron data is adjusted to approach the right yield of 15.6 at very high energies, while that for helium ions approaches the right yield of 3.6 at zero energy. The above five equations are assembled in Table III, and curves showing the fit of all these equations to the data are shown in Figs. 4 and 5.

Table III

Empirical Yield–Energy Relationships

For deuterons:

$G_i = 3.6 + 12.0/(1 + 0.45(-dE/dx))$	(A)
$G_0 = 5.9 + 9.6/(1 + 13.6/E_0)$	(B)

For helium ions:

$G_i = 3.6 + 12.0/(1 + 0.37(-dE/dx))$	(C)
$G_i = 3.6 + 14.0/(1 + 0.47(-dE/dx))$	(D)
$G_0 = 3.6 + 10.0/(1 + 38/E_0)$	(E)

Comparison with Other Investigations.—The ferrous sulfate oxidation yields of Hart, Ramler and Rocklin with deuteron beams[7] lie consistently 6–8% below our results. About half the discrepancy arises from differences in the values assumed for the charge displacement factor and for the ferric iron extinction coefficient. Insufficient stirring of their solutions might possibly account for some of the discrepancy. Their value of the molecular hydrogen yield for 18-Mev. deuterons, deduced not from direct measurement of hydrogen but from yields of $FeSO_4$ oxidation in the presence of $CuSO_4$, show a much greater difference from ours; they find 0.53 compared to our value of 0.72–0.81. The difference is presumably due to actual decrease in the hydrogen yield in solutions containing $CuSO_4$, owing to scavenging of H atoms which would otherwise combine to form molecular H_2. Copper sulfate has been shown to decrease the yield of mo-

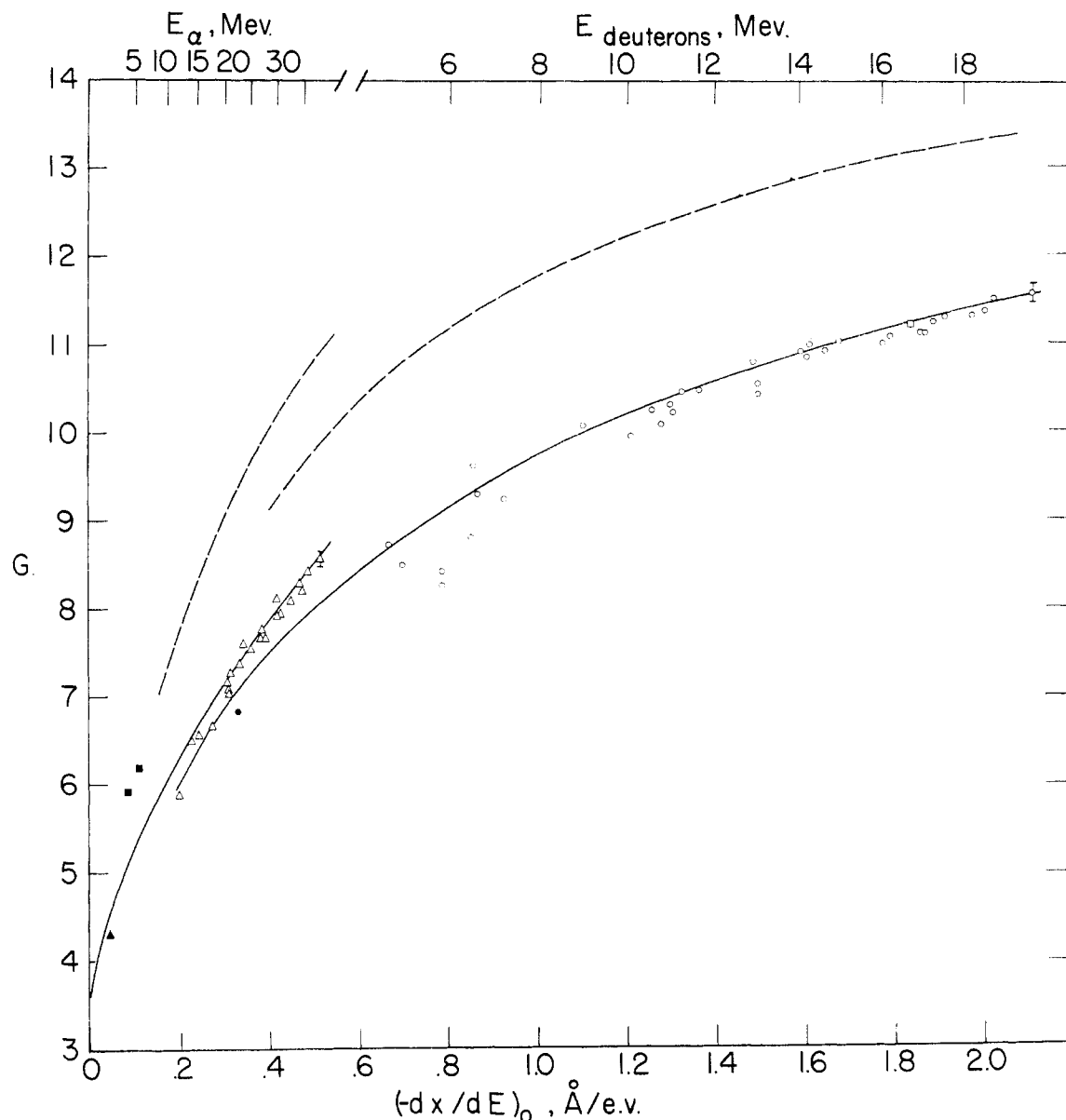(20) R. H. Schuler and A. O. Allen, J. Chem. Phys., 24, 56 (1956).

