formic acid, as described earlier by Pleskov.[2] The effect of hydration of these ions may be compared to complex formation, causing a shift of the half-wave potential to more negative values.

It is significant that the value of −0.29 volt *vs.* S.C.F.A.E. for the half-wave potential of thallium is well in accord with the corresponding value in aqueous solution.

Conclusion

The disadvantages of anhydrous formic acid as a solvent for polarographic investigations are due largely to its acidic nature. The use of supporting electrolytes such as cyanides, hydroxides or ammonia is excluded; due to its reducing properties, formic acid solutions of iodides and nitrates are also unsuitable. Further, the range of measurable potentials is restricted to values between +0.2 and −0.8 volt *vs.* S.C.F.A.E.

Anhydrous formic acid does, however, show some very useful advantages. Besides being a solvent with small solvating power the addition of as much as 2% (v./v.) of water has been shown to exert little effect. Dissolved oxygen, the presence of which is so undesirable, is more readily removed than from aqueous solution by bubbling nitrogen through the solvent; ten minutes degassing is usually sufficient. Polarographic maxima (overcurrents) were seldom encountered in this investigation, their irregular appearance being discussed elsewhere.[11]

Acknowledgment.—The authors wish to express their sincere appreciation to the Council for Scientific and Industrial Research, Pretoria, for a bursary to T.A.P.

(11) F. Sebba and T. A. Pinfold, *J. Colloid Sci.*, **11**, in press (1956).

CAPETOWN, SOUTH AFRICA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

The Radiation Induced Decomposition of Ferrous Ammonium Sulfate[1]

BY EVERETT R. JOHNSON[2]

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The radiation induced decomposition of ferrous ammonium sulfate has been studied by the dissolution of the irradiated salt in deaerated water with subsequent wet and gaseous analyses. The products of decomposition were found to be ferric ion, sulfite ion and hydrogen.

This report concerns some results obtained from a study of the radiation induced decomposition of crystalline ferrous ammonium sulfate and ferrous sulfate (anhydrous and crystalline). More exactly, this work may be described as a study of the chemical effects produced upon the dissolution of irradiated ferrous salts in deaerated water. This research is part of a general program on radiation chemistry being initiated in this Laboratory.

Experimental

C.P. $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (small crystals), $FeSO_4 \cdot 7H_2O$ (small crystals) and $FeSO_4$ (anhydrous powder) as purchased were irradiated with 2 Mev. cathode rays. The sample (about 11 g.) to be irradiated was put into the sample holder and connected to a vacuum line and pumped to a pressure of 10^{-5} mm. Helium at atmospheric pressure was then admitted to the system and the sample holder now filled with gas was removed from the vacuum line and capped. The sample was then irradiated for varying times at room temperature. The irradiated sample was removed from the holder and placed in the vacuum system. When the vacuum was 10^{-6} mm. that portion of the line containing the irradiated sample was isolated and deaerated water distilled onto the sample at liquid N_2 temperature. The sample plus water was warmed to about 40° and maintained at this temperature until the sample dissolved. The solution was now frozen and any liberated gases toeplered over into the analysis portion of the vacuum system. The gases were then analyzed in the usual manner.[3]

The sample holder was simply a shallow aluminum cylinder (1/2 in. thick, 2 in. i.d., 3/16 in. deep) covered with a mica window (0.038 g./cm.^{2}). A 1/4 in. o.d. piece of brass tubing threaded on one end and soldered to a commercial Kovar-glass tapered joint on the other end, served as a connection to the vacuum system. The mica window was held in place by sandwiching it between the aluminum cylinder and a 1/2 in. thick Micarta toroid, 2 in. i.d.

All irradiations were done with 2 Mev. cathode rays from a Van de Graaff accelerator purchased from the High Voltage Engineering Corp.

Ferric ion was determined by dissolving a separate sample in 0.8 *N* H_2SO_4 and measuring the extinction at 305 mμ. Sulfite ion was determined by a method described elsewhere.[4] No interference in the determination of sulfite ion was found by the presence of ferric ion in the concentration range studied.

All chemicals were C.P. and were used as purchased.

Results

Figure 1 shows a plot of the Fe^{3+}, $SO_3^=$ and H_2 produced as a function of dose for a dose rate of approximately 0.63×10^{18} e.v./g./sec. As can be seen the yield of decomposition products is linear up to a dose of 30×10^{19} e.v./g.,[5] after which there was a definite falling off (not shown in Fig. 1) of the yield with absorption of radiation. At a total dose of 3.8×10^{21} e.v./g., the yield of ferric ion was 0.67 molecule 100 e.v. absorbed. A similar decrease in yield with dose has been found by others. Hydrogen was the only gas produced. Careful analyses showed in all cases that no oxygen or nitrogen was formed during the radiation. Stoichiometry requires that for each H_2 formed two ferric ions must be found, and the same applied to sulfite formation.

The arithmetic mean value for the rate of $SO_3^=$ formation is 0.43 molecule 100 e.v., and that for H_2 is 0.35 molecule/100 e.v. The mean value of

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) Chemistry Department, Stevens Institute of Technology, Hoboken, New Jersey.

(3) E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

(4) C. J. Hochanadel, J. A. Ghormley and T. J. Sworski, *ibid.*, **77**, 3215 (1955).

(5) These results indicate that ferrous ammonium sulfate can be used as a dosimeter for very high intensity radiation.

