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force is compared to the inter-atomic force it assures an Einstein transition. The preceding comparison seems to indicate that a treatment of the non-ideal helium gas on the basis of the ideal B.E. fluid, where the non-ideal character, i.e., the inter-atomic force, is considered as a perturbation, cannot well be justified. The treatment where the non-ideal classical fluid is taken as the zero-order approximation, and where the symmetry in phase space would be considered as a perturbation, might lead to more plausible results.

Similar results have been obtained recently[6] through detailed and laborious studies on the theory of the second virial coefficient of helium at low temperatures.

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[6] Cf. J. De Boer and A. Michels, Physica 9, 409 (1938) and also B. Kahn, Dissertation, Utrecht (1938).

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The Photolysis of Persulfate*

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The photochemical efficiency, ϕ, for the decomposition of persulfate by light of λ254 mμ is determined by comparison with ϕ for the uranyl oxalate actinometer. The persulfate content was followed by the method of Kurtenacker and Kubina and in representative cases the hydrogen ion produced also was determined. The equation $S_2O_8^{=}+H_2O+h\nu=2HSO_4^{-}+O_2/2$ accounts quantitatively for the data. Evidence is given to show that the main reaction is not the decomposition of SO_4^{-}. Six tenths of a mole of persulfate is decomposed per Einstein absorbed by persulfate in dilute neutral and alkaline solutions when all oxidizable material is absent. Acetic acid increases this yield to unity but non-oxidizable ions have a depressing effect. Many of the observations of Morgan and Crist also are verified. At constant ionic strength, ϕ remains nearly unchanged in alkali, but drops abruptly to less than 0.01 when solutions are acidified suggesting the formation of a weak acid containing photochemically inert persulfate. Absorption spectra and conductivity measurements, however, give no indication that such a weak acid is formed. The explanation offered for these facts is that the hydrogen ion associates with and thereby stabilizes the persulfate ion after the latter absorbs a photon. The stabilizing effects of other ions, except perhaps bisulfate, is much less than hydrogen which is thought to be related, among other things, to their larger size. Hydrogen peroxide was not found in any of the solutions.

ULTRAVIOLET light of λ254 mμ decomposes colorless aqueous solutions of persulfate, the reaction $H_2O+S_2O_8^{=}+h\nu=2HSO_4^{-}+O_2/2$ accounting quantitatively for the increase in acidity accompanying the loss of persulfate[1] as found in experiments 9c and 12 summarized in Table I and in the text under H^+ ion yields.

Crist[2] precipitated the liberated sulfate as the barium salt and found it corresponded to the loss of one mole of persulfate per Einstein absorbed at λλ302, 265, and 254 mμ by $0.05M$ $K_2S_2O_8$ when the solution undergoing photolysis was alkaline or had not been acidified. The presence of electrolytes decreased[1–4] the photochemical efficiency, ϕ, sulfuric acid being especially effective.

Since this work, Kurtenacker and Kubina[5] have improved greatly the method for determining persulfate. Their method as used in this research gives values for ϕ about 0.6 as large as

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* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 493.

[1] J. L. R. Morgan and R. H. Crist, J. Am. Chem. Soc. 49, 960 (1927) mentioned this fact but gave no data.

[2] R. H. Crist, J. Am. Chem. Soc. 54, 3939 (1932).

[3] J. L. R. Morgan and R. H. Crist, J. Am. Chem. Soc. 49, 16 (1927).

[4] J. L. R. Morgan and R. H. Crist, J. Am. Chem. Soc. 49, 338 (1927).

[5] A. Kurtenacker and H. Kubina, Zeits. f. anal. Chemie 83, 14 (1930).

those published by Crist.[2] Ammonium, potassium, and sodium persulfates give practically the same results. Most of the work was done on the very soluble sodium salt (at least 2 F.W. dissolve per liter at 25°) because solutions could be made concentrated enough to absorb all but a negligible part of λ254 mμ before it could reach the stirrer.

EXPERIMENTAL WORK

The ammonium, potassium, and sodium persulfates were recrystallized specimens of the best commercial products. The crystals were formed usually from alkaline solutions at less than 35° by evaporation of the colorless mother liquors to 50–70 percent solids. The white crystals were stored in the dark in a vacuum over anhydrone. When added to water, they cooled the solution.

