However, the agreement of the results shows that in some cases the error due to the method of obtaining the ratio $(OBr^-)/(HOBr)$ was considerably greater. Any estimate of total error must be from the fluctuation in numerical results at each temperature.

TABLE I

IONIZATION CONSTANT OF HYPOBROMOUS ACID

Temp., °C.	Ionization constant, $K_i \times 10^9$
15.65	1.57 ± 0.22
25.28	2.53 ± .28
35.55	3.43 ± .18
45.55	4.33 ± .003

The ionization constant may be expressed as a function of the temperature as

$$\log K_i = 2802.49 + 0.7335T - 80670/T - 1115.1 \log T$$

From the equilibrium constants expressed as functions of the temperature the values were calculated for the thermodynamic relations; change in heat content, free energy and entropy of the three processes: distribution of bromine from carbon tetrachloride to water, evaporation of bromine from aqueous solutions and the ionization of hypobromous acid. The data are reported in Table II.

TABLE II

THERMODYNAMIC PROPERTIES OF AQUEOUS BROMINE SOLUTIONS

Temp., °C.	log K	ΔH, cal.	ΔF^0, cal.	ΔS^0, cal./°K.
Distribution from carbon tetrachloride				
15.00	−0.391	−1900	516	−8.5
25.00	− .430	−1600	587	−7.2
35.00	− .457	−1200	645	−6.0
45.00	− .474	− 850	690	−4.8
Evaporation of bromine				
15.00	−0.061	8400	80	28.8
25.00	+ .148	8500	−202	29.1
35.00	.345	8600	−487	29.5
45.00	.532	8700	−775	29.9
Ionization of hypobromous acid				
15.00	− 8.83	9300	11600	− 8.2
25.00	− 8.60	6800	11700	−16.6
35.00	− 8.47	5000	11900	−22.6
45.00	− 8.37	3800	12200	−26.2

The values for ΔH in calories per mole expressed as functions of the temperature are

$$\Delta H_d = -12250 + 35.84T$$

$$\Delta H_v = 12250 - 35.84\,T + 0.0779T^2$$

$$\Delta H_i = 3.69 \times 10^5 - 2215T + 3.355T^2$$

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Oxidation of Ferrous Sulfate by Ionizing Radiations from (n, α) Reactions of Boron and Lithium[1a]

BY ROBERT H. SCHULER[1b] AND NATHANIEL F. BARR[1c]

RECEIVED MAY 3, 1956

The high degree of reproducibility of irradiations carried out in the thermal-neutron facility of the Brookhaven reactor makes possible detailed study of chemical reactions produced by the very densely ionizing radiations from (n,α) activation of boron and lithium. The respective 100 e.v. yields for oxidation of ferrous ion by these radiations have been found to be 4.22 ± 0.08 and 5.69 ± 0.12 for 1 mM ferrous sulfate in aerated 0.8 N sulfuric acid solution and 3.77 ± 0.10 and 4.10 ± 0.10 in deaerated solution. From the above values, a yield of 6.7 in aerated solutions is estimated for the 2.7 Mev. tritium recoil produced in the neutron activation of lithium. The yields of ferric ion are increased slightly by saturating the solutions with oxygen and also by increasing the concentration of ferrous sulfate from 1 to 10 mM.

The over-all effects of radiation on aqueous systems can be described in terms of the formation of radicals $H\cdot$ and $\cdot OH$ and molecular products H_2 and H_2O_2. It has long been evident[2] that, while for sparsely ionizing radiations such as fast electrons the predominant effect is radical production, very densely ionizing radiations tend to produce high yields of molecular products. Although cyclotron beams provide a convenient tool for quantitative studies of the effect of ionization density on the yields of radiation-chemical reactions,[3] these measurements do not give accurate yields for α particle energies less than ~10 Mev. and deuteron energies less than ~5 Mev. For the purpose of establishing limiting values, independently determined yields for particles of high ionization density are desirable. Pertinent data are provided from studies of chemical reactions induced by the recoil particles from (n,α) activation of boron and lithium salts in solution. Such measurements also eliminate difficulties inherent in particle-beam experiments due to the presence of zones of high local radiation intensity.

Absolute radiation yields[4] for the oxidation of aerated ferrous sulfate have previously been determined by McDonell and Hart[5,6] as 4.2 for the radiations from the reaction B^{10} (n,α)Li^7 and 5.2 for the

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[1] (a) Research performed under the auspices of the U. S. Atomic Energy Commission. Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September 20, 1956; (b) Department of Radiation Research, Mellon Institute, Pittsburgh, Pa.; (c) Department of Biophysics, Sloan-Kettering Institute, New York, N. Y.

(2) A. O. Allen, (a) *J. Phys. Colloid Chem.*, **52**, 479 (1948); (b) *Radiation Research*, **1**, 85 (1954).

(3) R. H. Schuler and A. O. Allen, THIS JOURNAL, **77**, 507 (1955).

(4) All radiation yields are expressed as molecules reacting per 100 e.v. of absorbed energy (G). The symbols G_B and G_{Li} are used to represent the yields of the chemical reactions induced by heavy particle recoils from the nuclear reactions $B^{10}(n,\alpha)Li^7$ and $Li^6(n,\alpha)H^3$.

(5) W. R. McDonell, A.E.C. Document ANL-4949 (1952).