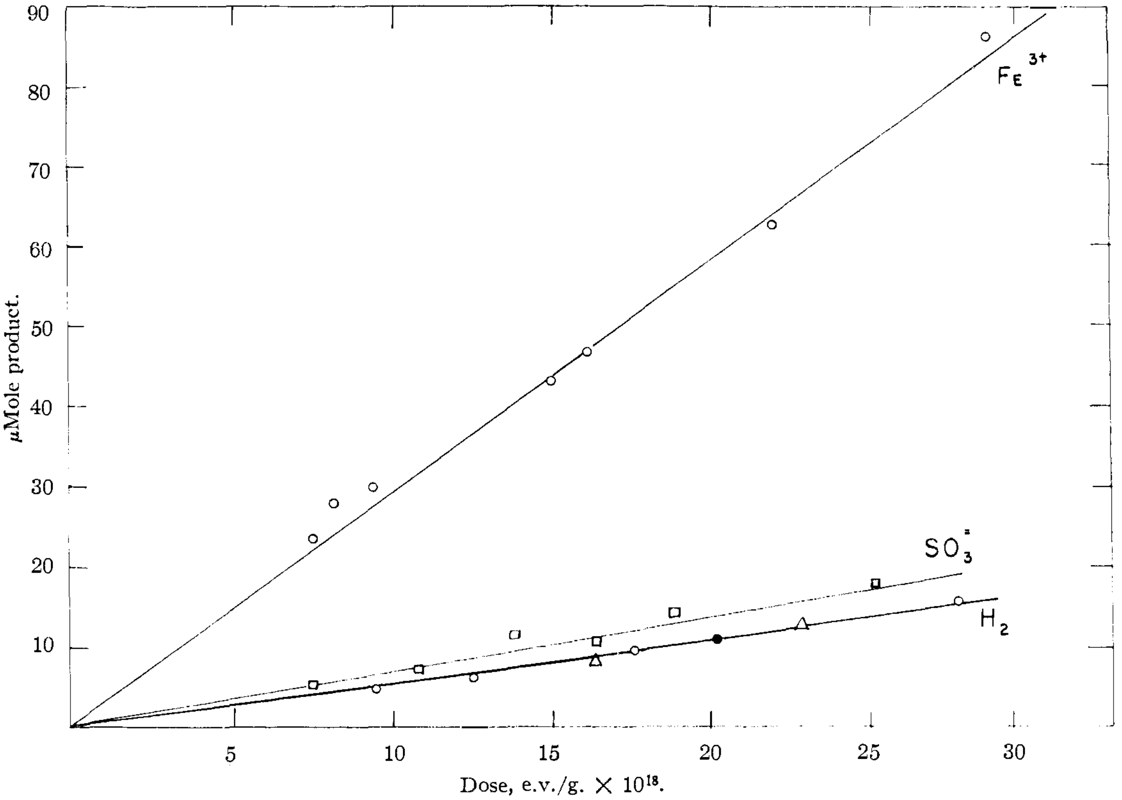

Fig. 1.—Yield of ferric ion, sulfite and hydrogen as a function of dose: hydrogen, O; $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$; Δ, $FeSO_4 \cdot 7H_2O$; ●, $FeSO_4$ anhydrous. (Hydrogen yields only were determined on $FeSO_4 \cdot 7H_2O$ and $FeSO_4$ anhydrous.)

ferric ion was found to be 1.8 molecules/100 e.v. abs. This figure is 20% higher than that required by stoichiometry and could possibly be due to experimental error. The dispersion in the ferric ion yield is at least 10%. The remaining discrepancy would have to come from the sulfite and hydrogen determinations, or from additional products which have not been found. The degree of accuracy of these analytical procedures is not sufficient to warrant a definite choice of these possibilities at this time.

Hydrogen production was the same regardless of whether there was ammonium ion or water of crystallization present in the crystal. This definitely indicates that the hydrogen arises from the action of the irradiated salt with water during dissolution. Furthermore it was found that it was not necessary to dissolve the irradiated salt completely to obtain all the hydrogen. This would indicate that trapped electrons are at the surface of the small crystallites. Annealing the irradiated salts at 60° in an atmosphere of helium did not reduce the ferric ion concentration.

It appears that those salts which have available other accessible oxidation or reduction states, *viz.*, nitrates,[6,7] azides,[8] chlorates[9] and ferrous sulfates undergo extensive damage under radiation while those salts which do not have these states available are resistant to radiation, *e.g.*, alkali halides[10,11] and alkali sulfates.[12]

The results for ferrous ammonium sulfate may be summarized as

$$2Fe^{2+} + 2H_2O \longrightarrow 2Fe^{3+} + H_2 + 2OH^-$$
$$2Fe^{2+} + 2H^+ + SO_4^{=} \longrightarrow 2Fe^{3+} + SO_3^{=} + H_2O$$

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UPTON, N. Y.

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[8] H. G. Heal, *Can. J. Chem.*, **31**, 1153 (1953).

[9] L. J. Sharman and K. J. McCallum, *J. Chem. Phys.*, **23**, 597 (1955).

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[11] As a comparison NaCl was irradiated with a total dose of 20 × 10^{19} e.v./g. At this dose the yield of H_2 from irradiated ferrous sulfate was 10.2 μmoles. The yield from NaCl was less than 0.1 μmole.

[12] Results from one experiment with K_2SO_4.