Fig. 6.—$G(Fe^{+3})$ in 10 mM, air-saturated solutions: O, G_0 for cyclotron deuterons; △, G_0 for cyclotron He^{++}; □, G_0 for cyclotron protons; ●, G_0 for T$^+$ recoil from Li(n, α) (ref. 14); ▲, G_0 for recoils from B(n, α) (ref. 14); ■, G_0 for Po α-particles (refs. 23, 25); dotted curves, G_i from eq. A and D; solid curves, G_0 from integration of the same equations.

lecular hydrogen with γ-radiation.[21] Their calculated values of net water decomposition yield are correspondingly low. Their results on ferrous sulfate oxidation by low energy protons from an electrostatic generator are in fairly good agreement with the extrapolation of our deuteron results.

The ferrous sulfate oxidation yield by the β-rays of tritium may be compared with our deuteron results if we assume that the same G_i value is obtained by deuterons and electrons having the same values of $-dE/dx$, and that equation A may be used to describe the yields at $-dE/dx$ values considerably below the range of the deuteron measurements. In making this calculation we used for the calculation of LET for electrons a slightly modified

formula[16] in which the factor 4 under the logarithm in eq. 1 is replaced by the number 1.16, equal to $\sqrt{e/2}$. The value of G_0 for a series of electron energies was then obtained by numerical integration of G_i and finally the net yield was integrated numerically over the spectrum of tritium β-rays.[22] Since the yield increases with the electron energy, the final yield obtained corresponds to an electron of energy greater than the mean energy (5.5 kev.) of the tritium β-rays. The calculated value of the tritium beta yield was 12.6, in good agreement with the experimental results of 12.9 (McDonell and Hart[23]) and 12.7 (Hardwick[24]). Schuler and Barr

(21) H. A. Schwarz, This Journal, **77**, 4960 (1955).

(22) S. C. Curren, J. Angus and A. L. Cockcroft, Phil. Mag., [7] **40**, 53 (1949).
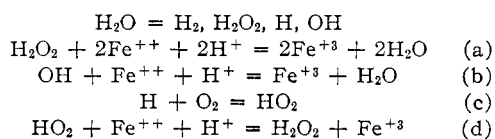(23) W. R. McDonell and E. J. Hart, This Journal, **76**, 2121 (1954).
(24) T. J. Hardwick, personal communication.

have determined the ferrous sulfate oxidation yields in aerated and deaerated solution for the recoils from the boron (n,α) reaction and our figure of 3.6 as the limiting value for particles of zero energy is based in part on these results. The yield due to the helium and tritium ion recoils from the (n,α) reaction on lithium also was determined, and by assuming the appropriate value for the slow helium ion yield it was possible to calculate a yield for the faster tritium ion. This value is also shown on Fig. 6 and agrees well with the extrapolation of the present deuteron measurements.

The reported $G_0(Fe^{+3})$ values for the α-rays of polonium[23,25] lie near 6.2, which is considerably above the number expected from our cyclotron measurements (Fig. 6). It is of course possible that these results are all correct and that the curve of G_0 vs. $-dx/dE$ actually shows a knee. However, the value of the hydrogen yield also was determined by Miller and Wilkinson with Po α-rays in oxygenated $FeSO_4$ solutions.[25] Their observed ratio of the hydrogen yield to the ferrous sulfate oxidation yield, 0.262, will lead to a reasonable value of 3.6 for the net water decomposition yield (see below) only if the absolute value for the ferrous sulfate oxidation yield is taken as 5.6, which would be the number expected from our helium ion measurements made at higher energies.