(6) W. R. McDonell and E. J. Hart, THIS JOURNAL, **76**, 2121 (1954).

recoil particles from $Li^6(n,\alpha)H^3$. Similar results have been obtained by Ehrenberg and Saeland.[7] Studies of more limited scope have also been reported by Draganic and Sutton.[8]

From the data of McDonell and Hart, G for the oxidation of ferrous ion by the 2.7 Mev. tritium recoil from lithium activation is estimated to be 5.8. This value appears to be low and inconsistent with the radiation yields of 6.2 ± 0.2[6] and of 5.9 ± 0.2[9] reported for the more densely ionizing α particles from Po^{210} since only a slight difference is expected between the yields for singly charged tritons and doubly charged α particles that have the same rate of energy loss.[3] The apparent discrepancy in the yields could arise from errors in the absolute dosimetry scales involved or from a low ratio of $G_{Li}(Fe^{+++})$ to $G_B(Fe^{+++})$.

The Biology Department of the Brookhaven National Laboratory maintains at the Brookhaven reactor a thermal-neutron irradiation facility[10] which provides highly thermalized neutrons with a very low γ-ray background. This facility is highly suitable for the determination of radiation-chemical yields in (n,α) activation experiments and has made possible considerable reduction of the uncertainty in the absolute yields of ferrous-ion oxidation. Since highly reproducible results (± 0.8%) could be obtained, details of the radiation-chemical reactions such as small variations in the yields due to changes in ferrous and oxygen concentrations could be studied. Yields for the oxidation of ferrous ion in deaerated ferrous sulfate, which previously had not been studied, have also been determined.

Experimental

Ferrous sulfate solutions in 0.8 N sulfuric acid and similar solutions containing added boric acid and lithium sulfate were irradiated for 10–20 hours at a flux of approximately 6.5×10^8 n. cm.$^{-2}$ sec.$^{-1}$. Quartz ampoules, 15 mm. in diameter and 30 mm. high, containing about 7 cc. of solution were supported in a horizontal block of Styrofoam in positions diagrammed in Fig. 1. This assembly was inserted into the thermal column while the reactor was running at full power. In the figure are indicated the neutron flux as well as absorbance (optical density) changes in ferrous sulfate solutions with and without added lithium sulfate. These values are from a typical run and indicate the precision obtained as well as the uniformity of the neutron flux.

Flux Measurements.—The neutron flux in the central volume used in these irradiations has been shown by gold monitoring to be uniform within a few per cent. There is little variation (±0.7%) in the horizontal plane although the flux does decrease by about 4% from the bottom to the top of the cells.[11] The neutrons are highly thermalized, as shown by a cadmium ratio of 1:4000.[10] Three weighed 0.001 in. gold foils were irradiated along with each set of boric acid–ferrous sulfate solutions, and the flux ϕ was determined from the standard relation

$$\phi = A/[n\sigma_{Au}(1 - e^{-\lambda t})] \qquad (1)$$

where A/n is the specific activity of the gold in disintegrations/sec./atom of gold, λ the Au^{198} decay constant, and t the duration of irradiation. It was assumed that the flux was constant during the course of the irradiation and that the gold activation cross-section σ_{Au} is 98×10^{-24} cm.^{2}. A correction of 0.6% has been applied for self-shielding of the gold monitors.

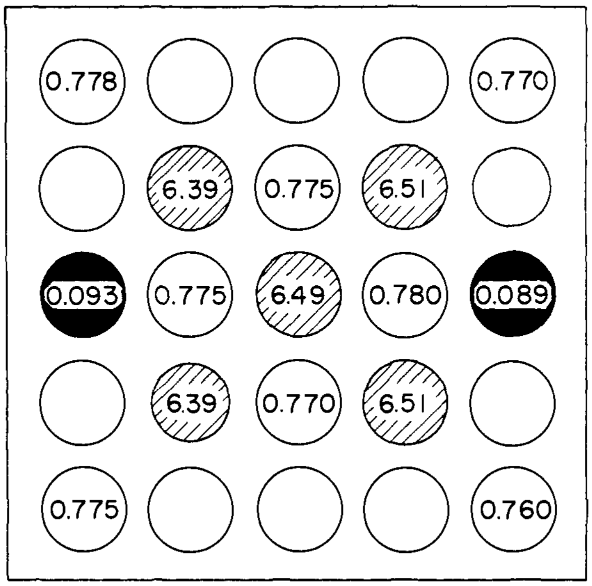

Fig. 1.—Irradiation matrix consisting of Styrofoam block 6″ × 6″ × 2″ having $^3/_4$″ holes on 1″ centers for positioning samples. The numbers in the open circles represent the absorbance (optical density) of 1 mM ferrous sulfate solutions containing 0.355 N lithium ion which were irradiated for 18.0 hours. The data in the darkened circles represent the absorbance of irradiated ferrous sulfate solutions not containing lithium sulfate. The neutron flux (n. cm.$^{-2}$ sec.$^{-1}$ × 10^{-8}) as determined by individual gold monitors is given in the shaded circles.

Absolute Counting of Au^{198}.—The activities of the gold samples were determined by absolute β-γ coincidence counting.[12] Because the high activity of the samples ($\sim 10^6$ disintegrations/sec.) necessitated a decay period of 10–15 days before coincidence measurements could be made, auxiliary measurements were made immediately after irradiation on a calibrated low geometry scintillation counter.

