total effect will be a ratio of 1.013 to 1.020 for k_{12}/k_{13}. Unfortunately, the carbon isotope effect does not help one decide whether the carbon–mercury bonds are broken simultaneously or not.

DEUTERIUM ISOTOPE EFFECTS IN THE PHOTOCHEMICAL EVOLUTION OF HYDROGEN FROM AQUEOUS FERROUS SOLUTIONS

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The dependence of the isotope separation factor in the photochemical evolution of hydrogen from aqueous solutions of ferrous sulfate on the concentration of H^+, ferrous, and ferric ions and on the concentration of an organic scavenger (methanol) was investigated. The results are interpreted in terms of a consecutive mechanism involving isotope separation in each of two steps. The respective separation factors in the first step (leading to H atom formation) and in the second (involving oxidation of Fe^{2+} by H) are derived. Isotope effects in radiation and photochemistry are compared. The isotope separation factors obtained support the intermediate hydride formation mechanism for the oxidation of Fe^{2+} by H atoms.

Introduction

The first investigation of the separation of hydrogen isotopes in the photochemical liberation of hydrogen from aqueous ionic solutions was carried out by Farkas and Farkas.[1] The purpose of their work was the investigation of the isotope separation in a homogeneous system. In the irradiation of 0.05 *M* ferrous sulfate solutions in 0.05 *N* H_2SO_4, isotope separation factors of 3.8–4.8 were obtained depending on the deuterium content of the solutions.[1]

The use of hydrogen isotope effects in photochemistry and radiation chemistry[2] permits the study of primary photochemical radical formation processes by the technique of competitive reactions. In previous work[3,4] on the photochemistry of the ferrous ion in aqueous solution, the mechanism of H atom formation and the oxidation mechanism by atomic hydrogen were investigated. In the present work we attempt to apply the isotope separation technique to obtain further information on the dissociation of the photoexcited ferrous ion in aqueous solution and the reactivity of H atoms.

Experimental

Procedure.—Irradiations were carried out in fused silica vessels using 10 cc. of solution, and a low pressure Hg lamp operated at 1000 v. and 100 ma. was employed as a light source. The light was filtered by 0.5 cm. of 0.1 *M* NaCl solution, eliminating wave lengths below 2000 Å. Approximately 95% of the incident light was at 2537 Å. Irradiations were carried out at 20 ± 1°. The light intensity as determined by the uranyl oxalate actinometer was about 2×10^{-8} einstein $l.^{-1}$ $min.^{-1}$. Evacuation of the solutions was carried out as previously described.[3] After irradiation the gas was transferred by a Toepler pump for isotope analysis.

Materials and Solutions.—Deuterium oxide was purified by triple distillation from alkaline permanganate and $KHSO_4$. Triple-distilled water and A.R. grade sulfuric acid and ferrous ammonium sulfate were used.

Isotope Analysis.—The deuterium content of the liberated gas was determined by using the mass spectrograph built in this Department. The instrument was calibrated using hydrogen–deuterium mixtures prepared by decomposition of standard solutions on Zn at 400°. The analysis was performed on mixtures of relatively low deuterium content so that H_2 and HD only need be considered. The isotopic composition was determined by the mass ratio 2:3 (H_2:HD). Calibration and analysis were carried out at the same gas pressure, which was in the region 10^{-5}–2×10^{-5} mm. The experimental results were reproducible within ±5%.

Results

Ferrous Sulfate-H_2SO_4 Solutions.—The experiments were carried out in solutions of relatively low deuterium content $(D/H)_l \sim 0.2$. We measured the isotope separation factor defined by

$$S = (D/H)_l \times (H/D)_g \qquad (I)$$

where l and g refer to the liquid and the gas, and D and H are in moles.

The dependence of the isotope separation factor on the irradiation time *t* (at constant light intensity) and sulfuric acid concentration was investigated. The results are presented in Table I.