The fresh air dried ammonium salt was found to be a dihydrate by analysis for persulfate. Some of it after standing in a vacuum was used in experiment 1 where it still contained 1.6 moles of water per mole of persulfate. The other persulfates were anhydrous even when only air dried.

A blue crust formed on the crystals of sodium persulfate when allowed to dry in air while in contact with alkali. The phenomenon was reversible so that solutions of the material were colorless. However, when all alkali was washed from the colorless sodium persulfate crystals before they were allowed to dry, they remained colorless on drying and did not change on standing out of direct sunlight. The reflection spectrum of the blue compound is being investigated.

Uranyl oxalate and sulfate and the oxalic acid used in the actinometer were air dried, recrystallized specimens stored in the dark. The other chemicals were of analytical reagent or C.P. quality. Solutions were made with distilled water of $p\mathrm{H} \sim 6$.

The apparatus and part of the *experimental procedure* have been described.[6] A shutter of stainless steel tubing was used as it corroded less in tap water than the aluminum shutter formerly used.[6a]

The actinometric procedure was like that described.[7] The actinometer contained per liter 0.0017 mole of uranyl *oxalate* and 0.0040 mole of oxalic acid. It gave the same value for ϕ at λ254 mμ as the one $0.001M$ in uranyl *sulfate* and $0.0067M$ in oxalic acid.[6b] Photolysis in the actinometer was held, by varying the time of photolysis, to correspond to about 2.5 g of permanganate titer for all values of the light intensity.

The volume of the irradiated solution was always 11 ml measured at 26±1°. All the photochemical experiments were conducted at fairly constant temperature in the range 10 to 21°. A variation of 10° was found to be without measurable effect on the results.

Analyses for persulfate were made at 26±1°. They differed in detail somewhat from that published[5] and several additional precautions were taken. All solutions were weighed to 1 mg. Ferrous ion was added only to acid solutions.

The end-point was determined by electrometric titration using apparatus and a procedure described elsewhere.[8] The bulb was omitted from A in Fig. 1c of that article[8] and the water level in the outer beaker F surrounded the inner beaker E up to the cork ring G. The end-point was always accompanied by a change in color, but it did not shift although the color end-point often faded. It was proved in separate experiments that the evaluation of persulfate was not affected by the ammonium, perchlorate, and the other ions sometimes present.

The ferrous solutions were standardized against permanganate each day they were used. Both solutions were stored in the dark. Permanganate solutions were standardized against Bureau of Standards sodium oxalate at the beginning, about the middle, and at the end of the research and the proper factors at other times interpolated. The latter solutions changed less than 2 percent during the course of the research covering a period somewhat less than a year.

The permanganate used for the analyses for oxalate and persulfate contained, respectively, 0.00183 and 0.0197 formula weight $KMnO_4$ per kg of solution. Some entries in Table I have been adjusted up to 1.5 percent to put them on this basis.

End-points were determined to one drop of permanganate titer independent of the persulfate or oxalate content of the solution titrated. This

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[6] L. J. Heidt, (a) Science **90**, 473 (1939), and (b) J. Am. Chem. Soc. **61**, 3223 (1939).

[7] Reference 6b, under column II, p. 3225.

[8] L. J. Heidt, J. Am. Chem. Soc. **61**, 3455 (1939).

TABLE I. Quantum yield, ϕ, measurements. The column headings are explained further in the text.

