univalent chloride systems. S appears to decrease rapidly in the more dilute solutions and to approach constancy at the higher concentrations. When the sensitivity of this test is taken into account, it appears that equations 2 and 3 yield a close approximation to the actual behaviors of these mixtures.

For purposes of future comparison, we record in Table IV the hypothetical osmotic coefficients of the mixtures and the water vapor pressure of the solutions as calculated by equations 7 and 8.

TABLE IV

OSMOTIC COEFFICIENTS AND VAPOR PRESSURES AT 25° OF THE SYSTEM $HCl–AlCl_3–H_2O$

$\mu = 1$			$\mu = 3$			$\mu = 5$		
m	ϕ_x	p	m_1	ϕ_x	p	m_1	ϕ_x	p
1.0	1.039	22.88	3.0	1.348	20.54	5.0	1.680	17.55
0.9	1.026	22.96	2.7	1.327	20.79	4.5	1.651	18.00
.8	1.013	23.02	2.4	1.306	21.03	4.0	1.622	18.44
.7	1.000	23.09	2.1	1.282	21.27	3.6	1.592	18.89
.6	0.985	23.15	1.8	1.257	21.51	3.0	1.560	19.33
.5	.968	23.22	1.5	1.230	21.75	2.5	1.526	19.78
.4	.950	23.28	1.2	1.199	21.99	2.0	1.488	20.23
.3	.929	23.34	0.9	1.164	22.22	1.5	1.447	20.67
.2	.904	23.48	.6	1.123	22.46	1.0	1.399	21.12
.1	.872	23.49	.3	1.072	22.69	0.5	1.343	21.57
.0	.831	23.52	.0	1.006	22.91	0.1	1.272	22.01

Conclusions

(1) Equation 2 represents within narrow limits the variation of the logarithm of the activity coefficient of hydrochloric acid in aluminum chloride solutions. The values of α_{12} change little with ionic strength in these solutions. A like behavior is found for hydrochloric acid–cerium chloride–water systems.

(2) The calculated values of the quantity α_{21}, vary with ionic strength, and consequently $S = 12\alpha_{12} + 4\alpha_{21}$ is found to decrease with increasing concentration. The magnitude of this decrease indicates that in these concentrated solutions, small deviations from results calculated by equation 3 will occur.

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Mechanism of Complex Electrode Reactions

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Several possible mechanisms may be envisaged to explain any complex electrode reaction. By assuming a single step to be rate determining, any postulated mechanism may be reduced to an "equivalent reaction pair," which embodies all the kinetic properties of the mechanism. Account is taken of concentration polarization by including transport processes in the treatment. The procedure is easily extended to cover cases of mixed rate determination. From the equivalent reaction pair, current-voltage relationships can be derived in which it is possible to recognize regions of specific control. The converse operation, the determination of the reaction mechanism from current-voltage curves, is subject to severe limitation. The most direct method, examination of the regions of specific control, is applicable only for intermediate values of the rate constant. Under favorable conditions, experimental data will enable the equivalent reaction pair to be constructed, from which possible mechanisms may be inferred. Mechanisms yielding the same equivalent pair are kinetically indistinguishable.

Analysis of conditions at an electrode surface is greatly simplified if one variable, time, can be ignored; hence steady-state conditions only will be treated here. A steady-state electrode system is one in which the activities of all substances present, both at the electrode surface and in the bulk, do not vary appreciably with time, at any potential within the experimental range. Constancy of current is a necessary, though not a sufficient, criterion of steady-state conditions.

The term "electrode reaction" will here denote those processes intimately concerned in the transfer of electrons between an electrode and substances in solution. An electrode reaction may thus involve, in addition to the actual electron transfer, many other reactions, all occurring within a few molecular diameters of the electrode surface. It is convenient to consider the volume in which electrode reactions occur as a zone in which concentrations are uniform and to refer to the activities of substances in this reaction zone as activities "at" the electrode surface. It must be borne in mind that the reaction zone is also occupied by the electrical double layer, but no further mention will be made of this layer on the assumption that any effect of it will be nullified by an excess of indifferent electrolyte, the presence of which will be assumed throughout.