In the coincidence measurements a 95 mg./cm.^{2} beryllium absorber was interposed between the sample and the β-detector to eliminate the conversion electrons from the 411-kev. γ-ray. A 284 mg./cm.^{2} beryllium absorber shielded the β-radiation from the γ-detector. Measurements were made on the relative β, γ, and β-γ coincidence rates and measured corrections were applied for γ-γ and chance coincidences, γ-ray detection by the β-counter, and background. The absolute decay rate of the sample was calculated as

$$A = \frac{1}{1.01}\,\frac{N_\beta N_\gamma}{N_{\beta\gamma}} \qquad (2)$$

where the 1% correction has been applied for the excess γ-radiation originating from the 290-kev. β-transition.[13]

All activities were corrected for Au^{198} decay assuming a half-life of 2.698 days.[12] Coincidence measurements of the absolute activity of one gold sample during the period 10 to 21 days after bombardment gave a half-life of 2.695 days and eight determinations of the activity during this period, when corrected to the end of irradiation ($t_{1/2}$ = 2.698 days) had a standard deviation of ±0.5%.

Ferric Iron Analysis.—Ferric iron was determined by measurement of the absorbance of solutions at 305 mμ with a Beckman DU spectrophotometer. The extinction co-

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(7) N. Ehrenberg and E. Saeland, Joint Establishment for Nuclear Energy Research, Report No. 8, Kjeller per Lillestrom, Norway (1954).

(8) I. Draganic and J. Sutton, *J. chim. phys.*, **52**, 327 (1955).

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

(10) Described by H. J. Curtis, S. R. Person, F. B. Oleson, J. E. Henkel and N. Delihas, *Nucleonics*, **14**, No. 2, 26 (1956).

(11) N. Delihas, private communication.

(12) H. H. Seliger and A. Schwebel, *Nucleonics*, **12**, No. 7, 54 (1954).

(13) Seliger and Schwebel (ref. 12) have compared the β-γ coincidence method to other absolute standardization methods. Recent work at the National Bureau of Standards (H. H. Seliger, private communication) has given almost identical values (6.971 as compared to 6.969) for β-γ and $4\pi\beta$ methods.

efficient of ferric iron in 0.8 *N* H_2SO_4 in the absence of added sulfate is taken as 2174 (mole/l.)$^{-1}$ cm.$^{-1}$ at 23.7°.[14] The addition of lithium sulfate to 0.8 *N* sulfuric acid increases the effective ferric iron extinction coefficient as shown in Fig. 2. The addition of boric acid has a negligible effect on the extinction coefficient.

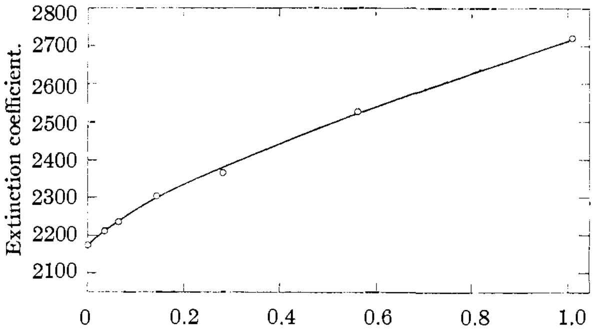

Fig. 2.—Molar extinction coefficient at 305 mμ for ferric iron in 0.8 *N* sulfuric acid as a function of the concentration of added lithium sulfate. Measurements were made on 0.2 m*M* Fe^{+++} solutions at 23.7° with Beckman DU spectrophotometer.

Materials.—All chemicals were reagent grade. The sample of lithium sulfate monohydrate used was found from loss in weight at 600° to have the composition $Li_2SO_4 \cdot 1.009H_2O$. Flame-photometric analysis showed the sodium and potassium content of this lithium sulfate sample to be negligible.

Sample Preparation.—All solutions to be irradiated contained 0.8 *N* sulfuric acid and 1 m*M* sodium chloride and except where noted were air-saturated. Weighed samples of boric acid and lithium sulfate monohydrate were dissolved in the ferrous sulfate solution. Degassed solutions were prepared in an apparatus similar to that described by Johnson and Allen.[15] The solution to be irradiated was degassed in a large flask and transferred under vacuum to quartz ampoules connected to the flask through 4 cm. of 1 mm. quartz capillary tubes and a graded seal. After completely filling the cells and capillaries, the latter were broken. The capillary ends remained exposed to air. Contact of the solution and oxygen was prevented by the low rate of diffusion through the long capillary. Solutions similarly deaerated were allowed to stand for 48 hours and then irradiated in a Co^{60} source. The observed rate of oxidation was 54% of that of aerated solutions in agreement with yields obtained for deaerated solutions using vessels sealed after deaeration.[16] The solution remaining in the degassing apparatus was then equilibrated with air and transferred to stoppered irradiation vessels. Oxygen-saturated solutions were prepared by bubbling the gas, which had been passed through concentrated sulfuric acid and 10 m*M* ferrous sulfate, through the solution to be irradiated and inserting a stopper so as to leave no gas space above the liquid.

