[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Radiolysis of Eder's Solutions

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Satisfactory consistency in the observed rate of Eder's reaction when induced in deaerated solutions by γ-radiation, may be achieved through (i) use of redistilled water to prepare necessary solutions, (ii) use of recrystallized salts and (iii) avoidance of contact between reactants and stopcock grease. The reaction, in the presence of 3×10^{-6} M ferric chloride, proceeds at a rate proportional to the concentration of the complex ion, $Hg_2Cl_2(C_2O_4)_2^{=}$, and independent of the ionic strength of the solution. In the presence of 3×10^{-6} M $FeCl_3$, and with irradiation rates of 0.095 to 0.34 r./min., the amount of reaction is proportional to the total radiation dosage and is independent of the rate of irradiation. Chromic, cupric, ferric and ruthenium(III) salts at concentrations from 0.5 to 60 μM are effective inhibitors. A reaction sequence consistent with the observations is proposed. The 10° temperature coefficient is 1.5.

The oxidation in solution of oxalates by such oxidizing agents as permanganate, persulfate, halogens and mercuric salts appears[1] to proceed as a chain reaction. Half oxidized oxalate ion, $C_2O_4^-$ or CO_2^-, is usually regarded as one of the chain-propagating intermediates[2] and when the oxidizing agent is mercuric chloride, the other intermediate has been variously taken to be Hg^+ ions,[2d] chlorine atoms[1c] and active calomel radicals.[1c] The oxidation of oxalate by mercuric chloride is often referred to as Eder's reaction after its discoverer.[3] Its remarkable chain length[1a,1c,4] of nearly 10^6 recommends its use in actinometry including X-ray actinometry[5] although its erratic behavior severely limits its usefulness in this respect and some consider it worthless.[6]

Eder's reaction may be induced by several oxidizing or reducing agents.[2d,7] Several fluorescent dyes, quinine and ferric chloride act as photochemical sensitizers[8] and several substances act as inhibitors including dyes,[7] many phenols,[1d] oxygen,[8] ferric chloride[1a,1b,7a,9] and other inorganic chlorides.[10]

In the study here reported, the effect of various foreign substances on the γ-ray-induced reaction was investigated, in part qualitatively and in part quantitatively. The influence of dosage rates, of reactant concentrations and of temperature was determined also.

Experimental

Method.—The reaction was followed by measurement of the volume of carbon dioxide produced at constant pressure. Control of pressure was maintained automatically by means of mercury contacts, a relay, and a reversing motor that served to raise or lower a levelling bulb. An electrically-powered vibrator provided agitation to prevent over-saturation of the solution by carbon dioxide.

Materials.—Specially distilled water was necessary. At first we observed that even without irradiation, solutions of mercuric chloride in laboratory-distilled water when mixed with solutions of either ammonium or potassium oxalate and then deaerated react quickly. Previous authors have been in disagreement as to the rate of the thermal reaction. Some[2] have observed it at 30° and others[1b,3] at 100°. The variations undoubtedly are due to variability in the quality of the water and in the amounts of inhibitors and inducing agents present in the solutions. When we used water that had been redistilled through a one-foot packed column, thermal reaction rates in deaerated solutions at 28° were negligible and in dilute solutions were immeasurably small. Care had to be taken to use redistilled water not only for preparing the reactant solutions but also for recrystallization of the salts and for cleaning the apparatus. The nature of the impurity in the laboratory-distilled water that promoted the thermal reaction was not identified.

Mercuric chloride was prepared by two recrystallizations from redistilled water followed by drying at 70°. Stock solutions were prepared from this product by weighing the salt and adding an appropriate amount of solvent.

Potassium oxalate was also twice recrystallized from hot water. Solutions were standardized by permanganate titration. Potassium and ammonium oxalate appeared to behave identically.

Carbon dioxide was drawn from a tank and was sent through copper turnings at 400° to remove oxygen.

The salts used in trace amounts as inhibitors were C.P. reagents not further processed.

Procedures.—Solutions and redistilled water were drawn as necessary from burets attached to 500-ml. bulbs which served as storage vessels. These articles were made of Pyrex brand glass. To avoid contamination of the solutions by grease, beads in Tygon tubing were used in place of stopcocks to control flow.