Reaction Rates

Any electrode reaction can be represented by a pair of opposed reactions

$$\text{over-all reactants} + Ne^- \rightleftarrows \text{over-all products} \quad (1)$$

expressing the over-all stoichiometry of the reaction. Only for very simple electrode reactions, such as $Tl^+ + e^- \rightleftarrows Tl$, however, can it be hoped that (1) will depict the mechanism of the process. For a more complex reaction the most likely mechanism is a sequence of a number, say m, of pairs of opposed reactions

$$\begin{array}{rcll} \text{initial reactants} & \rightleftarrows & \text{initial products} & (2:1) \\ \text{second reactants} & \rightleftarrows & \text{second products} & (2:2) \\ \cdots\cdots & & \cdots\cdots & \\ \text{penultimate reactants} & \rightleftarrows & \text{penultimate products} & (2:m-1) \\ \text{final reactants} & \rightleftarrows & \text{final products} & (2:m) \end{array}$$

all proceeding at the electrode surface. The possibility of parallel reaction paths is considered in an appendix. At least one pair, and possibly more than one, of these $2m$ reactions will involve electrons.

The rate of each of these reactions is governed by the usual kinetic laws of heterogeneous reactions, provided no electrons are involved. Thus, if the jth pair of reactions is

$$r_1\mathrm{R}_1 + r_2\mathrm{R}_2 + \ldots\ldots \rightleftharpoons p_1\mathrm{P}_1 + p_2\mathrm{P}_2 + \ldots\ldots \tag{2:j}$$

involving r_1 moles of R_1, etc., and yielding p_1 moles of P_1, etc., the rates of each reaction, in moles cm.$^{-2}$ sec.$^{-1}$, are

$$\overrightarrow{\text{rate}}_{\text{j}} = \overrightarrow{k}_{\text{j}}[\mathrm{R}_1]^{r_1}[\mathrm{R}_2]^{r_2}\ \ldots \tag{3}$$

$$\overleftarrow{\text{rate}}_{\text{j}} = \overleftarrow{k}_{\text{j}}[\mathrm{P}_1]^{p_1}[\mathrm{P}_2]^{p_2}\ \ldots \tag{4}$$

where $[\mathrm{R}_1]$, $[\mathrm{R}_2]$, $[\mathrm{P}_1]$, etc., are the activities of R_1, R_2, P_1, etc., at the electrode surface, considered as dimensionless quantities. The terms $\overrightarrow{k}_{\text{j}}$ and $\overleftarrow{k}_{\text{j}}$ are heterogeneous rate constants having the dimensions moles cm.$^{-2}$ sec.$^{-1}$; these rate constants are defined somewhat differently than is usual,[1] being equal to the actual rates of the opposed reactions when all reactants are at unit activity.

If electrons are also involved in the reaction pair $(2{:}j)$, *e.g.*, if the forward reaction as written is a reduction involving n_{j} electrons, then the rate laws are[2]

$$\overrightarrow{\text{rate}}_{\text{j}} = \overrightarrow{k}_{\text{j}}[\mathrm{R}_1]^{r_1}\,[\mathrm{R}_2]^{r_2}\exp\left\{-n_{\text{j}}\alpha_{\text{j}}\,\frac{FV}{RT}\right\} \tag{5}$$

$$\overleftarrow{\text{rate}}_{\text{j}} = \overleftarrow{k}_{\text{j}}[\mathrm{P}_1]^{p_1}\,[\mathrm{P}_2]^{p_2}\exp\left\{n_{\text{j}}(1-\alpha_{\text{j}})\,\frac{FV}{RT}\right\} \tag{6}$$

where F, R and T are, respectively, the faraday, the gas constant and the absolute temperature, α_{j} is the transfer coefficient of the reduction (a symmetry factor taking some value between zero and unity) and V is the potential across the interface. The dimensions of $\overrightarrow{k}_{\text{j}}$ and $\overleftarrow{k}_{\text{j}}$ are the same as before but their magnitudes are dependent on the potential scale used to measure V. We shall choose the scale that gives $V = 0$ when (1) is at equilibrium with all reactants and products at unit activity. In view of (5) and (6) it would seem that the mechanism is most aptly represented by

$$r_1\mathrm{R}_1 + r_2\mathrm{R}_2 + \alpha_{\text{j}}n_{\text{j}}\mathrm{e}^- \rightleftharpoons p_1\mathrm{P}_1 + p_2\mathrm{P}_2 - (1-\alpha_{\text{j}})n_{\text{j}}\mathrm{e}^- \tag{2:j'}$$

If $n = 0$, equations 5 and 6 reduce to (3) and (4) and these latter can, therefore, be regarded as special cases of the former.