Reaction Mechanism.—The mechanism of ferrous sulfate oxidation in aerated solution by γ or X-rays has frequently been discussed[3–5] and a similar mechanism presumably holds for other types of radiation. It is summarized in the equations

$$H_2O = H_2, H_2O_2, H, OH$$
$$H_2O_2 + 2Fe^{++} + 2H^+ = 2Fe^{+3} + 2H_2O \quad (a)$$
$$OH + Fe^{++} + H^+ = Fe^{+3} + H_2O \quad (b)$$
$$H + O_2 = HO_2 \quad (c)$$
$$HO_2 + Fe^{++} + H^+ = H_2O_2 + Fe^{+3} \quad (d)$$

The quantities of interest are the amounts of the four products H, OH, H_2 and H_2O_2, which are produced from the water. The four primary chemical yields will be denoted here by the symbol G with the appropriate subscript, while observed yields of various reaction products are denoted by the symbol G with the formula of the product following in parentheses. Thus the yield of molecular hydrogen supposed to be produced initially from the decomposition of water will be denoted by G_{H_2}, while the actually observed yield of hydrogen gas in a solution will be denoted by $G(H_2)$. The total amount of water decomposed to form the primary products is called the net water decomposition and is given by $G_{-H_2O} = G_{OH} + 2G_{H_2O_2} = G_H + 2G_{H_2}$.[26] The ferrous sulfate oxidation yield according to the above mechanism may be expressed as

$$G(Fe^{+3}) = G_{OH} + 2G_{H_2O_2} + 3G_H = G_{-H_2O} + 3G_H \quad (2)$$

(25) N. Miller and J. Wilkinson, *Trans. Faraday Soc.*, **50**, 690 (1954).

(26) We are not using in this paper the notation involving the quantities F, R and E, used in previous publications,[5,15] since the meaning of these letters seems to have been misunderstood, frequently. It is often convenient, however, to use F, R and E or a similar system of notation in working out the yields to be expected on the basis of various reaction mechanisms. The relations between the quantities in the two systems are: $G_{H_2} = F$; $G_{H_2O_2} = F + E$; $G_{OH} = R$; $G_H = R + 2E$; $G_{-H_2O} = R + 2E + 2F$.

According to the mechanism the reactions in this solution are independent of the relative yields of OH and H_2O_2; but the observed yields can tell us the net water decomposition yield and the hydrogen atom yield as a function of the nature of the radiation.

Calculation of Net Water Decomposition Yield.— If we substitute for G_H in eq. 2 its value in terms of G_{-H_2O} and G_{H_2}, we obtain

$$G_{-H_2O} = 0.25G(Fe^{+3}) + 1.5G_{H_2} \quad (3)$$

In applying this equation we have a small correction for the fact that not quite all the hydrogen atoms react with dissolved oxygen as required by the above mechanism. Some may react with ferrous sulfate in the presence of acid to form ferric salt and hydrogen.

$$H + H^+ + Fe^{++} = H_2 + Fe^{+3} \quad (e)$$
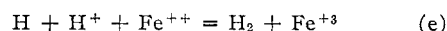
Insofar as reaction (e) occurs instead of (c) the yield of ferrous oxidation is reduced and that of hydrogen production increased. W. Rothschild, working in our laboratory, found that the ratio of rate constants for reactions (c) and (e) is 1200 in 0.8 N H_2SO_4. The yields of iron oxidation and hydrogen gas formation are then given by the formulas

$$G(Fe^{+3}) = G_{-H_2O} + G_H \left(1 + \frac{1}{1 + \frac{(Fe^{++})}{1200(O_2)}}\right)$$

$$G(H_2) = G_{H_2} + \frac{G_H}{1 + \frac{1200(O_2)}{(Fe^{++})}}$$

On putting in the appropriate numbers we then find a slightly corrected formula for the net water decomposition in air-saturated 10 mM $FeSO_4$

$$G_{-H_2O} = 0.241G(Fe^{+3}) + 1.52G(H_2) \quad (3')$$

This is the integral yield (G_0) for net water decomposition. The precision and number of the results is hardly sufficient to warrant a calculation of G_i for the net water decomposition as was attempted by Hart.[7] Table II shows the values of G_{-H_2O} and related quantities.

The Free Radical Theory of Water Radiolysis.— Current thinking on the mechanism of water decomposition assumes that all or most of the molecular products, H_2 and H_2O_2, arise by combination of free radicals, H and OH, formed close to one another in the tracks of secondary electrons. A little group of radicals formed close together along the track of such an electron is called a spur. With increasing LET the spurs must come close together and overlap, so that more radicals will form in close proximity with correspondingly greater probability of reacting with one another to produce the molecular products or to recombine to water. One therefore expects to find that the radical yields decrease, the molecular yields increase, and the net water decomposition yield decreases with increasing LET, which is certainly borne out qualitatively by the present data. The slightly higher H atom yield apparently found for helium ions as compared to deuterons (or protons) of the same LET is to be explained by the slightly greater mean energy of secondary electrons (δ-rays) from the heavier he-

lium ions,[27] which will penetrate to a greater average distance from the actual particle track, and so lead to a slightly greater dispersion of the initial radical positions around the track. Thus, comparing a helium ion with a deuteron having the same linear energy transfer, the actual mean initial volume density of radicals will be somewhat greater along the track of the deuteron.