A reaction vessel containing 20 ml. of solution of appropriate concentration was attached to a manifold through a ground glass joint. Attached to the manifold also were a manometer, a mercury-filled gas buret and connections to a source of carbon dioxide and to a vacuum pump. After attachment, the reaction vessel was evacuated to a pressure within 5 mm. of the vapor pressure of the solution in order to remove most of the dissolved air. Carbon dioxide was then added to bring the pressure to 1 atm., and this gas was in turn removed by pumping to reduce still further the content of residual air in the solutions. During both the removal of gas and the readmission of carbon dioxide, the apparatus was mechanically shaken to promote vapor–liquid equilibrium. Nine flushings by carbon dioxide were found by Roseveare sufficient to remove all significant quantities of oxygen from the solutions and that is the number used in the present investigation. Further flushings

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(1) (a) W. E. Roseveare, THIS JOURNAL, **52**, 2612 (1930); (b) W. E. Roseveare and A. R. Olson, *ibid.*, **51**, 1716 (1929); (c) E. V. Shpolskii, *Nature*, **126**, 647 (1930); (d) K. Weber, *Z. physik. Chem.*, **A169**, 224 (1934).

(2) (a) E. Abel and H. Schmid, *Naturwissenschaften*, **23**, 501 (1935); (b) E. Abel, R. Jokisch, R. Lavisch and H. Sassmann, *Z. Elektrochem.*, **43**, 629 (1937); (c) A. Berthoud and H. Bellenot, *Helv. Chim. Acta*, **7**, 307 (1924); (d) G. H. Cartledge, THIS JOURNAL, **63**, 906 (1941); (e) H. F. Launer, *ibid.*, **54**, 2597 (1928); **55**, 865 (1929); **56**, 2571 (1930); (f) E. V. Shpolskii, *Acta Physicochim. U.R.S.S.*, **3**, 1269 (1935).

(3) J. M. Eder, *Ber.*, **13**, 166 (1880).

(4) E. V. Shpolskii, *Acta Physicochim., U.R.S.S.*, **3**, 255 (1935).

(5) E. H. Quimby and H. R. Downes, *Radiology*, **14**, 468 (1930); H. Q. Woodard, E. H. Quimby and H. R. Downes, *Am. J. Roentgenol. Radium Therapy*, **29**, 308 (1933); R. W. G. Wyckoff and L. E. Baker, *ibid.*, **22**, 551 (1929).

(6) (a) F. Krauss and K. Berge, *J. prakt. Chem.*, **136**, 257 (1933); (b) C. Winther, *Z. wiss. Phot.*, **8**, 197 (1910); (c) C. Ellis, A. A. Wells and F. F. Heyroth, "Chemical Action of Ultraviolet Rays," Reinhold Publ. Corp., New York, N. Y., 1941, p. 443.

(7) (a) C. Winther, *Z. wiss. Phot.*, **7**, 409 (1909); (b) J. H. Kastle and W. A. Beatty, *Am. Chem. J.*, **24**, 182 (1900).

(8) (a) A. Jodlbauer and H. von Tappeiner, *Ber.*, **38**, 2602 (1905); (b) C. Winther, *Z. wiss. Phot.*, **9**, 205 (1911); (c) G. Kornfeld, *Sci. et inds. Phot.*, [2] **23**, 377 (1952).

(9) E. V. Shpolskii and N. I. Kolesnikova, *J. Phys. Chem. (U.S.S.R.)*, **5**, 1199 (1934); E. V. Shpolskii, *Acta Physicochim., U.R.S.S.*, **21**, 958 (1946); F. Feigl, *J. Chem. Ed.*, **21**, 479 (1944); *ibid.*, **22**, 36 (1945); *cf.* N. Semenoff "Chemical Kinetics and Chain Reactions," Clarendon Press, Oxford, 1935, p. 159.

(10) G. Berger, *Rec. trav. chim.*, **40**, 387 (1921).

were without effect. After the ninth removal of gas, carbon dioxide was added to a selected partial pressure and the apparatus shaken until equilibrium between gas and liquid was established. Thereafter the solution was exposed to radiation and the volume of carbon dioxide released by the reaction was read at appropriate intervals. There was usually an induction period of one to ten minutes[2f,6b] following which carbon dioxide appeared at constant rate until several percentage of the reactants had been destroyed.

Cleaning of Reaction Vessels.—To avoid the accumulation of impurities, the reaction vessels were cleaned in the following way. A vessel, after removal of grease from the ground glass joint, was filled with cleaning solution and heated to 100°. It then stood until the temperature fell to that of the room. The cleaning solution was poured out and the vessel was rinsed several times with distilled water. Thereafter the vessel was steamed out in an inverted position for a half-hour, about 150 g. of steam being used in the process. Not only were the reaction vessels treated thus but also the burets, the bulbs used for storage of solutions, and the glassware used during recrystallization of the salts.