TABLE I

ISOTOPE SEPARATION IN THE PHOTOCHEMISTRY OF THE FERROUS ION

$[H_2SO_4]$, *N*	$[Fe^{2+}]_0$, mole $l.^{-1}$	*t*, min.	$10^3[Fe^{3+}]$, mole $l.^{-1}$	*S*
0.78	0.10	20		4.0
.78	.10	33		4.0
.78	.20	36		3.9
.70	.10	60	4.0	4.2
.031	.10	47		4.0
.0074	.10	60		4.1
.0065	.10	130	1.10	4.0
.0032	.10	140	1.10	3.8
.0009	.10	150	0.35	3.7

These results indicate that within the experimental error the isotope separation factor is independent of the concentration of the ferric ion during irradiation. These results also indicate that the isotope separation factor is independent of the acid concentration in the region 0.8–0.01 *N*. In this region the rate of primary radical formation is pH dependent.[4]

Isotope Separation in KF Solutions.—At low acid concentration (pH > 2) the accuracy of the isotopic analysis was reduced because of the low

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[1] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1120 (1938).

[2] J. Jortner and G. Stein, *Intern. J. Appl. Radiation Isotopes*, **7**, 198 (1960).

[3] J. Jortner and G. Stein, *J. Phys. Chem.*, **66**, 1258 (1962).

[4] J. Jortner and G. Stein, *ibid.*, **66**, 1264 (1962).

gas yields obtained under irradiation. Therefore additional experiments were carried out in 0.1 M KF solutions. The increase of the photochemical yield in the presence of the fluoride ion is due to two factors.

(a) There is a reduction of the inner filter effect[3] of the ferric ion. The molar extinction coefficient of the ferric ion in 0.8 N H_2SO_4 at 2536 Å. is reduced from ϵ = 2800 to 600 l. mole^{-1} cm.$^{-1}$ by the addition of 0.1 M KF. The molar absorption coefficient of the ferrous ion is unaffected.

(b) The ferric–fluoride ion pair is stable to reduction by H atoms,[5] compared to the reactivity of $Fe^{3+}OH^-$ ion pairs present in sulfuric acid solution at high pH.[4,5]

The experimental results presented in Table II indicate that the pH effect on the separation factor is rather small. A slight decrease is observed at high pH, within the range of experimental error.

TABLE II

ISOTOPE SEPARATION IN H_2SO_4 SOLUTIONS CONTAINING 0.1 M KF; $[Fe^{2+}]_0$ = 0.1 M

$[H_2SO_4]$, N	pH[a]	S
0.78		4.2
.78		3.9
.09	2.8	3.9
.044	3.8	3.7

[a] The pH was measured in identical solutions prepared from ordinary water.

The Effect of Methanol on Isotope Separation.— In an attempt to determine the isotope separation factor in the primary radical formation process, a series of experiments was carried out in solutions containing ferrous sulfate, methanol, and 0.8 N sulfuric acid. In this system the atomic hydrogen formed oxidizes ferrous ion[3,4]

$$Fe^{2+} + H + H^+ \longrightarrow Fe^{3+} + H_2 \quad (1)$$

or the organic solute[6,7]

$$CH_3OH + H \longrightarrow CH_2OH + H_2 \quad (2)$$

as in the radiation chemical investigation of this system.[6,7] The radical CH_2OH thus formed may react by dimerization and disproportionation

$$2CH_2OH \longrightarrow CH_2O + CH_3OH \quad (3)$$

$$2CH_2OH \longrightarrow (CH_2OH)_2 \quad (4)$$

In the presence of the ferric ion CH_2OH will act as a reducing agent

$$CH_2OH + Fe^{3+} \longrightarrow Fe^{2+} + CH_2O + H^+ \quad (5)$$

At high $[CH_3OH]/[Fe^{2+}]$ ratio the hydrogen atoms formed will react preferably in reaction 2 and the ferric ion formed will be reduced again according to reaction 5. Table III presents the experimental results.