If a steady state exists for the electrode reaction (1), the surface activities of all substances are invariant at a given potential and all $\overrightarrow{\text{rates}}$ and $\overleftarrow{\text{rates}}$ of each pair in (2) are constant. Moreover, each step in the sequence must proceed at the same net rate which will be the net rate of the over-all reaction. That is

$$\text{net rate} = \frac{\overrightarrow{\text{rate}}_1 - \overleftarrow{\text{rate}}_1}{q_1} = \ldots = \frac{\overrightarrow{\text{rate}}_{\text{j}} - \overleftarrow{\text{rate}}_{\text{j}}}{q_{\text{j}}} = \ldots = \frac{\overrightarrow{\text{rate}}_{\text{m}} - \overleftarrow{\text{rate}}_{\text{m}}}{q_{\text{m}}} \tag{7}$$

where the q's are numbers chosen such that when pair (2:1) is multiplied by q_1, pair (2:2) by q_2, etc., and the m pairs are then summed algebraically, the resultant reaction pair is (1).

Now, in general, one of the m opposed pairs will have the property of being "rate determining." By this is meant that if the net rate is far more dependent on the magnitude of $\overrightarrow{k}_{\text{j}}$ or $\overleftarrow{k}_{\text{j}}$ than on any other $\overrightarrow{k}$ or $\overleftarrow{k}$, then the jth pair is rate determining. A more precise consideration of the rate-determining pair is given below. Frequently the rate-determining pair will be the "slowest pair," *i.e.*, the pair for which rate/q is smallest, but this is not necessarily so except at equilibrium.

Equation 7 is of little use as an expression for the over-all net rate, since it will usually involve indeterminate activity terms, *i.e.*, terms expressing the activities of substances present only at the electrode surface.

Classification of Substances.—The environment of an electrode frequently contains many different substances. These may be classified as follows, in accordance with the role that each plays in the electrode reaction.

Class I: substances not involved in any way in the electrode reaction. The solvent, inert electrolytes and inert electrode materials would commonly belong under this heading. Class I substances are important only in so far as they affect the activities of other substances; in this discussion we shall assume activity coefficients to be constant.

Class II: substances involved in the electrode reaction which are present both in the bulk of the solution phase (or the electrode phase) and at the surface, but at different activities. It is usually possible to choose experimental conditions such that only one (or at the most, two) of the substances present in the system fall into Class II.

Class III: substances participating in the electrode reaction which are present both in the bulk and at the interface, and at activities that are not significantly different. It is convenient to subdivide Class III.

Class IIIa: those Class III substances whose activities are subject to experimental variation.

Class IIIb: those Class III substances whose activities are not subject to significant variation, such as a solvent or a pure electrode component which participates in the electrode reaction. It is usual to consider the activities of all such substances as unity, and this convention will be followed here.

Class IV: substances present only at the electrode surface, where they are formed transiently and only at low concentrations. These substances are too unstable in the environment of the electrode to be transported into the bulk.

Class V: substances produced at the electrode surface where they are capable of further reaction, but which are stable enough to allow some fraction to escape from the interface. When such substances are present, a side reaction may be said to occur; such systems will be excluded from subsequent discussion.

Class VI: substances present at the interface that cannot properly be considered as part of

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(1) J. E. B. Randles, *Trans. Faraday Soc.*, **48**, 828 (1952).

(2) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 577. See also J. O'M. Bockris, *Ann. Rev. Phys. Chem.*, **5**, 477 (1954), and many of the references cited therein.

either the solution phase or the electrode phase. Gas bubbles and certain films fall under this heading. Systems containing Class VI substances will not be considered.

To exemplify this classification, consider the system consisting of a silver-plated platinum electrode in contact with an aqueous solution of 0.1 M KCN and 10^{-3} M $AgNO_3$. The over-all electrode reaction could then be written

$$Ag(CN)_2^- + e^- \rightleftharpoons Ag + 2CN^-$$

Pt and the ions K^+ and NO_3^- fall into Class I; $Ag(CN)_2^-$ is a Class II substance; CN^- belongs to Class IIIa and Ag to Class IIIb. Water might be placed in Class I, but since solvation of the ions may be an important factor, a rigorous classification would assign it to Class IIIb. The species AgCN and Ag^+ might be speculated to belong to Class IV.