Radiation Source.—A 1.25-curie sample of cobalt-60 provided a source of radiation. Normally a thick layer of mercury was interposed between the cobalt and the rest of the system, but when the mercury was withdrawn a beam of gamma radiation sprayed upward through the reaction vessel. Ionization chambers were used to estimate the power of the beam both with and without lead absorbers interposed between the source and the reactants.

Results

Roseveare[1a] could not secure consistent reaction speeds in Eder's solutions when the solutions contained from 0.2 to 7.0×10^{-6} mole of ferric chloride per liter. With small concentrations of inhibitor, the effect of accidental impurities led to great variability. We adopted, as standard procedure, the practice of making all our solutions 3×10^{-6} *M* with respect to ferric chloride. At this selected concentration, the effects of accidental impurities were largely masked. It is our present opinion, however, that the techniques finally developed make the introduction of the inhibitor unnecessary.

Absence of Carbon Dioxide Effect.—The pressure of gas over the solutions seemed to have no effect on the rate of reaction.[8a] In a series of duplicating runs, agreement was independent of the pressure at which carbon dioxide was collected and hence, over a small range, independent also of the *p*H of the reactant solution.[11] A confirmation of the absence of a specific carbon dioxide effect is found in an experiment in which the shaking was intentionally interrupted at the end of 60 minutes. During the following 40 minutes, no increase in the volume of the gas was noted. All the additional carbon dioxide released by the reaction remained in the solution. Ten minutes after the shaking was resumed, the amount of carbon dioxide collected was exactly what would have been expected had the shaking been continuous. Thereafter the evolution of gas continued at the same rate as during the first 60 minutes. Neither the diminished *p*H of the solution nor the absence of agitation appeared to have any effect on the formation of carbon dioxide.

Dependence of Rates on Concentration of $Hg_2Cl_2(C_2O_4)_2^{=}$.—Cartledge and Goldheim[12] by means of freezing point and extraction measurements have shown that the important complex ion in Eder's solution is $Hg_2Cl_2(C_2O_4)_2^{=}$ rather than $HgCl_2C_2O_4^{=}$ as others had concluded earlier. Cartledge and Goldheim suggest that the rate of the Eder reaction is proportional to the concentration of this ion. Our results listed in Table I support this suggestion. It is to be noted in connection with this table that many species[12] other than $C_2O_4^{--}$ and $Hg_2Cl_2(C_2O_4)_2^{--}$ exist in the solutions, including $HgCl_2$, $HgCl_3^-$, Hg_2Cl_4, $Hg_2Cl_5^-$, etc.

TABLE I

DEPENDENCE OF REACTION VELOCITY ON CONCENTRATION OF $Hg_2Cl_2(C_2O_4)_2^{--}$

20 ml. soln., irradiation rate, 0.337 r./min.

Initial concn., *M*		Equilibrium concn.,[a] *M*				Rate of CO_2 evolution, µmoles/min.
$HgCl_2$	$K_2C_2O_4$	$HgCl_2$	$C_2O_4^{--}$	$Hg_2Cl_2(C_2O_4)_2^{--}$	$\mu^{1/2}$	
0.143	0.065	0.104	0.045	0.0100	0.12	2.95
.143	.065	.104	.045	.0100	.12	2.43
.107	.096	.073	.076	.0104	.18	2.98
.107	.096	.073	.076	.0104	.18	2.95
.116	.058	...	...	.0089	..	2.64
.061	.141	.039	.125	.0081	.27	2.10

[a] Data on equilibrium concentrations are taken from Cartledge and Goldheim[12] except those on the fifth line which are from M. C. Chen and C. J. Hsaio, *J. Chinese Chem. Soc.*, 10, 154 (1943).

To test further the proportionality between reaction rates and $Hg_2Cl_2(C_2O_4)_2^{=}$ concentration, a solution was made up of the same initial concentration as one prepared by Roseveare for which Chen and Hsaio have determined the point to point concentration as the reaction proceeded. The initial concentrations were 0.1164 *M* $HgCl_2$ and 0.058 *M* $K_2C_2O_4$. A plot of $\log A_0/A$ (where A_0 is the initial concn. of complex and A the concn. at time t) against time gives a straight line as shown in Fig. 1. This linearity is characteristic of a first-order reaction. The reaction was followed in this experiment to 47% destruction of the oxalate[13] corresponding to an 85% drop in concentration of the complex. The extent of reaction in other experiments was much less. The initial 100 e.v.-, or *G*-yield of carbon dioxide in this particular experiment was 4.6×10^5.

