TABLE I

VARIATION OF THE PSEUDO-FIRST-ORDER RATE CONSTANT WITH SULFATE ION CONCENTRATION[a]

235°			275°		
$[SO_4^=]_m$	$k' \times 10^2$, min.$^{-1}$	n[b]	$[SO_4^=]_m$	$k' \times 10^2$	n
0.05	3.7 ± 0.4	2	0.07	8.7 ± 0.4	2
.08	3.2	1	.10	7.7 ± 0	2
.10	2.8 ± .4	3	.15	5.6 ± 3	2
.125	2.2 ± .1	2	.20	4.9 ± 1	2
.15	2.0 ± .1	3	.225	4.2 ± 0	2
.175	1.8 ± .03	2	.25	3.8 ± 4	2
.20	1.5 ± .2	5	.30	3.3 ± 3	2
.21	1.5	1	.34(satd.)	3.5 ± 1	2
.22	1.6	1			
.25(satd.)	1.6 ± 0.1	3			

[a] Initial $S_2O_7^=$ concentration 0.01, 0.02, 0.03 m at 235°; 0.02 m at 275°. Nitrogen flow rate: 0.21 l./min. [b] n = number of runs.

TABLE II

RATE AND EQUILIBRIUM CONSTANT DATA FOR REACTIONS OF PYROSULFATE AND DICHROMATE WITH FUSED NITRATE

k (min.$^{-1}$)	T, °C.	$K_{S_2O_7^=}$	T, °C.	$K_{Cr_2O_7^=}$[a]
0.038	235	0.026	250	8.5×10^{-14}
0.096	275	0.038	300	3.8×10^{-12}
ΔH_a = 13 kcal.		ΔH = 5 kcal.		ΔH = 50 kcal.

[a] From extrapolation of data in ref. 2 and F. R. Duke and M. L. Iverson, *J. Phys. Chem.*, 62, 417 (1958).

TABLE III

SOLUBILITY OF Na_2SO_4 IN $NaNO_3$-KNO_3 EUTECTIC

T, °C.	Solubility (m) $\times 10^2$
235	25 ± 1
250	28.2 ± 0.7
275	34.2 ± .8
300	42.1 ± .5

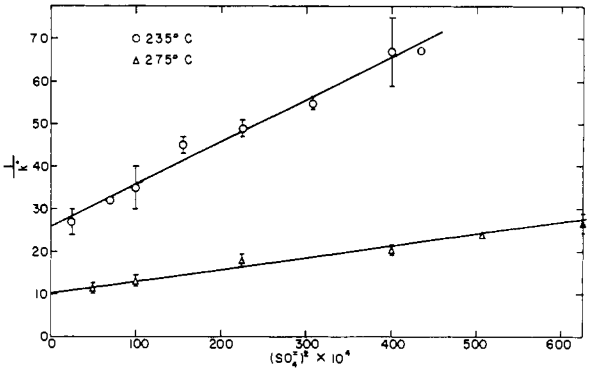

Fig. 1.—Plot of reciprocal rate data *vs.* $[SO_4^-]^2$ to determine k and K.

The plots of equation 7, $1/k'$ *vs.* the square of the initial sulfate ion concentration, are shown in Fig. 1. It should be noted that the sulfate ion concentration increases during the reaction and, therefore, the values for K obtained from these graphs may be slightly smaller than the true value.

Comparison with the Dichromate-Nitrate Reaction.—Since the dichromate and the pyrosulfate reactions have the same slow step and were studied under similar conditions, the rate constant obtained in this study can be used to calculate the equilibrium constant for the former. The result (see Table II) shows that $Cr_2O_7^{--}$ is a much weaker acid than $S_2O_7^{--}$. The rate of the dichromate reaction was brought into the measurable range by adding heavy metal ions to precipitate the chromate as it is formed. The large over-all apparent activation energy for the dichromate reaction (*ca.* 63 kcal.) is partly compensated by the increase in solubility of these chromate salts with temperature.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Kinetics of Discharge of Metal Ion Complexes with Preceding Chemical Reaction

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The kinetics of discharge of complexes with preceding formation of an intermediate by a purely chemical reaction are treated for faradaic impedance measurements and the galvanostatic and potentiostatic methods. Contributions from charge transfer and the preceding chemical reaction can be separated from experimental data. Analysis is given (a) for variations of the faradaic resistance (series equivalent circuit) and faradaic capacity with $1/\omega^{1/2}$ ($\omega = 2\pi f, f$ = frequency), (b) for potential–time curves, and (c) for current–time curves. The contribution from chemical kinetics vanishes for $1/\omega^{1/2} \rightarrow 0$ or $t = 0$, and the exchange current density can be computed from simple equilibrium considerations. The chemical kinetics component of the faradaic resistance is constant for large values of $1/\omega^{1/2}$ or t.