Expt.	Grams of persulfate in 50 cc at 26±1°	Moles of persulfate per liter found in dark sample	Wt. of a cc at 26±1°	Minutes the persulfate was irradiated	Δg of $KMnO_4$ soln ≃ persulfate photolyzed	% persulfate photolyzed	Δg of $KMnO_4$ soln ≃ oxalate photolyzed per min. in the actinometer	ϕ	Persulfate used if not the sodium salt, and other remarks. Concentrations are given in moles/liter
1 a	0.982	0.0854	1.005	31	1.83	9.5	0.85	0.46	ammonium
b		0.0854		31	1.75		.85	.44	salt
c		0.0854		87	4.12	22.	.85	.37	
d		0.0854		87	4.25		.85	.38	
2 abc	1.355	.099	1.012	40	1.55	7.	.52	.48	K salt
d		.10		29	1.6	8.	.66	.57	K with 0.02NaOH
3 abcd	2.513	.186	1.028	32	2.06	5.5	.77	.57	K with 0.02NaOH
4 abcd	1.192	.10	1.011	22.5	1.27	5.7	.80	.47	
ef		.10		69	3.19	14.	.8	.38	
g		.099		30	1.42	6.4	k		
hi		.099		30	1.37	6.4	k		
jk		.099		1056	2.42	11.3	.025	.60	
l		.099		2977	5.00	23.4	.025	.45	
5 ab	2.198	.185	1.023	15	1.13	2.7	.84	.59	
cd		.185		30	2.06	5.0	.80	.57	
e		.185		60.3	3.46	8.3	.80	.47	
fg		.185		180	7.43	17.8	.84	.33	
6 a	5.525	.464	1.064	45	2.08	2.0	.77	.40	
bc		.464		136	5.25	5.	.79	.34	
7 abc	2.201	.186	1.027	31	2.17^b	5.3	.82	.58	.02NaOH
de		.186		62	4.05^a	10	.82	.54	.02NaOH
8 a	2.200	.186	1.028	40	2.08^b	5.0	.65	.53	0.1NaOH
b		.186		90	4.87^b	11.7	.65	.55	0.1NaOH
cd		.186		1145	2.18^b	5.3	.020	.64	0.1NaOH
9 ab	13.200	1.12	1.167	144	7.79^b	3.07	.62	.59	0.1NaOH
c		1.12		963	21.2^a	8.4	.63	.24	0.1NaOH
10 abc	2.198	.185	1.065	90	5.57^b	13.5	.76	.51	1.0NaOH
11 ab	2.200	.186	1.136	65	2.44^b	5.8	.65	.38	$\begin{cases} .1NaOH+ \\ .9Na_2SO_4 \end{cases}$
12 ab	2.300		1.143	66.8	1.84^a	4.0	.69	.27	$1.0Na_2SO_4$
13 abc	2.205	.187	1.036	50	2.35	5.8	.71	.44	$0.08Na_2HPO_4$
14 abc	3.202	.271	1.156	76	3.27	5.4	.77	.37	$.8Na_2HPO_4$
15 abc	2.201	.186	1.129	102	4.44	10.7	.76	.38	$1PO_4$ at pH6.7
16 ab	2.207	.185	1.119	131	5.80^b	14.1	.70	.42	$1Na_2CO_3$
17 abc	2.203	.186	1.075	105	3.46	8.3	.82	.27	$1H_3PO_4$
18 abc	2.201	.186	1.027	79	3.00	7.1	.84	.31	$0.02\ NaHSO_4$
19 abc	2.202	.187	1.035	123	2.00	4.8	.87	.12	$.1NaHSO_4$
20 abc	2.203	.186	1.043	423	4.72	11.4	.83	.09	$.2NaHSO_4$
21 abc	2.203	.185	1.110	415	2.38	5.7	.94	.04	$1NaHSO_4$
22 abc	2.199	.186	1.024	100	3.09	7.4	.80	.26	$.02H_2SO_4$
23 ab	1.191	.10	1.043	629	3.40	15.5	.81	.005	$.5H_2SO_4$
24 ab	5.402		1.145	549	4.4	2.7	.77	.007	$.5H_2SO_4$
25 ab	2.201	.185	1.081	569	5.5	13.2	.73	.009	$1.05H_2SO_4$
26 ab	2.20	.187	1.113	127	1.2		.78	.008	$1HClO_4$
27 a	2.231	.188	1.032	5.5	.63	1.5	.80	.97	$1HC_2H_3O_2$
b				60	6.78	16.0	.80	.94	
c				180	18.4	44.0	.81	.86	

uncertainty plus all others amounted to less than ±3 percent in ϕ as can be seen by comparing the values for ϕ obtained in experiments 1 and 5 abcd under corresponding conditions.

Extinction coefficients, $\epsilon=[\log_{10}(I_0/I)]/cd$, where c is in moles per liter and d is in cm. ϵ was measured between 300 and 230 mμ in the same way as k on page 3224 of reference 6b. At 254 mμ,

ϵ for 0.186 molar (M) $Na_2S_2O_8$ equaled 22 compared to 20 obtained by Morgan and Crist[4] for the potassium salt at 0.1 and $0.01M$. They found ϵ was not affected by $0.02M$ sulfuric acid, and in this research ϵ was found to be affected less than 5 percent by $0.52M$ sulfuric acid.