TABLE III

ISOTOPE SEPARATION IN THE PHOTOCHEMISTRY OF Fe^{2+} ION IN THE PRESENCE OF METHANOL

$[H_2SO_4]$ = 0.78 N

$[Fe^{2+}]_0$, mole l.$^{-1}$	$[CH_3OH]_0$, mole l.$^{-1}$	t, min.	$10^3[Fe^{3+}]_t$, mole l.$^{-1}$	$\left(\frac{D}{H}\right)_l$	$\left(\frac{D}{H}\right)_g$	S
0.10	0	33	4.0	0.220	0.052	4.2
.10	0.26	52	1.05	.254	.055	4.6
.10	0.55	50	0.75	.240	.050	5.0
.20	1.18	51	.85	.240	.047	5.1
.10	1.25	47	.40	.241	.047	5.2
.05	1.22	49	.11	.241	.045	5.5
.025	1.20	47	.04	.235	.038	6.2

The formation of formaldehyde was confirmed by determination with chromotropic acid. The decrease of the yield of Fe^{3+} with increasing ratio $[CH_3OH]/[Fe^{2+}]$ is due to the competition between reactions 1 and 2. Under conditions of high $[CH_3OH]/[Fe^{2+}]$ ratio (~50) the limiting value of 6.2 ± 0.3 was obtained for the isotope separation factor. Under these conditions the yield of Fe^{3+} is only 1% of the yield obtained in the absence of methanol. Hence H atoms react almost entirely by reaction 2, and the oxidation reaction (1) may be neglected. The very low value of Fe^{3+} obtained implies that the value of S is a limiting one in view of the nearly total scavenging of H atoms by methanol.

Discussion

The contributions of the following steps to the isotope separation have to be considered: (a) primary radical formation; (b) interaction of H and D atoms with the solvent; (c) oxidation of ferrous ion by H and D atoms; and (d) reduction of the ferric ion by H and D atoms.

The secondary process b probably does not contribute to the isotope separation in our case. The exchange reactions with water and H^+ ions are relatively slow. Farkas and Farkas,[1] using kinetic data from gaseous phase experiments, claimed that for the exchange reaction of deuterium atom and water the activation energy is of the order of 16 kcal./mole. Friedman and Zeltman[8] found for this reaction in aqueous solution at pH 2 a rate constant of 2 sec.$^{-1}$.

Radiation chemical[9] and photochemical[4] evidence indicates that the reduction of Fe^{3+} by H atoms is negligible at low pH, the rate of reduction increasing with increasing pH. No isotope effect was observed in this reaction.[6] Thus reaction d does not contribute to the isotope separations. This conclusion is consistent with the independence of the isotope separation factor of the irradiation time and of the extent of photochemical oxidation. The separation factors presented in Tables I and II include (a) the contribution of the primary H and D atom formation, and (c) a subsequent contribution rising from the oxidation reaction of the ferrous ion by H and D atoms. The experimental results in the presence of methanol allow the separate determination of the two factors.

The rate of introduction into the bulk of the H

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[5] T. Rigg, G. Stein, and J. Weiss, *Proc. Roy. Soc.* (London), **A211**, 375 (1952).

[6] J. H. Baxendale and G. Hughes, *Z. physik. Chem.* (Frankfurt), **14**, 306 (1958).

[7] J. H. Baxendale and G. Hughes, *ibid.*, **14**, 323 (1958).

[8] H. L. Friedman and A. H. Zeltman, *J. Chem. Phys.*, **28**, 878 (1958).

[9] A. O. Allen and W. G. Rothschild, *Radiation Res.*, **7**, 591 (1957).

and D atoms, produced from the excited state of the ion, will be represented schematically by the reactions

$$\mathrm{Fe^{2+}{}_{aq}}^{*} \begin{cases} \xrightarrow{k_{pD}} \mathrm{D + Fe^{3+}} \\ \xrightarrow[k_{pH}]{} \mathrm{H + Fe^{3+}} \end{cases} \qquad (p)$$

k_{pH} and k_{pD} represent the rate constants for radical production at constant light intensity. These quantities consist of the quantum yields for atom production (as defined in ref. 3 and 4) multiplied by the light intensity absorbed by the ferrous ion. These constants include a contribution for the preferential solvation of the light absorbing ferrous ion, and of the H^+ ion which acts as a scavenger[4] transferring radicals into the bulk.