Results

Absolute Yields.—Table I summarizes data obtained for ferrous sulfate solutions containing added boric acid. The absolute yields listed in the last column are calculated from equation 3

$$G_{\mathrm{B}}(\mathrm{Fe}^{+++}) = \frac{(\mathrm{Fe}^{+++})}{(\mathrm{H_3BO_3})\sigma_{\mathrm{B}}\phi t E_0(\mathrm{B})\gamma} \times 100 \qquad (3)$$

The boron absorption cross-section, σ_B, is taken as 755×10^{-24} cm.^{2}.[17] The average energy absorbed by the solution from the heavy particle recoils, $E_0(B)$, is taken as 2.35×10^6 e.v. per nuclear event and is obtained by correcting the exothermicity of the (*n*,α) reaction, 2.79 Mev., for the 0.48 Mev. γ-ray which occurs in 93% of the reactions.[18] The term γ (= 1.007) is included to correct for the absorption of the γ-radiation from the (n, α) reaction and assumes 1% absorption of this radiation within the sample and a relative yield 3.6 times larger than for the heavy particles. The ferric-iron concentration is that due to the neutron irradiation, obtained by correcting for the effect of the γ-radiation present in the thermal column. This background was determined from the ferrous sulfate oxidation in boron-free solutions. Attenuation of the neutron flux by absorption within the sample is estimated from the apparent 16% drop in yield for the 0.361 *M* boric acid solution (Table I). It is assumed, from this measurement, that self-shielding decreases the average flux by 0.5% for each 0.01 *M* concentration of boric acid. This correction corresponds to an average neutron path length of 2.2 cm. within the sample. In column 2 of Table I data are given on the rate of ferrous sulfate oxidation of the various solutions in a Co^{60} source. No effect of the boric acid on the γ-ray induced oxidation is observed even for the most concentrated (0.36 *M*) solution.

A comparison of the oxidation of ferrous ion by neutron reactions on lithium and on boron is given in Table II. The yield due to the lithium reaction obtained from this comparison is calculated from eq. 4

$$G_{\mathrm{Li}}(\mathrm{Fe}^{+++}) = \frac{(\mathrm{Fe}^{+++})_{\mathrm{Li}}}{(\mathrm{Fe}^{+++})_{\mathrm{B}}}\,\frac{(\mathrm{H_3BO_3})}{(\mathrm{Li}^+)}\,\frac{\sigma_{\mathrm{B}}}{\sigma_{\mathrm{Li}}}\,\frac{E_0(\mathrm{B})\gamma}{E_0(\mathrm{Li})}\,G_{\mathrm{B}}(\mathrm{Fe}^{+++}) \qquad (4)$$

where $G_B(Fe^{+++})$ is taken as 4.22, σ_{Li} as 71×10^{-24} cm.^{2} and $E_0(Li)$ as 4.78 Mev. Self-shielding corrections of 0.5% for each 0.01 *M* concentration of boric acid and 0.1 *N* lithium ion have been applied. Irradiation of ferrous sulfate solutions containing added lithium sulfate in the Co^{60} source shows that the added salt has no effect on the rate of oxidation.

Errors.—The radiation yield in the boron recoil experiments is found to be 4.22 ± 0.08 where the standard error is estimated in the following manner. The standard deviation between the individual sets of experiments (1%) is in agreement with the mean standard deviations for individual values within a set of 0.8% in the chemical measurements and 0.8% in the flux measurements. Other sources of random error, therefore, appear to be absent. Among the systematic errors, the largest is due to the uncertainty in the absorption cross-sections of boron (± 0.5%) and gold (± 1%).[17] Since the cross sections of both boron and gold have the same dependence on neutron energy in the thermal region and since they enter into the determination as a ratio, no additional error is introduced by slight deviations of the neutron energy distribution from a thermal spectrum. The systematic error in the absolute counting of gold is largely due to the cor-

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

(15) E. R. Johnson and A. O. Allen, This Journal, **74**, 4147 (1952).

(16) N. F. Barr and C. G. King, *ibid.*, **78**, 303 (1956).

(17) D. J. Hughes and J. A. Harvey, A.E.C. Document BNL 325 (1955).

(18) Reference 7 contains an excellent discussion of the physics involved, particularly with respect to the contribution of minor nuclear reactions.

TABLE I

ABSOLUTE YIELD OF FERROUS SULFATE OXIDATION IN 1 m*M* SOLUTION INDUCED BY RECOILS FROM THE REACTION $B^{10}(n,\alpha)Li^7$

Boron concn., $[H_3BO_3]$, *M*	Rate of oxidn.[a] in Co^{60} source, moles l.$^{-1}$ min.$^{-1}$ $\times 10^6$	Irradiation period, hr.	Neutron flux, n cm.$^{-2}$ sec.$^{-1}$ $\times 10^{-8}$	Absorbance (A.) Boron soln.	Absorbance (A.) Blank[d]	Ferric ion[b] produced, moles/l. $\times 10^4$	Specific yield $\left(\frac{Fe^{+++}}{B}\right)$ / n./cm.^{2}	Self-shielding[c] corr.	$G(Fe^{+++})$, molecules/100 e.v.
0.0466	..	15.4	6.47	0.336(3)[e]	0.073(2)[e]	1.211	7.25	0.977	4.17
.0226	8.02	15.8[f]	6.48	.209(3)	.074(3)	0.621	7.45	.989	4.22
.0484	7.98	15.8[f]	6.48	.359(2)	.074(3)	1.310	7.34	.976	4.22
.0695	8.01	15.8[f]	6.48	.476(2)	.074(3)	1.849	7.21	.965	4.20
.0535	..	16.8	6.91	.380(4)	.075(2)	1.403	7.34	.974	4.23
.0312	8.00	17.8	6.61[i]	.298(4)	.083(2)	0.990	7.49	.984	4.28
.0361	7.98	18.5	6.35	.328(4)	.080(2)	1.140	7.44	.982	4.26
.0226	8.02	19.8[g]	6.98	.268(2)	.086(2)	0.837	7.24	.989	4.23
.0484	7.98	19.8[g]	6.98	.465(2)	.086(2)	1.743	7.25	.976	4.17
								Average	4.22
.361	8.04	3.35[h]	6.43	.407(2)	.020(2)	1.781	6.36	(.839)	
.0695	8.01	3.35[h]	6.43	.106(2)	.020(2)	0.395	7.33		

[a] Rate as of January 1, 1956. The oxidation rate in boron-free solutions is 8.04×10^{-6} mole l.$^{-1}$ min.$^{-1}$. [b] Oxidation corrected for background. [c] Calculated as 0.5% per 0.01 *M* $[H_3BO_3]$. [d] Boron-free ferrous sulfate irradiated simultaneously with other solutions. [e] Number of samples in parentheses. [f,g,h] Simultaneous irradiations. [i] Gold activity determined with scintillation counter only.