It is now well established[2] that discharge of certain metal ion complexes is preceded by a purely chemical reaction of the type

$$MY_p^{+(n-pz)} \rightleftarrows MY_\nu^{+(n-\nu z)} + (p-\nu)Y^{-z} \quad (1)$$

the exchange current for direct discharge being so low that reaction 1 followed by discharge of $MY_\nu^{+(n-\nu z)}$ is faster. The intermediate complex composition can be determined from variations of the exchange current with concentration of complexing agent, all other concentrations remaining constant. This method, which is similar to reaction order determination in chemical kinetics, was extended to electrode processes by Vetter[3] and Gerischer.[4] These authors assumed that chemical equilibrium is achieved but this assumption, while

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(2) For a review see, for instance, P. Delahay, *Ann. Rev. Phys. Chem.*, **8**, 229 (1957)

(3) (a) For a review see K. J. Vetter, *Z. Elektrochem.*, **59**, 596 (1955). (b) Also K. J. Vetter, "Transactions of Symposium on Electrode Processes," Philadelphia, May 1959, in course of publication.

(4) (a) For instance, H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953). (b) For a review see H. Gerischer, *Anal. Chem.*, **31**, 33–39 (1959).

entirely justified under proper experimental conditions, cannot always be made. The kinetics of the chemical step are considered here for the discharge of metal ion complexes on amalgam electrodes for faradaic impedance measurements, galvanostatic and potentiostatic methods.[5] Extension to other electrode processes with similar kinetics is immediate.

Current–Potential Characteristics.—The current density (positive for a net cathodic reaction) for the discharge of $MY_\nu^{+(n-\nu z)}$ is

$$I = nFk_s' \left\{ C_\nu \exp\left[-\frac{\alpha nF(E-E_s)}{RT}\right] - C_y^\nu C_a \exp\left[\frac{(1-\alpha)nF(E-E_s)}{RT}\right]\right\} \quad (2)$$

where C_ν is the concentration of $MY_\nu^{+(n-\nu z)}$ at the discharge site; C_a the amalgam concentration at the electrode surface; C_y the concentration of complexing agent at the discharge site; k_s' the formal rate constant at the standard potential E_s for the charge transfer reaction, *e.g.*, the discharge of $MY_\nu^{+(n-\nu z)}$ (*not* the over-all reaction); E the potential in the European convention; α the transfer coefficient; and F, R, T have their usual significance. Kinetic data can more conveniently be given at the standard potential E^0 for the over-all reaction, *e.g.*, the reduction of $MY_p^{+(n-pz)}$ to the amalgam. Equation 2 is applicable except that $E - E_s$ and C_ν are replaced by $E - E^0$ and C_ν/K, respectively, K being the instability constant for reaction 1.

The common value of the current densities for the forward and backward reactions is equal to the *exchange current density* I_0 at the equilibrium potential E_e for the bulk concentration of reactants. Thus, by application of the Nernst equation at E_e there follows

$$I_0 = nFk_s(C_p^0)^{1-\alpha}(C_a^0)^\alpha(C_y^0)^{\nu-p(1-\alpha)} \quad (3)$$

where C_p^0 is the bulk concentration of $MY_p^{+(n-pz)}$, and C_a^0 and C_y^0 the bulk concentrations of amalgam and complexing agent, respectively. Note (a) that I_0 does not include any kinetic parameter for the preceding chemical step and (b) that I_0 and k_s are formal kinetic parameters depending on the double layer structure (Frumkin). For correction of the double layer effect, see a previous paper from this Laboratory.[6]