A calculation of the competition, in the expanding track, between radical recombination and capture by such active solutes as ferrous sulfate and oxygen is too complicated to be carried out rigorously. The most elaborate attempt at an approximate computation is that of Ganguly and Magee.[28] They found it necessary to assume, among other approximations that the concentration of the scavenger solutes remained constant at all points throughout the expanding track. This assumption can hardly be true for tracks of moderately high LET, since it is readily calculated from their own figures that the initial mean radical concentration in the track of a 36-Mev. helium ion is about 0.15 M, which is orders of magnitude higher than the concentrations of ferrous sulfate and oxygen used as scavengers in this work. The scavengers will then be entirely depleted near the center of the track, where a large fraction of the molecular products are formed. The calculations of Ganguly and Magee therefore underestimate the fraction of radicals combining with one another, and the error should increase with increasing LET. Comparison with experiment is also confused by the fact that two kinds of radicals are in fact formed, while Ganguly and Magee assumed the radicals to be all alike, and calculated only a quantity S, the fraction of all radicals which react with scavengers. We have compared the ratio of our yields for H atoms and molecules, $G_H/2G_{H_2}$, with their calculated values of $S/(1 - S)$. The results showed that the change in radical yield with LET was somewhat faster than predicted for a given concentration of scavengers, as expected on account of neglect in the calculations of scavenger depletion in the track.

(27) E. Pollard, Advances in Biol. and Med. Phys., **3**, 153 (1953).

(28) A. K. Ganguly and J. L. Magee, J. Chem. Phys., **25**, 129 (1956).

The change of radical yield with scavenger concentration, as shown in our experiments by the effect of oxygen concentration on the ferrous oxidation yields, seems to be of about the magnitude predicted by Ganguly. The effect of ferrous ion concentration on the oxidation yield must be interpreted as an increase in total net water decomposition caused by greater scavenging of the OH radicals by the ferrous ions. It thus appears that in general the system conforms to the predictions of the theory, and that closer agreement with experiment would be expected if calculations were to take into account the depletion of solute concentration within the expanding track.

There is however one feature of the present results which does not appear to conform to expectations. The net water decomposition appears to change very little or not at all over the range of LET's from zero energy up to 38-Mev. helium ions, in which range the hydrogen yield G_{H_2} changes by about 0.5. In passing over the rest of the range from 38-Mev. helium ions up to fast electrons we find that the hydrogen yield undergoes a further drop of about 0.6 while the net water decomposition increases by 1.0. According to the free radical theory, the yields of hydrogen and net water decomposition should change in a smoothly complementary manner. A possible explanation for the discrepancy would be that an extra source of water decomposition exists which comes into play with especial prominence in dense radical tracks and thus counterbalances the increased recombination of radicals to water which is expected in such tracks. The extra source of water decomposition might consist of a species of excited water molecules which normally decay without decomposition, and produce net chemical reaction only if formed in adjacent sites; or they might be regarded as H-OH radical pairs formed together (in a "cage") which normally recombine rapidly, and can react with one another to form H_2 and H_2O_2 molecules only if formed in adjacent sites. Further work is needed on determination of the net water decomposition yields under different conditions at moderate to high LET's.

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Sexadentate Chelate Compounds.　IX

By Francis Lions and Kenneth V. Martin[1]

1ε,3ε,5ε-Triaminocyclohexane has been prepared by an improved process and condensed with salicylaldehyde and pyridine-2-aldehyde, giving 1ε,3ε,5ε-tris-salicylideneaminocyclohexane and 1ε,3ε,5ε-tris-(α-pyridylmethyleneamino)-cyclohexane, respectively. Each of these condensation products has been shown to be capable of functioning as a sexadentate chelate compound of novel type.

The ability of an organic compound to function as a sexadentate chelate compound, whose molecule can supply six donor atoms to occupy without undue strain the six octahedrally disposed coördination positions about a six-covalent metal atom,

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depends upon the manner of construction of the molecule, on the nature of the atoms which function as donor atoms, and on the nature of the metal atom. Three different types of sexadentate chelate compound appear, so far, to have been prepared and studied. The first of these, shown diagrammatically in Fig. 1a, may be considered as