TABLE II

COMPARISON OF THE YIELDS OF FERROUS SULFATE OXIDATION IN 1 m*M* SOLUTION INDUCED BY RECOILS FROM THE REACTIONS $Li^6(n,\alpha)H^3$ AND $B^{10}(n,\alpha)Li^7$

Lithium concn. $[Li^+]$, *N*	Co^{60} [a,b] rate, moles l.$^{-1}$ min.$^{-1}$ $\times 10^6$	Ferric ion[b,c] produced in lithium soln., moles/l. $\times 10^4$	Boron concn. $[H_3BO_3]$, *M*	Ferric ion[c] produced in boron soln., moles l.$^{-1}$ min.$^{-1}$ $\times 10^6$	$G_{Li}(Fe^{+++})$
0.0494[d]	8.08	0.891(4)[e]	0.0312	2.150(3)[e]	5.73
.240	8.07	1.796(4)	.0589	1.700(3)	5.67
.265	7.99	1.509(4)	.0484	1.061(4)	5.70
.294[f]	8.06	2.509(2)	.0312	1.046(2)	5.65
				Av.	5.69

[a] Rate of oxidation of lithium sulfate solution in Co^{60} source, as of January 1, 1956. [b] Obtained using extinction coefficients of Fig. 1. [c] Corrected for γ background. [d] Irradiated 42 hours. [e] Number of samples in parentheses. [f] Solution made up from weighed sample of Li_2CO_3 which was dissolved in an equivalent amount of concentrated sulfuric acid.

rection applied for excess γ-radiation and is estimated to be ± 0.5%. Because of the vertical variation of the flux, an error of ±0.5% must be included for uncertainty in neutron sampling by the gold. The correction applied for self-absorption of the 0.48 Mev. γ-radiation introduces an error of ±0.5% and the uncertainty in the extinction coefficient of ferric ion an additional ±0.5%. Errors due to variation of the flux with time, correction for decay of the gold, instrumentation in the coincidence counting of gold, self-shielding of the samples, and boric acid composition are considered negligible. The above errors give a combined standard error of 1.8% in the absolute value of G_B.

The errors in the relative yields for oxidation of iron by the recoils from boron and lithium (n, α) reactions consists entirely in the uncertainties associated with the precision of the measurements (±0.6%) and in the systematic errors involved in the recoil energies (±0.5%) and in the relative absorption cross sections of boron (±0.5%) and lithium (±1.4%). A combined standard deviation of 1.7% is obtained for the value $G_{Li}(Fe^{+++})$ relative to $G_B(Fe^{+++})$. Taking into account duplication of certain systematic errors involved both in the determination of $G_B(Fe^{+++})$ and in the relative yields for the boron and lithium (n, α) radiations, a standard deviation of 2% is estimated for the absolute yield in the lithium experiments ($G_{Li}(Fe^{+++}) = 5.69 \pm 0.12$).

Deaerated Solutions.—Data on relative yields in the presence and absence of dissolved air are given in Table III. The γ-radiation background correction for the deaerated solutions is taken as 53% of that observed in the aerated solutions.[16] In these studies, 10 m*M* ferrous sulfate was used since at lower concentrations back reaction due to the build-up of ferric ion results in a drop in the apparent yield of oxidation of deaerated solutions.[19]

Oxygen-saturated Solutions.—Comparative data on air- and oxygen-saturated 1 m*M* ferrous sulfate solutions, given in Table IV, show slight increases in the yields due to the increased oxygen concentration. The effects while small are greater than the errors involved. A similar comparison with Co γ-radiation did not show an increase in yield. The observed increase in the heavy particle yields is, therefore, presumably not an impurity effect.

Effect of Ferrous Ion Concentration.—Data on the effect of increasing the concentration of ferrous ion from 1 to 10 m*M* on the radiation yield are given in Table V. The production of ferric iron due to the γ-ray background in the thermal column is the same for 1 and 10 m*M* solutions after correction for the appreciable rate of spontaneous oxidation in 10 m*M* solution. Initially measurements were made using solutions containing different concentrations of boric acid and lithium sulfate and can be compared only after these concentration differences are taken into account. More direct comparisons

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(19) A. O. Allen and W. Rothschild, *Radiation Research*, 3, 210 (1955).