By combination of eq. 3 with eq. 2, as written in terms of E^0 and K, one obtains in the same fashion as in a previous paper[7]

$$I = I_0 \left\{ \frac{C_\nu}{C_\nu^0} \exp\left[-\frac{\alpha nF(E-E_e)}{RT}\right] - \frac{C_a}{C_a^0} \exp\left[\frac{(1-\alpha)nF(E-E_e)}{RT}\right]\right\} \quad (4)$$

where C_ν^0 is the bulk concentration of $MY_\nu^{+(n-\nu z)}$. This is the general current–potential equation for processes with preceding reaction 1. The concentrations C_ν and C_a of eq. 4 will be derived from the Fick equation modified for the occurrence of the preceding step of eq. 1. This approach is based on the ideas originally developed by Koutecky and Brdicka[8] in their classical paper on polarographic kinetic currents. It will be assumed that (a) the reaction site is at $x = 0$, x being the distance from the electrode; (b) there is practically no concentration polarization of Y; and (c) the overvoltage, $E - E_e$, except for the potentiostatic method, does not exceed a few millivolts. Equation 4 then can be linearized in terms of E by expansion in series of the exponentials. Thus

$$I = I_0\left[\frac{C_\nu}{C_\nu^0} - \frac{C_a}{C_a^0} - \frac{nF}{RT}(E-E_e)\right] \quad (5)$$

for $(E - E_e) << RT/nF$, $|C_\nu^0 - C_\nu| << C_\nu^0$, and $|C_a^0 - C_a| << C_a^0$.

Faradaic Impedance Measurements.—The derivation is quite similar to Gerischer's analysis[9] of the simpler process with control by a chemical step and diffusion (*e.g.*, $I_0 \rightarrow \infty$). The elements r_s and c_s of the series equivalent circuit in the usual case in which $C_\nu^0 \ll C_p^0$, *i.e.*, $K \ll 1$, are

$$r_s = \frac{RT}{nF}\left[\frac{1}{I_0} + \frac{1}{2^{1/2}nF}\left(\frac{1}{C_p^0D^{1/2}} + \frac{1}{C_a^0D_a^{1/2}}\right)\frac{1}{\omega^{1/2}}\right] + Z_r \quad (6)$$

$$\frac{1}{\omega c_s} = \frac{RT}{nF}\left[\frac{1}{2^{1/2}nF}\left(\frac{1}{C_p^0D^{1/2}} + \frac{1}{C_a^0D_a^{1/2}}\right)\frac{1}{\omega^{1/2}}\right] + Z_c \quad (7)$$

with

$$Z_r = \frac{RT}{2^{1/2}n^2F^2}\,\frac{(C_y^0)^{p-\nu}}{D^{1/2}KC_p^0}\left\{\frac{[\omega^2 + k_b^2(C_y^0)^{2(p-\nu)}]^{1/2} + k_b(C_y^0)^{p-\nu}}{\omega^2 + k_b^2(C_y^0)^{2(p-\nu)}}\right\}^{1/2} \quad (8)$$

and Z_c being given by eq. 8 with $-k_b(C_y^0)^{p-\nu}$ instead of $k_b(C_y^0)^{p-\nu}$ in the numerator. New notations are: D the common value of the diffusion coefficients of $MY_p^{+(n-p\nu)}$ and $MY_\nu^{+(n-\nu z)}$ which are assumed to be equal; D_a the diffusion coefficient of M in the amalgam; and k_b the rate constant for the backward reaction of eq. 1.

Equations 6 and 7 are of the same form as for direct discharge except for Z_r and Z_c. The terms in $1/\omega^{1/2}$ and $1/I_0$ in eq. 6 represent the contributions of diffusion and slow discharge, respectively. Two limiting cases will be examined according to whether $\omega \ll k_bC_y^{0(p-\nu)}$ or $\omega \gg k_bC_y^{0(p-\nu)}$. In the first case $Z_c = 0$ and the component

$$Z_r = \frac{RT}{n^2F^2D^{1/2}}\,\frac{(C_y^0)^{(p-\nu)/2}}{Kk_b^{1/2}C_p^0} \quad (9)$$

is independent of frequency. By comparison of Z_r from eq. 9 with $(RT/nF)(1/I_0)$ of eq. 8 one can readily establish conditions under which Z_r is negligible at low frequencies. This case can be encountered since one easily has $k_b = 10^8$ sec.$^{-1}$ mole^{-1} l.) *cf.* the case of cadmium cyanide discussed below) and $C_y^0 = 0.1$ mole l.$^{-1}$, *i.e.*, for $p - \nu = 1$, $\omega << 10^7$ radians per sec.