Several other series of solutions with different concentrations of oxalate and mercuric salt were prepared and irradiated. Roughly the rates varied as the two-thirds power of both oxalate and mercuric chloride concentrations. While these observations are empirically useful, they are best interpreted, in view of the variety of equilibria in these solutions, in terms of the concentration of $Hg_2Cl_2(C_2O_4)_2^{=}$.

Kinetic Salt Effects.—It is observed from the data in Table I that the reaction rates are independent of ionic strength (μ) over at least a moderate range of concentrations. This independence suggests that ion–ion reactions are not rate-determining in the radiolysis of Eder's solutions.

Inhibition.—The effect of chromic, cupric, ferric and ruthenium(III) chlorides in the radiation-induced reaction has been determined over a concen-

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(11) *Cf.* M. Roloff, *Z. physik. Chem.*, **13**, 327 (1894), who found that hydrogen ions at higher concentrations inhibit the photal reaction.

(12) G. H. Cartledge and S. L. Goldheim, THIS JOURNAL, **55**, 3583 (1933).

(13) The weight of calomel from this experiment matched the carbon dioxide production within 4%.

tration range of 0.5 to 60 × 10^{-6} M (depending on the degree of inhibition). Plotting the reciprocals of the reaction speeds against inhibitor concentration produces a series of straight lines, one for each salt. The relative slopes are 1.0, 25, 3.1 and 45 for the salts in the order listed above. Three micromoles of $CuCl_2$ per liter cut the reaction rate in half. The linearity of the plots, reciprocal rates *vs.* concentration, may be expressed algebraically in the familiar relation

$$\text{reaction rate} = \frac{k_1}{1 + k_2(\text{In})} \qquad (1)$$

where k_1 is the rate in the absence of added inhibitor, (In) is the inhibitor concentration and k_2 is a coefficient reflecting the efficiency of the inhibitor.

The four salts noted by no means exhaust the list of powerful inhibitors in this reaction. In further experiments, we introduced sodium nitroprusside ($3\mu M$) and potassium thiocyanate ($15\mu M$) into two separate solutions hoping as a result of complex formation to reduce the concentration of some of the cationic inhibitors accidentally present and thus to increase the observed rate of reaction. These reagents had the opposite effect, reducing the speed of reaction some 60 to 70% as a consequence presumably of their own inhibitory action. On the other hand, introduction of a little solid manganous permutit or pretreatment of the water by Amberlite Resin MB 1 with the idea again of removing cationic inhibitors resulted in uncontrollably fast thermal reactions.

Incidental observations during the present work showed that cotton fibers have no effect on the reaction. It should be possible, therefore, to use paper for filtering solutions, when necessary, but we made no direct test of this idea. Stopcock grease (apiezon) such as was used to lubricate the ground joint above the reaction vessel appears to be a powerful inhibitor. Momentary contact of the solution with this grease as a result of foaming during carbon dioxide removal was followed by lowered reaction rates. Even glass surrenders an inhibitor on long-standing. At one point in this work, water which had been redistilled three months earlier and stored in a soft-glass bottle was used to dilute the reactant solutions. The observed rates were about half the expected ones. Use of freshly distilled water brought the rates back to normal. Even Tygon tubing during a week's contact with mercuric chloride seemed to surrender an inhibitor. Despite the considerable number of contaminants that will cause inhibition and another considerable number that will induce the thermal reaction, it is possible with care to observe consistent radiochemical rates. We found agreement to 10% as a usual occurrence with occasional deviations greater than that.

Effects of Temperature and Intensity.—In Table II data are presented that show the speed of Eder's reaction (in presence of 3 × 10^{-6} M $FeCl_3$) to vary linearly with the intensity of the γ-radiation inducing it.

TABLE II

REACTION VELOCITY AS A FUNCTION OF RADIATION INTENSITY

20 ml. solution, temp. = 28.0°.