TABLE III

COMPARISON OF FERROUS ION OXIDATION IN DEAERATED AND AERATED 10 mM SOLUTIONS

Solution	Absorbance (A)	Correction for γ background	Cor. absorbance	$\frac{G(\text{Fe}^{+++})\text{aer.}}{G(\text{Fe}^{+++})\text{ deaer}}$
	$B^{10}(n,\alpha)Li^7$			
10 mM Fe^{++}	0.080(2)[a]	...	...	
+0.04 M H_3BO_3 (aerated)	.385(2)	0.080	0.305	1.12 ± 0.02[b]
+ .04 M H_3BO_3 (deaerated)	.313(4)	.042	.271	
	$Li^6(n,\alpha)H^3$			
10 mM Fe^{++}	.076(2)	...	...	
+0.6 N Li_2SO_4 (aerated)	.917(2)	0.089[c]	0.828	1.38 ± 0.01[b]
+ .6 N Li_2SO_4 (deaerated)	.646(4)	.047	.599	
10 mM Fe^{++}	.034(2)	...	...	
+0.6 N Li_2SO_4 (aerated)	.588(2)	0.038[c]	0.550	1.40 ± 0.02[b]
+ .6 N Li_2SO_4 (deaerated)	.412(4)	.020	.392	

[a] Number of samples in parentheses. [b] Standard deviations calculated from the precision of the individual determinations. [c] Blank corrected for increased extinction coefficient of ferric ion in the presence of 0.6 N Li_2SO_4.

TABLE IV

COMPARISON OF AIR- AND OXYGEN-SATURATED 1 mM SOLUTIONS

Solution		Absorbance (A) Solution	Correction for γ background	Corrected	$\frac{G(\text{Fe}^{+++})\text{air sat.}}{G(\text{Fe}^{+++})\text{oxy. sat.}}$
		$B^{10}(n,\alpha)Li^7$			
0.046 M H_3BO_3	air-satd.	0.420(3)[a]	0.104	0.316	1.022 ± 0.018[b]
	oxygen-satd.	.427(3)	.104	.323	
.046 M H_3BO_3	air-satd.	.344(3)	.080	.264	1.022 ± 0.017[b]
	oxygen-satd.	.350(3)	.080	.270	
		$Li^6(n,\alpha)H^3$			
.312 N Li_2SO_4	air-satd.	.636(3)	.082[c]	.554	1.058 ± 0.013[b]
	oxygen-satd.	.668(3)	.082	.586	
.321 N Li_2SO_4	air-satd.	.584(3)	.077[c]	.507	1.079 ± 0.010[b]
	oxygen-satd.	.624(3)	.077	.547	

[a] Number of samples in parentheses. [b] Standard deviations calculated from the precision of the individual determinations. [c] Blank corrected for increased extinction coefficient of ferric iron in the presence of 0.3 N Li_2SO_4.

TABLE V

COMPARISON OF FERROUS OXIDATION IN 1 AND 10 M SOLUTIONS

Solution	$[Fe^{++}]$, mM	Absorbance (A) Solution	Blank	Rel. yield $\frac{\text{moles Fe}^{+++}}{\text{mole B or Li}}$	$\frac{G(\text{Fe}^{+++})10}{G(\text{Fe}^{+++})1}$
		$B^{10}(n,\alpha)Li^7$			
0.0466 M H_3BO_3	1	0.336(3)[a]	0.073	2.597	1.043 ± 0.010[b]
.0472 M H_3BO_3	10	.351[c](3)	.072[c]	2.708	
.0535 M H_3BO_3	1	.380(4)	.075	2.621	1.036 ± 0.011[b]
	10[d]	.391[c](4)	...	2.719	
		$Li^6(n,\alpha)H^3$			
.199 N Li_2SO_4	1	.376(3)	0.063	6.65	1.027 ± 0.010[b]
.203 N Li_2SO_4	10	.391[c](3)	.062[c]	6.83	
.241 N Li_2SO_4	1	.514(4)	.084	7.45	1.028 ± 0.007[b]
	10[d]	.526[c](4)	...	7.66	

[a] Number of samples in parentheses. [b] Standard deviation calculated from precision of the individual determinations. [c] Corrected for an increase in A (∼0.015) due to the spontaneous oxidation of ferrous ion during irradiation. [d] Solid ferrous ammonium sulfate added to 1 mM solution to increase ferrous 10 N concentration to 10 mM.

were made by the addition of solid ferrous ammonium sulfate to 1 mM solutions.

Discussion

Complete agreement is found between the present measurements of $G_B(Fe^{+++})$, 4.22 ± 0.08, and the previous determinations of McDonell and Hart, 4.2 ± 0.4,[6] and of Ehrenberg and Saeland, 4.1 ± 0.4.[7] The increased accuracy of the present work is important in comparing absolute yields observed for these heavy particle radiations with the yields measured under other dosimetric conditions, *e.g.*, cyclotron radiations.[3]

The value given here for $G_{Li}(Fe^{+++})$, 5.69 ± 0.12, is somewhat higher than the reported values of 5.2 ± 0.4[6] and 5.4 ± 0.4.[7] The ratios of $G_{Li}(Fe^{+++})/G_B(Fe^{+++})$ observed here and in the work of Ehrenberg and Saeland[7] are in somewhat better agreement than the absolute yields. However, in the work of McDonell and Hart[6] the yield of 5.2 was obtained without applying a correction for the increased ferric ion extinction coefficient in the presence of added sulfate. Application of this correction lowers their yield to 4.5. This value is, in addition to being in disagreement with the present results and those of Ehrenberg and Saeland, inconsistent with the yield for the very much more densely ionizing (n, α) products from boron. The results of Draganic and Sutton[8] on ferrous sulfate oxidation by the recoils from the $Li^6(n,\alpha)H^3$ reaction are only of qualitative value owing to large uncertainties in the nature of the neutron spectrum.