When $\omega \gg k_bC_y^{0(p-\nu)}$

$$r_s = \frac{RT}{nF}\left\{\frac{1}{I_0} + \frac{1}{2^{1/2}nF}\left[\frac{1}{C_p^0D^{1/2}}\left(1 + \frac{(C_y^0)^{p-\nu}}{K}\right) + \frac{1}{C_a^0D_a^{1/2}}\right]\frac{1}{\omega^{1/2}}\right\} \quad (10)$$

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[5] For an analysis of polarographic waves *cf.* H. Matsuda, unpublished investigation.

[6] M. Breiter, M. Kleinerman and P. Delahay, This Journal, **80**, 5111 (1958).

[7] T. Berzins and P. Delahay, *ibid.*, **77**, 6448 (1955). See references therein.

[8] J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

[9] H. Gerischer, *Z. physik. Chem.*, **198**, 286 (1951); **201**, 55 (1952).

and $1/\omega C_s$ is given by eq. 7 in which Z_c is made equal to zero and the term in $1/\omega^{1/2}$ is the same as in eq. 10. Note that the term in $1/C_p^0$ in eq. 10 is practically $1/C_p^0 D^{1/2}$, *i.e.*, r_s at sufficiently high frequencies depends on the equilibrium concentration of the discharged species and not on the kinetics of reaction 1. For $1/\omega^{1/2} \rightarrow 0$, $r_s = (RT/nF)\cdot(1/I_0)$, *e.g.*, r_s solely depends on the exchange current when $\omega \rightarrow \infty$. The influence of the kinetics of reaction 1 progressively decreases with increasing frequency, *i.e.*, with decreasing $1/\omega^{1/2}$.

The foregoing analysis accounts for certain not yet fully explained observations on faradaic impedance. For instance, Gerischer[4a] found it necessary to use very high salt concentrations (5 M sodium chloride) in measurements on the discharge of $Cd(CN)_4^{--}$ and $Cd(CN)_3^-$ on a cadmium-amalgam electrode. Discharge of $Cd(CN)_4^{--}$ is preceded by transformation[6,10] into $Cd(CN)_3^-$. Dissociation into $Cd(CN)_2$ also is observed[11] at sufficiently low cyanide concentrations. The rate of formation of $Cd(CN)_3^-$ and/or $Cd(CN)_2$ increases with the foreign salt concentration[6,10] because of the double layer effect, and the condition $\omega \gg k_b(C_y^0)^{p-\nu}$ is fulfilled at relatively low frequencies in 5 M sodium chloride. Furthermore, the chemical contribution is then quite negligible.

Galvanostatic Method.—The exchange current in this method is determined from potential–time curves observed at constant cell current in unstirred solution. An analysis was reported[7] previously for potential–time curves for direct discharge in which the effect of the capacity current (charging of the double layer) was considered. This correction for the capacity current also holds here. The concentrations C_a and C_ν in eq. 5 are known from the Sand equation[12] and a previous paper[13] from this Laboratory. Thus ($K << 1$)

$$E - E_e = - \frac{RT}{nF} I \left\{ \frac{1}{I_0} + \frac{2}{\pi^{1/2} nF} \left[\frac{1}{C_p^0 D^{1/2}} + \frac{1}{C_a^0 D_a^{1/2}} \right] t^{1/2} + \frac{1}{nFD^{1/2}C_p^0} \frac{\operatorname{erf}[k_b^{1/2}(C_y^0)^{(p-\nu)/2}\, t^{1/2}]}{K k_b^{1/2} (C_y^0)^{-(p-\nu)/2}} \right\} \quad (11)$$

This equation, except for the last term, is the same as the one previously derived[7,14] for a process without preceding chemical step. The error function in eq. 11 is equal to zero for $t = 0$, and consequently I_0 can be calculated directly from the overvoltage at $t = 0$. Thus, the kinetics of reaction 1 need not be considered at $t = 0$ just as for the faradaic impedance for $\omega \rightarrow \infty$. Conversely, the error function in eq. 11 is practically equal to unity for $k_b^{1/2} (C_Y^0)^{(p-\nu)/2} t^{1/2} < 2$, and the overvoltage extrapolated with $t^{1/2}$ to $t^{1/2} = 0$ for sufficiently large t's includes a chemical kinetic term independent of time. This situation corresponds to $\omega \rightarrow 0$ for faradaic impedance measurements.