The exchange of the atoms thus produced with the solvent is neglected, and only scavenging reactions have to be considered. The oxidation of the ferrous ion will be presented in the form

$$\begin{array}{l} \mathrm{H + Fe^{2+}} \begin{cases} \xrightarrow{k_{\mathrm{OXH}}} \mathrm{H_2 + Fe^{3+}} \\ \xrightarrow{k_{\mathrm{OXD}}} \mathrm{HD + Fe^{3+}} \end{cases} \\ \mathrm{D + Fe^{2+}} \begin{cases} \xrightarrow{k_{\mathrm{OXH}}} \\ \xrightarrow{k_{\mathrm{OXD}}} \mathrm{D_2 + Fe^{3+}} \end{cases} \end{array} \qquad (1')$$

Assuming that these rate constants are independent of the nature of the attacking atom, k_{OXH} and k_{OXD} represent the rate constants for the oxidation of the ferrous ion depending on whether H or D is detached.

The atoms produced from the excited state of the ion may alternatively react with methanol

$$\mathrm{H + CH_3OH \longrightarrow H_2 + CH_2OH} \qquad (2')$$

$$\mathrm{D + CH_3OH \longrightarrow HD + CH_2OH}$$

As reaction 2′ leads in both cases to a rupture of a C–H bond, the isotope effect in this reaction is negligible.

At high scavenger concentration and at low pH, second-order recombination of H and D atoms may be neglected. From this reaction scheme

$$\frac{d[\mathrm{H_2}]}{dt} = k_2[\mathrm{CH_3OH}][\mathrm{H}] + k_{\mathrm{OXH}}(1 - W)[\mathrm{H}][\mathrm{Fe^{2+}}]$$

$$\frac{d[\mathrm{HD}]}{dt} = k_2[\mathrm{CH_3OH}][\mathrm{D}] + k_{\mathrm{OXD}}W[\mathrm{H}][\mathrm{Fe^{2+}}] + k_{\mathrm{OXH}}(1 - W)[\mathrm{D}][\mathrm{Fe^{2+}}] \qquad (\mathrm{II})$$

$$\frac{d[\mathrm{D_2}]}{dt} = k_{\mathrm{OXD}}W[\mathrm{D}][\mathrm{Fe^{2+}}]$$

where

$$W = \left(\frac{\mathrm{D}}{\mathrm{H + D}}\right)_{\mathrm{l}}$$

The steady state concentrations of the H and D radicals are presented by

$$[\mathrm{H}] = \frac{(1 - W)k_{pH}}{k_2[\mathrm{CH_3OH}] + \{k_{\mathrm{OXH}}(1 - W) + k_{\mathrm{OXD}}W\}[\mathrm{Fe^{2+}}]} \qquad (\mathrm{III})$$

$$[\mathrm{D}] = \frac{Wk_{pD}}{k_2[\mathrm{CH_3OH}] + \{k_{\mathrm{OXH}}(1 - W) + k_{\mathrm{OXD}}W\}[\mathrm{Fe^{2+}}]}$$

The experimentally determined quantity is

$$\left(\frac{\mathrm{H}}{\mathrm{D}}\right)_{\mathrm{g}} = \frac{2[\mathrm{H_2}] + [\mathrm{HD}]}{2[\mathrm{D_2}] + [\mathrm{HD}]} \qquad (\mathrm{IV})$$

which at low deuterium content of the solution is reduced to

$$\left(\frac{\mathrm{H}}{\mathrm{D}}\right)_{\mathrm{g}} = 1 + \frac{2[\mathrm{H_2}]}{[\mathrm{HD}]} \qquad (\mathrm{IV}')$$

In the integration of eq. II the contribution of the inner filter effect[3] should be taken into account. However, as the right hand side of eq. IV′ is only dependent on the ratio of amounts of the hydrogen isotopes produced, the contribution of the inner filter effect cancels out.