Intensity, r./min.	0.095	0.128	0.188	0.217	0.246	0.337	0.337
μmoles CO_2/min.	.34	.40	.53	.75	.82	1.10	1.10

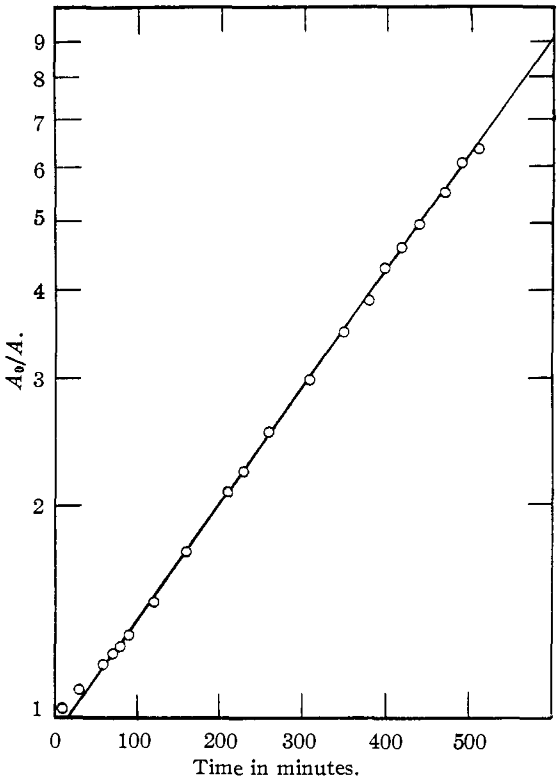

Fig. 1.—Linearity of log A_0/A plotted against time in Eder's solution: initial $HgCl_2$ = 0.1164 M; initial $K_2C_2O_4$ = 0.058 M.

Roseveare reported two values for the 10° temperature coefficient of the X-ray-induced reaction, namely, 1.51 and 1.54. A determination in the present work produced the value 1.47, which, considering the difficulty of reproducing conditions for long-chain reactions, is in satisfactory agreement with Roseveare's figures.[1a] Temperature coefficients ranging in value from 1.05 to 1.75 depending on the wave length of the exciting light have been reported for the photochemical reaction.[14]

Discussion

The following reaction scheme is consistent with the principal experimental features of Eder's reaction

$$H_2O + \text{radiation} \longrightarrow H + OH \qquad (2)^{15}$$

$$H + Hg_2Cl_2(C_2O_4)_2^{=} \longrightarrow$$
$$H^+ + Hg_2Cl_2 + C_2O_4^- + C_2O_4^{=} \qquad (3)$$

$$C_2O_4^- + HOH \longrightarrow H + 2\,CO_2 + OH^- \qquad (4)$$

$$H + M \longrightarrow H^+ + \text{other products} \qquad (5)$$

$$H + In^{+++} \longrightarrow H^+ + In^{++} \qquad (6)$$

M represents a reducible impurity in the solution and In^{+++} represents a cationic poison.

Applying the usual steady-state assumption to the concentration of the intermediate species and

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[14] G. Kistiakowsky, "Photochemical Processes," Chem. Catalog Co., New York, N. Y., 1928, p. 186.

[15] M. Burton, *J. Phys. Chem.*, **51**, 611 (1947); A. O. Allen, *ibid.*, **52**, 479 (1948); A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *ibid.*, **56**, 575 (1952).

assuming that the chain terminators in (5) and (6) do not change in concentration, one arrives at the rate law

$$\text{rate} = \frac{k(Hg_2Cl_2(C_2O_4)_2^- \times I}{k_5(M) + k_6(In^{+++})}$$

where I is the intensity of the γ-radiation. The reduction products whose formation breaks the main reaction chain may be regenerated in reactions of the type[16]

$$Fe^{++} + OH \longrightarrow Fe^{+++} + OH^-$$

The suggestion that H atoms are chain initiators in γ-induced reactions in solution is not an original one. Hart explains the decomposition of formic acid solutions partly in terms of a reaction between the H atoms liberated from water and formic acid molecules.[17]

The reaction sequence proposed above is in accord with the observations that the rate (1) is proportional to the concentration of $Hg_2Cl_2(C_2O_4)_2^{=}$, (2) is independent of ionic strength, (3) is proportional to the radiation intensity and (4) is affected by inhibitors as shown in equation 1.

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[16] H. S. Dainton, *J. Phys. Chem.*, **52**, 490 (1948).