A depth of 2 cm of the colorless 71 percent perchloric acid, used in experiment 26 to acidify the solution, absorbed less than 5 percent of visible and ultraviolet light down to $\lambda 230$ mμ.

Quantum yields, ϕ, were calculated as moles of persulfate disappearing per Einstein of $\lambda 254$ mμ absorbed by the system since the persulfate and particles containing it absorbed all but a negligible fraction of this light. The quantum yield data are summarized in Table I.

Averages are given for separate values of ϕ differing within experimental error but averaging over greater differences in ϕ to conserve space would misrepresent the dependence of ϕ upon the fraction photolyzed.

$\phi = 19.7\phi_a$(Δg of $KMnO_4$ soln equal to the persulfate photolyzed)/1.83 (min. the persulfate was irradiated) (Δg of $KMnO_4$ soln equal to the oxalate photolyzed per min. in the actinometer). ϕ_a is the quantum yield for the actinometer, and was taken as 0.63 at 254 mμ and 25° with a positive ten degree temperature coefficient of 1.03.

Moles of persulfate photolyzed $= 2.5 \times 1.97 \times 10^{-5}$ (Δg of $KMnO_4$ soln equal to the persulfate photolyzed).

Einsteins absorbed per min. $= (2.5/\phi_a)(1.83 \times 10^{-6})$($\Delta g$ of $KMnO_4$ soln equal to the oxalate photolyzed per min.).

The volume of stock solution of persulfate was usually 50 cc and contained the weight of persulfate recorded in Table I. The specific gravities also were determined to obtain the volume of the weighed solutions analyzed, and are recorded in Table I since no data were available in the literature from which to calculate them.

Alongside the weights of persulfates in the 50-cc stock solution are listed the moles of persulfate found per liter in the portion kept in the dark. In every case, except experiment 1, these two quantities are equivalent; hence analyses are internally consistent, the dark reaction is negligible and pure materials were used. In experiment 1, the value $0.0854M$ instead of 0.1 is caused, as noted above, by the presence of 1.6 mole of water of hydration left in the originally dihydrated ammonium persulfate.

The acetic acid in experiment 27 increased ϕ to unity and thus acts as an oxidizable acceptor for persulfate activated by light. Thus more easily oxidized substances like chloride in acid and cellulose also would be likely to increase ϕ. To avoid their presence, the persulfate solutions and crystals during purification and afterward were allowed to contact only themselves and glass, and especial care was taken to avoid introducing material containing copper, manganese, and silver which are known to catalyze the reduction of persulfate in thermal reactions.

Neither acetic acid nor any of its products of oxidation by persulfate activated by light reduce persulfate in the dark under the prevailing conditions because in the photolyzed solutions in experiment 27 the conc. of persulfate was the same immediately after photolyses as it was after they had stood a day in the dark. The dark reaction in the unphotolyzed samples also was negligible.

The perchloric acid in experiment 26 probably contained some chloride for an initial fast reaction occurred during photolysis until the oxidizable impurities were consumed. The data given in Table I for this experiment represent differences between photolyses in which the fast reaction had been extinguished.

Air does not affect the reaction as was found also by Morgan and Crist.[4] In experiments 1b and d and 4 hi, the solutions were photolyzed under their own vapor pressure all air having been pumped off, yet these experiments gave the same results as the corresponding ones in air, namely, experiments 1a, 1c, and 4g, respectively. In experiments 4g and hi, the k signifies that the same average light intensity was used although its absolute value was not determined.

Stirring in the solutions photolyzed under their own vapor pressure was accomplished as follows: A horse-shoe Alnico magnet was rotated by a motor and drove an iron bar attached at right angles to the shaft holding the quartz stirrer. The iron bar and shaft were jacketed with gas tight brass and turned freely with graphite as a lubricant. A glass tube connected the jacket and reaction cell and made gas tight connections through rubber joints. The glass tube contained a side arm fitted with a stopcock, through which

TABLE II. Conductivity measurements showing the additivity of the conductances of sulfuric acid and persulfate. Conductances given equal $100/R$ where R is the observed resistance in ohms. The cell constant was 0.296, and the temp., 25.0°. Solution B contained 6.004 g $Na_2S_2O_8$ in 25 ml which weighed 28.880 g. Values in columns D and E are for an equal volume of water instead of $0.04N$ H_2SO_4 or B, respectively. Conductances are additive when $A=D+E$.