Using eq. II, III, and IV′, we obtain

$$\left(\frac{\mathrm{H}}{\mathrm{D}}\right)_{\mathrm{g}} = 1 + \frac{\dfrac{k_2[\mathrm{CH_3OH}]}{k_{\mathrm{OXH}}[\mathrm{Fe^{2+}}]} + (1 - W)}{\dfrac{k_2[\mathrm{CH_3OH}]}{2k_{\mathrm{OXH}}[\mathrm{Fe^{2+}}]}\dfrac{k_{pD}}{k_{pH}}\dfrac{W}{1 - W} + \dfrac{W}{2}\left\{\dfrac{k_{\mathrm{OXD}}}{k_{\mathrm{OXH}}} + \dfrac{k_{pD}}{k_{pH}}\right\}} \qquad (\mathrm{V})$$

Applying this equation to some limiting cases, the isotope separation factors in the primary radical production process, and in the oxidation reaction, can be obtained. Under limiting conditions when most of the radicals produced react with the organic scavenger, the separation factor observed is solely determined by the isotope separation in the primary process. This condition will be fulfilled when $[\mathrm{CH_3OH}]/[\mathrm{Fe^{2+}}] >> 1$. Then we get

$$\left(\frac{\mathrm{H}}{\mathrm{D}}\right)_{\mathrm{g}} = 1 + \left(2\frac{k_{pH}}{k_{pD}} \times \frac{1 - W}{W}\right) \qquad (\mathrm{VI})$$

Defining the separation factor S_p in the primary process for the introduction of H and D atoms into the bulk by

$$S_p = \frac{k_{pH}}{k_{pD}} \qquad (\mathrm{VII})$$

and using the definition of W we readily get

$$S_p = \frac{\{(\mathrm{H/D})_{\mathrm{g}} - 1\}}{2} \times \left(\frac{\mathrm{D}}{H}\right)_{\mathrm{l}} \qquad (\mathrm{VIII})$$

Application of the experimental results obtained under these limiting conditions (Table III) leads to the value $S_p = 2.9 \pm 0.3$.

The isotope separation factor for the oxidation of ferrous ion by H and D atoms will be defined by

$$S_{OX} = \frac{k_{OXH}}{k_{OXD}} \qquad (IX)$$

This value can be obtained from the experimental results obtained for ferrous ion–H_2SO_4 solutions in the absence of methanol when sufficient Fe^{2+} is present for total scavenging of the atoms. Setting $[CH_3OH] = 0$, the following expression is obtained for consecutive isotope separation at relatively low deuterium content

$$\left(\frac{H}{D}\right)_g = 1 + \frac{2(1 - W)}{W} \frac{1}{\dfrac{k_{OXD}}{k_{OXH}} + \dfrac{k_{pD}}{k_{pH}}} = 1 + \frac{2(1 - W)}{W} \frac{1}{\dfrac{1}{S_{OX}} + \dfrac{1}{S_p}} \qquad (X)$$

Using the experimental results in the absence of methanol and the value of S_p previously obtained from eq. X we get $S_{OX} = 5 \pm 0.5$.

The separation factors presented in Table III depend on the concentration ratio $[CH_3OH]/[Fe^{2+}]$. The gradual increase of the isotope separation factors with the increase of this ratio results from the competition between the scavenging reactions 1 and 2. The dependence of the isotope separation factors on the concentration ratio $[CH_3OH]/[Fe^{2+}]$ could be interpreted adequately by eq. V using the values of S_p and S_{OX} previously obtained and setting $k_2/k_{OXH} = 0.15$. The comparison between the calculated data and the experimental results is presented in Fig. 1. The rate constants ratio which was found to yield best agreement with the experimental results is in good agreement with the value of 0.17 obtained in ordinary water at pH 1[6,7] in acid solutions irradiated with ionizing radiations.

In our previous work[3,4] on the photochemistry of Fe^{2+} ions it was shown that the mechanism of radical introduction into the bulk involves two distinct mechanisms: (a) a pH dependent process involving essentially electron scavenging by the H^+_{aq} ion, and (b) a residual pH independent yield involving dissociative electron capture by a solvent molecule in the solvation layer of the excited ion. The H (or D) atom thus formed diffuses into the bulk.