Studies of chemical reactions induced by the recoils from (n, α) reactions in lithium are important because they provide data on the radiation chemical effects for low energy protons. Of the energy released in the reaction 57.1% or 2.71 Mev. goes to the recoiling triton which has the same rate of energy loss as that of a 0.9 Mev. proton. Since the yield of the simultaneously emitted α-particle can be estimated from the boron activation experiments, the yield due to the triton can be calculated from eq. 5.

$$G_T = G_\alpha + (G_{Li} - G_\alpha)/0.57 \qquad (5)$$

Taking into account the lower ionization density of the α radiation produced in the activation of lithium, a value of 4.4 is estimated for $G\alpha$ in aerated solutions. From this the triton yield is calculated to be 6.7. This yield is higher than the values reported for the more densely ionizing Po^{210} α-radiation but is slightly lower than the value of 7.3 observed for cyclotron helium ions having the same rate of energy loss.[20]

If it is assumed that the ratios of aerated to deaerated yields (measured in 10 m*M* solutions) are unaffected by ferrous ion concentration, radiation yields of $G_B(Fe^{+++})_{deaerated} = 3.77$ and $G_{Li}(Fe^{+++})_{deaerated} = 4.10$ are obtained for 1 m*M* solutions. From these values a yield of 4.4 is estimated for the lithium recoil triton in deaerated solution. The values for the observed yields and those calculated for the lithium recoil triton are summarized in Table VI.

TABLE VI

FERROUS OXIDATION YIELDS

	Radiations from $B(n,\alpha)$-Li^7	Radiations from Li^6-$(n,\alpha)H^3$	2.7 Mev. Triton[a] (calcd.)
1 m*M* ferrous sulfate—air-satd.	4.22	5.69	6.66
—deaerated	3.77[b]	4.10[b]	4.35
—oxygen-satd.	4.31	6.02	7.16
10 m*M* ferrous sulfate—air-satd.	4.38	5.85	6.82
—deaerated	3.91	4.26	4.52

[a] Rate of energy loss equivalent to 0.9 Mev. proton. [b] Calculated assuming the ratio of aerated to deaerated yields is the same as at 10 m*M*.

The relative importance of the hydrogen atom and molecular product yields can be calculated from the yields of oxidation of iron in aerated and deaerated solution provided the mechanism of the reactions are understood. In aerated solution reaction 1–4

$$H\cdot + O_2 \longrightarrow HO_2\cdot \qquad (1)$$

$$HO_2\cdot + Fe^{++} + H^+ \longrightarrow H_2O_2 + Fe^{+++} \qquad (2)$$

$$H_2O_2 + Fe^{++} \longrightarrow OH^- + \cdot OH + Fe^{+++} \qquad (3)$$

$$\cdot OH + Fe^{+++} \longrightarrow OH^- + Fe^{+++} \qquad (4)$$

lead to the oxidation of ferrous ion. In deaerated solutions hydrogen atoms oxidize ferrous ion according to (5)

$$H\cdot + H^+ + Fe^{+++} \longrightarrow H_2 + Fe^{+++} \qquad (5)$$

If the primary yields for production of hydrogen atoms, hydroxyl radicals and hydrogen peroxide are represented by $G(H\cdot)$, $G(\cdot OH)$ and $G(H_2O_2)$, the yield of ferrous oxidation in deaerated solutions is given as

$$G(Fe^{+++})_{deaerated} = G(\cdot OH) + 2G(H_2O_2) + G(H\cdot)$$

or

$$= G(-H_2O) + G(H\cdot)$$

where

$$G(-H_2O) = G(\cdot OH) + 2G(H_2O_2)$$

In aerated solutions

$$G(Fe^{+++})_{aerated} = G(-H_2O) + 3G'(H\cdot)$$

where

$$G'(H\cdot) = G(H\cdot) + \Delta$$

and Δ is the increase in hydrogen atom yield due to scavenging effects of oxygen in the track.[21]

From the above, the hydrogen atom yield is calculated as

$$G(H\cdot) = 1/2[G(Fe^{+++})_{aerated} - G(Fe^{+++})_{deaerated}] - 3/2\Delta$$

and the net water decomposition yield is given by

$$G(-H_2O) = G(Fe^{+++})_{deaerated} - G(H\cdot)$$

If we neglect scavenging effects on the track, *i.e.*, take $\Delta = 0$, then for the recoils from the boron (n,α) reaction $G_B(H\cdot) = 0.23$ and $G_B(-H_2O) = 3.6$. The almost negligible difference in yield in this case between air- and oxygen-saturated ferrous sulfate indicates that the scavenging effect of oxygen is small. The net water decomposition by the 2.7 Mev. tritons from lithium is, however, significantly influenced by the effect of oxygen on the molecular yield and must be deferred until further measurements are made for this radiation.[22] The above value of the net water decomposition yield, 3.6, may be compared to the value of 3.5 estimated from measurements at the Oak Ridge National Laboratory[23] on hydrogen production induced by the recoil fragments from uranium fission. It is seen that the net decomposition of water is little affected by changes in the rate of energy loss of the ionizing particle above 10 e.v./Å. The yield is, however, considerably less than 4.5, the value calculated from measurements of the oxidation of aerated and deaerated ferrous ion by Co^{60} γ-radiation.

The effect of oxygen on the track processes for these densely ionizing radiations is not unexpected in view of considerations of the competition involved in the track. The qualitative relationship between the molecular hydrogen yield and the

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[20] A. O. Allen and R. H. Schuler, to be published.

[21] H. A. Schwarz, THIS JOURNAL, **77**, 4960 (1955).

[22] A preliminary estimate of $G(-H_2O) = 3.4$–3.6 for these tritons may be made if we assume that 5–10% of the yield of oxidation in aerated solution is due to the effect of oxygen on the track processes.