	A	D	E	$D+E$
		(Water instead of acid)	(Water instead of persulfate)	
20 ml of 0.04 N H_2SO_4	3.85	6×10^{-5}		
" " +1 ml B	6.75	3.07	3.70	6.77
+2 ml B	9.01	5.44	3.59	9.03
+3 ml B	10.9	7.47	3.45	10.92
+5 ml B	14.0	10.89	2.20	14.09

the system was evacuated and its pressure determined. Care was taken to pump air from the solution only while stirring vigorously. This prevented boiling over.

Efficient stirring was exhibited by the constancy of ϕ in experiments 3 abcd where the rate of stirring was about doubled, trebled, and quadrupled yet ϕ remained at 0.58 ± 0.03. When stirring was slower ϕ dropped to 0.42, varying from 0.35 to 0.44. This drop in ϕ is probably caused in part by the local accumulation of hydrogen ions in the zone absorbing most of the actinic light. The same cause is also at least partly responsible for the low values for ϕ in experiment 6; also the increase in ϕ as the light intensity was decreased as observed in experiments 4 jh and l and possibly even in the otherwise alkaline solution in experiment 8 cd.

Correction for loss of solvent by evaporation was made by determining the loss in weight of the solution during an experiment. In no case, did this exceed 2 percent of the original amount of solvent and was negligible when gas was not pumped from the solution.

The evolution of oxygen during photolysis was exhibited by an increase in the pressure of the colorless vapor in equilibrium with the system when made gas tight. No corresponding increase in pressure occurred in the dark.

Tests for peroxide were made with titanium sulfate and vanadic acid. In experiments 23 and 24 no peroxide was found in the photolyzed or dark samples although positive tests were obtained when a drop of 3 percent hydrogen peroxide was added. Neither could any peroxide be detected by titration with permanganate under conditions where the permanganate would have been bleached by hydrogen peroxide but not by the persulfate.

The H^+ *ion yield* was determined by titration with $0.025N$ sodium hydroxide and $0.011N$ sulfuric acid using phenolphthalein as the indicator. In experiment 9 c, 5 ml of the dark and photolyzed samples were neutralized, respectively, with 44 ml of the acid and 16.5 ml of the base. This gives 1.97 milli-equivalents of acid liberated in the photolysis corresponding to the loss of 2.09 milli-equivalents of $Na_2S_2O_8$. The corresponding milli-equivalents in experiment 12 were 0.187 and 0.181.

In experiments 7–12, and 16, the superscripts attached to some of the values in the borderline cases mean that the solution was acidic, a, or basic, b, at the end of the photolysis.

*p*H *measurements* also were made. The glass electrode gave 2.2, 1.9, 1.7, and 1.5 for the final *p*H of the solutions after photolysis in experiments 5 ab, cd, e and fg, respectively, and 2.7 for that of the freshly prepared dark samples for experiments 5 and 6. These *p*H values although showing the correct trend are doubtless too low because bromthymol blue indicated a *p*H of 6.8, about that expected, for 4.79 g $Na_2S_2O_8$ (compared to 2.2 g in experiment 5 and 5.53 g in experiment 6) in enough water to make 50 cc of solution at 25°. *p*H values obtained with the quinhydrone as well as the chloranil (plus its hydroquinone) electrode were even lower than those obtained with the glass electrode, e.g., they indicated negative values for the *p*H of $0.33M$ sodium persulfate.

Conductivity measurements were made with student type apparatus kindly put at my disposal by Professor Dietrichson of this laboratory. The measurements are summarized in Table II.

DISCUSSION

Ammonium, potassium, and sodium persulfates give practically the same results when conditions are otherwise similar as is evident by comparing experiment 1 a with 2 abc and 4, and experiments 3 abcd with 5 cd. The value of 0.58 ± 0.02 for ϕ is, however, less than the previously reported value of unity[2] for 0.05 formal $K_2S_2O_8$.

The difference cannot be due to the dark reaction for in both researches this was negligible.