At pH 0.4, the contributions of these two reaction paths to the total quantum yield are about equal.[3,4] In both these reactions roughly the same intramolecular isotope effect is expected.[2]

The primary photochemical isotope separation factor S_p obtained in the present work is identical within the experimental range of error with the separation factor in the primary production of H and D atoms in the radiolysis of aqueous solutions, $S_A = 2.7 \pm 0.1$ obtained at low D content.[10,11]

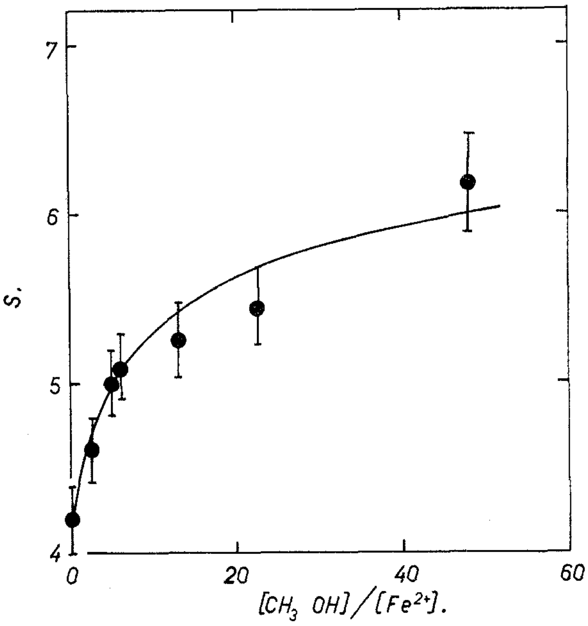

Fig. 1.—The dependence of the isotope separation factor in the presence of methanol on the concentration ratio $[CH_3OH]/[Fe^{2+}]$. $[H_2SO_4] = 0.8$ *N*; $(D/H)_l = 0.22$ to 0.25. Solid curve calculated from eq. V with $k_{H+CH_3OH}/k_{H+Fe^{2+}} = 0.15$.

S_p is equal to the separation factor in the radiation chemistry of aqueous solutions[12,13] where H atoms are formed by the interaction of e_{aq} with H^+_{aq}.

For the oxidation of Fe^{2+} ion by H atoms, the separation factor $S_{OX} = 5 \pm 0.5$ at low deuterium content is obtained. Baxendale and Hughes[7] derived a rate constants ratio of 2.4 between the rate constants for the oxidation of the ferrous ion in H_2O and D_2O. They considered this result as evidence against the oxidation mechanism involving the intermediate formation of the H_2^+ molecule ion. The conclusions are not unambiguous,[2] as an isotopic effect may be observed when the rates of an electron transfer reaction are compared in H_2O and D_2O. However, the marked isotope effect observed in the present work at low D content definitely rules out the oxidation mechanism involving H_2^+, since in the present case electron transfer in a medium of constant composition does occur. From the value[10] of

$$S_{H^+} = \frac{(H/D)_{H_3O^+}}{(H/D)_{H_2O}} = 1.66$$

at low deuterium content, the isotope separation factor for the oxidation reaction can be derived, corrected for the preferential solvation of the hydroxonium ion. Denoting this corrected separation factor by S'_{OX} we set $S'_{OX} = S_{OX}/S_{H^+}$. Using the experimental value $S_{OX} = 5 \pm 0.5$ we get $S'_{OX} = 3$, in fair agreement with the results of Baxendale and Hughes. Investigations of the oxidation of Fe^{2+} by H atoms externally generated[14] or produced photochemically[3,4] showed that this oxidation mechanism may involve the formation of a hydride intermediate[14]

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[12] J. T. Allan and G. Scholes, *Nature*, **187**, 218 (1960).

[13] G. Czapski and A. O. Allen, *J. Phys. Chem.*, **66**, 262 (1962).

[14] G. Czapski, J. Jortner, and G. Stein, *ibid.*, **65**, 956, 960 (1961).

$$\mathrm{Fe^{2+}_{aq} + H \rightleftarrows FeH^{2+}_{aq}} \qquad (6)$$

$$\mathrm{FeH^{2+}_{aq} + H^{+}_{aq} \longrightarrow Fe^{3+}_{aq} + H_2} \qquad (7)$$

The isotope effect in the oxidation reactions is consistent with this reaction mechanism, as reaction 7 involves the rupture of an O–H bond in the hydroxonium ion.