[17] E. J. Hart, THIS JOURNAL, **73**, 68 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Deuterium Isotope Effect in the Reaction of Water Vapor with Zinc

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The deuterium isotope effect in the reaction of water vapor with zinc was measured over the range 295–415°. The fractionation factor, defined as the ratio of the specific rates of reaction of HOH and HOD with zinc, was found to be 1.6 ± 0.1 at 400°. The temperature dependence of the fractionation factor over the above range was -0.0011 (°C.)$^{-1}$. The magnitude of the isotope effect observed is somewhat smaller than the theoretical upper limit given by Eyring and Cagle for the case of the rupture of an isolated oxygen–hydrogen bond. From the present results it has been possible to evaluate the correction required for incomplete conversion of water to hydrogen in the usual analytical procedure for deuterium.

Introduction

In the course of the unidirectional reaction of water with metals, fractionation of the hydrogen isotopes occurs because of the difference in specific rates of reaction of the isotopic molecules HOH and HOD. The fractionation factor is defined $\alpha = [(H)/(D)]/[(H)_0/(D)_0]$, where (H)/(D) represents the ratio of the atom fraction of protium to deuterium in the first fraction of the evolved hydrogen and $(H)_0/(D)_0$ is the corresponding ratio for the initial substrate water.

Horiuti and Szabo[2] reported a single value of α = 2.2 for the reaction of water vapor with sodium at room temperature. Johnston and Davis[3] investigated the reaction of liquid water with Li, Na, K and Ca at 30°, obtaining values of α = 1.85, 2.60, 1.44 and 1.40, respectively. The reaction of water vapor with iron at 500° was studied by Horiuti and Polanyi[4a] and Bleakney and Gould[4b] who obtained α = 1.3 and 1.2, respectively. Since the reaction $Fe + H_2O = FeO + H_2$ is reversible under the conditions of these experiments, the observed fractionation is associated with the attainment of the isotopic exchange equilibrium $HOH + HD = HOD + H_2$ on the metal surface rather than with a rate process.

It appears that no detailed study has been carried out for the case of the irreversible reaction of water vapor with a metal. The present investigation was concerned with measurement of the deuterium isotope effect in the unidirectional reaction of water vapor with zinc over the temperature range 295–415°.

Experimental

The procedure for the measurement of the fractionation factor was to allow a sample of water vapor to pass rapidly through a bed of zinc maintained at a temperature in the range 295–415°, under conditions such that a small fraction of the water reacted. The apparatus used (Fig. 1) was very similar to that of Rittenberg[5] for conversion of water to hydrogen with hot zinc. To minimize volume and surface, all tubing was 4 mm. o.d. The two U-tube traps were 4 cm. long. The Toepler pump volume was 200 cc., for rapid removal of hydrogen. The conversion zone was a loop of 4 mm. o.d. Pyrex tubing 50 cm. long which contained 11 ± 1 g. of 20-mesh zinc (Coleman and Bell Co., C.P.). A spectrographic analysis revealed no detectable impurities in the zinc.

Enriched water was used in order to obtain better analytical accuracy. Samples from stock solutions of two different (known) isotopic compositions were used: $(D)_0/(H)_0$ = 0.01060 and 0.00872, respectively. The water sample (10–20 mg.) was introduced with a syringe into a small weighing ampoule, provided with a stopcock and ₸ joint, which was then connected to the vacuum line, frozen and outgassed several times, and weighed. The sample was then distilled *in vacuo* from the ampoule to the first U-tube trap where it was outgassed and stored (as a vapor) while the ampoule was reweighed empty to determine the quantity of water taken. After the sample had become completely vaporized in the first trap it was allowed to diffuse rapidly through the bed of hot zinc to the second trap at −195° which removed the unreacted water from the stream of hydrogen entering the evacuated Toepler volume. The hydrogen was then compressed into a sample bulb and held for mass spectrometric assay. The unreacted water was distilled into the ampoule and reweighed so that the percentage

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[1] (a) Taken from the M.S. thesis of W. G. H. (1954); (b) Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

[2] J. Horiuti and A. R. Szabo, *Nature*, **133**, 327 (1934).

[3] H. L. Johnston and C. O. Davis, THIS JOURNAL, **64**, 2613 (1942).

[4] (a) J. Horiuti and M. Polanyi, *Nature*, **132**, 819 (1933); (b) W. Bleakney and A. J. Gould, *Phys. Rev.*, **44**, 265 (1933).

[5] J. Graff and D. Rittenberg, *Anal. Chem.*, **24**, 878 (1952).