These considerations are readily extended to the double pulse galvanostatic method developed by Gerischer and Krause.[15]

Potentiostatic Method.—The calculations follow the same pattern as for simple electrode processes treated by Gerischer and Vielstich.[16a] These authors' treatment in its turn is inspired from theoretical treatments of irreversible polarographic waves.[16b] The analysis of the preceding chemical step follows Koutecky and Brdicka.[8] The general equation of the current–time curve is quite involved, and only the particular case when $k_b(C_y^0)^{p-\nu}t << 1$ ($K << 1$) will be considered. One then has

$$I = I_0 \left\{ \exp\left[-\frac{\alpha nF}{RT}(E - E_e) \right] - \exp\left[\frac{(1-\alpha)nF}{RT}(E - E_e) \right] \right\} \left\{ \exp(\gamma^2 t)\operatorname{erfc}(\gamma t^{1/2}) + k_b C_y^{0\,2(p-\nu)} \frac{a}{\gamma^3 K} \left[\frac{2\gamma t^{1/2}}{\pi^{1/2}} - 1 - (\gamma^2 t - 1)\exp(\gamma^2 t)\operatorname{erfc}(\gamma t^{1/2}) \right] \right\} \quad (12)$$

with

$$a = \frac{I_0}{nF} \frac{1}{D^{1/2} C_p^0} \exp\left[-\frac{\alpha nF}{RT}(E - E_e) \right] \quad (13)$$

$$b = \frac{I_0}{nF} \frac{1}{D_a^{1/2} C_a^0} \exp\left[(1-\alpha)\frac{nF}{RT}(E - E_e) \right] \quad (14)$$

$$\gamma = \frac{a}{K} + b \quad (15)$$

By expansion in series of the exp and erfc functions in eq. 12 one can show (a) that the current decreases linearly with $t^{1/2}$ for very short times and (b) that the extrapolated current to $t = 0$ is

$$I_0 \left\{ \exp\left[-\frac{\alpha nF}{RT}(E - E_e) \right] - \exp\left[\frac{(1-\alpha)nF}{RT}(E - E_e) \right] \right\}$$

i.e., the extrapolated current has the value corresponding to the equilibrium for reaction 1. This situation corresponds to $1/\omega \rightarrow 0$ for the faradaic impedance and $t \rightarrow 0$ for the galvanostatic method.

These considerations could be transposed easily to the voltage-step method.[17]

Conclusion

Determination of the reaction order for electrode processes is possible for processes preceded by a pseudo-first-order chemical reaction even when equilibrium is not achieved for the chemical reaction. Conditions in which equilibrium is practically reached can be deduced from the foregoing kinetic analysis.

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(11) J. Koryta, *Z. Elektrochem.*, **61**, 423 (1957).

(12) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishing Co., New York, N. Y., 1954, p. 180. See eq. 8-6.

(13) P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953). See eq. 21.

(14) T. Berzins and P. Delahay, *J. Chem. Phys.*, **23**, 972 (1955). See also ref. 7.

(15) (a) H. Gerischer and M. Krause, *Z. physik. Chem.*, *N. F.*, **10**, 264 (1957); **14**, 184 (1958); (b) H. Matsuda, S. Oka and P. Delahay, THIS JOURNAL, **81**, 5077 (1959).

(16) (a) H. Gerischer and W. Vielstich, *Z. physik. Chem.*, *N.F.*, **3**, 16 (1955); **4**, 10 (1955); (b) see ref. 12, pp. 72–86.

(17) W. Vielstich and P. Delahay, THIS JOURNAL, **79**, 1874 (1957)