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COULOSTATIC METHOD FOR THE KINETIC STUDY OF FAST ELECTRODE PROCESSES. I. THEORY

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A new method (*charge-step* or *coulostatic*) for the kinetic study of fast electrode processes is discussed. The method involves: (a) charging of the electrode with a known quantity of electricity by means of a *coulostat* to cause a departure from the equilibrium potential, and (b) recording of the overvoltage–time curve during the subsequent discharge of the double layer capacity c_d by the electrode reaction. Overvoltage–time curves are derived for the following cases: constant c_d and linearized current–overvoltage (I–η) characteristic without mass transfer control or with mass transfer controlled by semi-infinite linear diffusion; constant c_d and quadratic and cubic approximations of the I–η characteristic in the absence of mass transfer control; and variable double layer capacity. Conditions for pure control by either diffusion or the charge transfer reaction are derived, and it is shown that conditions can be selected for which diffusion need not be considered when the apparent standard rate constant does not exceed 0.2–0.3 cm. sec.$^{-1}$. The method has about the same potentialities as the potentiostatic and single-pulse galvanostatic methods but has the advantage of somewhat greater simplicity of technique and interpretation of results. The coulostatic method also allows the determination of the differential capacity of the double layer even when a fast charge transfer reaction occurs on the electrode.

A method, which is new to the writer's knowledge, recently was suggested in this Laboratory for the study of fast adsorption processes at a metal–electrolyte interface[1] and for electroanalytical determinations in the 10^{-5}–10^{-7} M concentration range.[2] The method also can be applied to the kinetic study of fast electrode processes. The theory for the latter application is reported here, and experimental results are given in part II.[3] The principle is as follows. The electrode being studied is initially at equilibrium. The charge density on the electrode is changed abruptly (perhaps in 0.1–1 μsec.) in such a way that the electrochemical cell is essentially at open circuit once charging is completed (part II[3]). The potential departs from the equilibrium value as a result of the change of charge density. The increment of charge supplied to the electrode is consumed progressively by the electrode reaction, and the potential drifts back to its initial equilibrium value (unless there is a permanent change of the electrode). The overvoltage–time variations depend on the charge increment, the double layer capacity, and the characteristics of the electrode process. Study of electrode kinetics from overvoltage–time curves therefore should be possible.

The expression "coulostatic method" was coined[1] for this method when it is applied to adsorption kinetics because the charge density on the electrode remains constant during recording of potential–time curves. Further, the instrument supplying a known charge might be called a "coulostat" by analogy with "potentiostat." The charge density varies in the study of electrode processes by this method since the double layer is discharged until the equilibrium potential is reached, and the expression "charge-step method" might be preferable for application to electrode kinetics. However, there hardly seems a need for two expressions.

The theory of the method will be developed for a simple charge transfer reaction, O + ne = R, for which O and R are soluble. Processes without diffusion control will be considered first, and the effect of diffusion will be analyzed afterward. It will be assumed, as usual, that a large excess of supporting electrolyte is present.

Control by the Charge Transfer Reaction

Overvoltage–Time Variations for the Linearized Current–Overvoltage Characteristic.—The increment of charge is

$$\Delta_q = q_m - q_i \qquad (1)$$

where q_i is the charge density at the equilibrium potential for the electrode reaction O + ne = R and q_m is the charge density immediately after charging. It is assumed that the charging time is so short that leakage by the charge transfer reaction can be neglected during charging. The overvoltage η($\eta = E - E_e$, E_e equilibrium potential) at time t after charging is

$$\eta = (q - q_i)/c_d \qquad (2)$$

where q is the charge density at time t and c_d is the differential capacity of the electrode. It is assumed that variations of E are so small ($|\eta| < 5$ mv. approximately) that c_d is constant. The case of a variable double layer capacity is considered below. The signs in eq. 2 are consistent with the definition, $\eta = E - E_e$, and the dependence of q on E, namely $\eta \gtrless 0$ for $q - q_i \gtrless 0$. The charge density q is

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