[23] J. W. Boyle, C. J. Hochanadel, T. J. Sworski, J. A. Ghormley and W. F. Kieffer, Proc. International Conf. on the Peaceful Uses of Atomic Energy, Vol. 7, p. 576 (1956).

oxygen concentration is of the type described by Schwarz[21] for diffusion controlled radiation processes. It is seen in the present work that the effect of increasing the oxygen concentration is small for the (n,α) recoils from boron although considerably larger for the lithium recoil triton ($\sim$8%). Yields of ferrous ion oxidation are increased by 0.08 and 0.6, respectively, for the 1–2 Mev. α-radiation and 2.7 Mev. triton in going from air- to oxygen-saturated solutions.[24]

The increase of the oxidation yield with increased ferrous sulfate concentration, though small, appears to be quite real. A mechanism by which the ferrous ion might increase the yield is not immediately obvious. Scavenging of the hydrogen atoms within the radiation track by the ferrous ion does not appear to be significant because of the low rate of this reaction. Reaction of ferrous ion with hydroxyl radicals does not directly increase the yield since one ferrous ion is oxidized for each hydroxyl equivalent whether or not peroxide is formed as an intermediate. Reaction of ferrous ion with hydroxyl radicals within the track can, however, indirectly influence the yield by decreasing the back reaction of ·OH with H· thereby freeing hydrogen atoms with an ultimate increase in the oxidation yield.

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[24] J. A. Ghormley and C. J. Hochanadel, *Radiation Research*, **3**, 227 (1955), have shown that for γ-rays the yield of hydrogen from oxygen-saturated KBr solutions is 13% less than for degassed solutions. However, because of the low contribution of the molecular yield to the over-all decomposition, $G_\gamma(\mathrm{Fe}^{+++})$ is increased by only a negligible amount.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Activity Coefficients of Electrolytes of High Charge: Potassium Octacyanomolybdate (IV) and Tris-(ethylenediamine)-Platinum(IV) Chloride

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The mean activity coefficients of potassium octacyanomolybdate(IV) and tris-(ethylenediamine)-platinum(IV) chloride in fairly concentrated aqueous solutions have been determined by isopiestic comparison with potassium chloride solutions. It appears to be possible to predict the activity coefficients of these salts in solutions up to about 0.1 *m* by the Debye–Hückel equation, using $\mathring{a}$ = 4.33 and 3.61, respectively.

In this Laboratory, we have been studying various equilibria involving complex ions of high charge and have found interpretation of these equilibria complicated by a notable lack of information on the activity coefficients for fairly concentrated solutions of such electrolytes. Prompted by these considerations, we have undertaken a program of measuring the activity coefficients of very stable complex salts with the view of using them as models for the estimation of activity coefficients of other complexes of similar type and configuration.

There is a paucity of information concerning the activity coefficients of electrolytes of the 1–4 and 4–1 types. Robinson has studied potassium hexacyanoferrate(II)[1] and thorium(IV) chloride,[2] but certainly the latter cannot qualify as a strong electrolyte and hydrolysis appears to disqualify it as a 4–1 electrolyte.

According to the work of Kolthoff and Tomsicek,[3] potassium octacyanomolybdate(IV) and the acid $[\mathrm{HMo(CN)_8}^{\equiv}]$ appear to be strong electrolytes and stable toward oxidation or reduction in aqueous medium. Tris-(ethylenediamine)-platinum(IV) chloride represents a somewhat less satisfactory example, as we shall see, but it is very stable and we have not been able to detect much hydrolysis.

Experimental

Potassium octacyanomolybdate(IV) was prepared and purified according to the directions of Furman and Miller.[4] The product, $\mathrm{K_4Mo(CN)_8{\cdot}2H_2O}$, was recrystallized three additional times by the recrystallization method of Furman and Miller. The salt was weighed as the air-dried dihydrate.[3]

Basolo, Bailar and Tarr have previously prepared tris-(ethylenediamine)-platinum(IV) chloride,[5] but we found that the product contained a small amount of dichlorobis-(ethylenediamine)-platinum (IV) chloride. We, therefore, put the mixture through a four step fractional crystallization (the tris-(ethylenediamine) compound was concentrated in the least soluble fraction) and thus obtained, after drying the product over barium oxide or at 75° in an oven, the compound in good purity. (*Anal.* Calcd. for $\mathrm{Pt(en)_3Cl_4}$ (en = ethylenediamine): Pt, 37.73; Cl, 27.41. Found for oven-dried material: Pt, 37.81; Cl, 27.29. Found for desiccated material: Pt, 37.85; Cl, 27.30. It appears that the compound originally precipitated from water at room temperature is the dihydrate, but water is quickly lost in the air and can be completely removed by drying over barium oxide. Once water is removed, the material does not absorb it rapidly and the anhydrous material can be weighed conveniently in the air.

The apparatus we have used for determining isopiestic molalities of the two salts and potassium chloride is a modified version of the one used by Scatchard, Hamer and Wood[6]

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[1] A. Robinson, THIS JOURNAL, **59**, 84 (1937).

[2] R. A. Robinson, *ibid.*, **77**, 6200 (1955).

[3] I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **40**, 247 (1936).

[4] N. H. Furman and C. O. Miller, "Inorganic Syntheses," Vol. 3, ed. by L. F. Audrieth, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 160.

[5] F. Basolo, J. C. Bailar and B. R. Tarr, THIS JOURNAL, **72**, 2438 (1950).

[6] G. Scatchard, W. J. Hamer and S. E. Wood, *ibid.*, **60**, 3061 (1938).