The effect of H^+ ion is to smother ϕ in a way similar to that suggested by the kinetic studies of Morgan and Crist.[1,3,4] These ions progressively decreased ϕ in experiments 5 and 17 through 26 from 0.6 in dilute neutral and alkaline solution to less than 0.01 when the total hydrogen ions exceeded those of persulfate. This is the primary reason that ϕ is less than 0.58 in experiments 1, 2, 4, and 5 efg in which experiments no alkali was present to neutralize the hydrogen ions produced by the photolysis; in experiments 5 abcd the fractions decomposed were small so that the effect of hydrogen ion concentration on ϕ was negligible.

The decrease in ϕ as the acidity increases suggests the formation of a weak acid containing photochemically inert persulfate. If the weak acid is $HS_2O_8^-$, the photochemical data give it a dissociation constant about 10^{-4}; however, the conductivity measurements suggest that its presence is improbable. Hydrogen ions furnished by sulfuric acid in experiments 23–25 and by perchloric acid in experiment 26 appear to be equally effective in decreasing ϕ, but the low values for ϕ in experiments 18, 19, and 22 imply also a specific effect of bisulfate; otherwise, e.g., in experiment 18, ϕ could hardly have been halved when there was less than one H^+ for five persulfates unless mixing was inadequate. The effects upon ϕ of $H_2PO_4^-$, $HPO_4^=$, $PO_4^\equiv$, $SO_4^=$, $CO_3^=$, and OH^- ions in themselves are much less than that of hydrogen ion because ϕ in experiments 10 through 16 is seen to have remained above half of 0.6, when the pH was greater than 5, although the concentrations of some of these ions had been increased to over five times the persulfate. Similar remarks can be made concerning the positive ions Na^+, K^+, and NH_4^+.

MECHANISM

The structure of the persulfate ion revealed by x-ray data[9] suggests a cause for the observations recorded above. The ion consists of two SO_4^- tetrahedrons held together by one single homopolar bond between two oxygen atoms at one corner of each of the two tetrahedrons. This structure is electrically unstable and should be stabilized by a positively charged particle especially if small enough to wedge between its parts and ought then to form a complex such as the weak acid suggested by the photochemical data. This must occur, however, only after the persulfate ion has been opened by the absorption of an actinic photon because neither the absorption spectra cited nor the conductivity measurements given in Table II indicate any association between any positive ion and persulfate in its compact normal or *thermally* excited state. In fact the rate of the thermal reaction is known to be increased by adding acid. On the other hand, the rapid decrease in ϕ is not caused by the onset of the production of hydrogen peroxide for none could be found.

The decomposition of SO_4^-, namely, $H_2O + SO_4^- + h\nu = HSO_4^- + OH$, followed by $OH + OH = H_2O + (O)$ and $(O) + (O) + M = O_2 + M$ where M in any third body cannot be responsible for the main reaction giving the quantum yield of 0.6. If SO_4^- were the initial reactant, ϕ as calculated could not exceed 0.5 unless there were subsequent reactions involving SO_4^- which would have increased ϕ with the persulfate concentration. Such an increase in ϕ does not occur as can be seen by comparing experiments 7 ab and 8 ab with 9. Moreover, the products of the reaction $OH + OH = H_2O + (O)$ should give way to the production of some H_2O_2 in acid solution and thereby lower the measured ϕ but no H_2O_2 was found although ϕ was lower. The near independence of ϕ upon temperature also makes improbable any reactions requiring thermal activation.

The main reactions responsible for the quantum yield of 0.6, therefore, probably are $H_2O + S_2O_8^= + h\nu = 2HSO_4^- + (O)$ followed by $O + O + M = O_2 + M$.

The increase in ϕ to unity by acetic acid in experiment 27 suggests that yields of less than unity are due to reformation of persulfate in the absence of an oxidizable acceptor or the presence of an environment inhibiting the separation of the primary photochemical fragments or both. These hypotheses I plan to test in the near future by a systematic study of the effects upon ϕ of ionic strength and ions like cupric, manganous, and silver which act as positive catalysts when persulfate acts as an oxidizing agent.

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[9] R. C.Evans, *Crystal Chemistry* (Cambridge University Press, New York, 1939), p. 253, and R. C. L. Zachariasen and W. H. Mooney, Zeits. f. Krist. **88**, 63 (1934).