The Equivalent Reaction Pair.—Let us now reexamine the over-all reaction pair (1) and the mechanistic scheme of reaction pairs, (2), in the light of the classification of substances. All substances in (1) must belong to Classes II or III. However, most of the groups of substances in (2)—"initial products," "second reacants," . . ., "penultimate products" and "final reactants"—may contain Class IV substances in addition to substances in Classes II or III. Let us rewrite the over-all reaction pair, thus

$$a_0A + b_0B + \ldots. + Ne^- \rightleftharpoons a_0'A + b_0'B + c_0'C + \ldots \quad (8)$$

where A, B, C, . . . represent Class II or III substances present at the electrode and a_0, a_0', b_0 . . . are numbers expressing the stoichiometry. Half of these numbers will be zero. Similarly, a general pair, the jth, of the opposed reactions constituting scheme (2) may be rewritten

$$a_jA + b_jB + \ldots. + z_jZ + y_jY + x_jX + \ldots. + n_j\alpha_je^- \rightleftharpoons a_j'A + b_j'B + \ldots. + z_j'Z + y_j'Y + \ldots. - n_j(1 - \alpha_j)e^- \quad (9:j)$$

where Z, Y, X, . . . represent substances in Class IV. Again, a_j, a_i', b_j, z_j, z_j', y_j, n_j, . . ., etc., are pure numbers expressing the stoichiometry of the reaction pair; most of these numbers will be zero. m such reaction pairs may be written. In accordance with the definition of q_j, the following relationships must be true

$$N = q_1n_1 + q_2n_2 + \ldots. + q_jn_j + \ldots. + q_mn_m \quad (10)$$

$$a_0 - a_0' = q_1a_1 + \ldots. + q_ja_j + \ldots + q_ma_m - q_1 a_1' - \ldots - q_ma_m' \quad (11:a)$$

$$0 = q_1z_1 + \ldots. + q_jz_j + \ldots. + q_mz_m - q_1z_1' - \ldots - q_mz_m' \quad (12:z)$$

and (11:b), (11:c) . . . (12:y), (12:x), . . . similar to (11:a) and (12:z).

If the jth reaction pair is completely rate determining, all reaction pairs other than the jth will behave as true equilibria. Hence we can set up (m − 1) equilibrium expressions, such as the following one for the gth pair ($g \neq j$):

$$\frac{[A]^{a_g'}[B]^{b_g'} \ldots. [Z]^{z_g'}[Y]^{y_g'} \ldots.}{[A]^{a_g}[B]^{b_g} \ldots. [Z]^{z_g}[Y]^{y_g} \ldots.} = \frac{\overrightarrow{k}_g}{\overleftarrow{k}_g} \exp \left\{ - n_g \frac{FV}{RT} \right\} \quad (13:g)$$

The intention is now to combine all the pairs preceding the jth and all those succeeding it, denoting quantities associated with these combinations by the subscripts "u" and "v," respectively. It is convenient to define the following terms: n_u, $\overrightarrow{k}_u$, $\overleftarrow{k}_u$, a_u, b_u, . . ., z_u, y_u, . . . The defining equations are

$$q_jn_u = q_1n_1 + q_2n_2 + \ldots. + q_{j-2}n_{j-2} + q_{j-1}n_{j-1} \quad (14)$$

$$\left(\overrightarrow{k_u}\right)^{qj} = \left(\overrightarrow{k_1}\right)^{q1}\left(\overrightarrow{k_2}\right)^{q2} \ldots. \left(\overrightarrow{k_{j-1}}\right)^{qj-1} \quad (15)$$

$$\left(\overleftarrow{k_u}\right)^{qj} = \left(\overleftarrow{k_1}\right)^{q1}\left(\overleftarrow{k_2}\right)^{q2} \ldots. \left(\overleftarrow{k_{j-1}}\right)^{qj-1} \quad (16)$$

$$q_ja_u = q_1(a_1' - a_1) + \ldots.. q_{j-1}(a_{j-1}' - a_{j-1}) \quad (17:a)$$

and equations analogous to (17:a) with "a" replaced by b, c, z, y, etc. The terms n_v, $\overrightarrow{k}_v$, $\overleftarrow{k}_v$, a_v, z_v, etc., are defined by equations similar to (14) through (17) except that the summations (or products) are taken over the (j + 1)th to the mth pair, rather than the first to the (j − 1)th. If (13:1) is raised to the q_1th power, (13:2) to the q_2th power, . . . and (13:j − 1) to the q_{j-1}th power, and the q_jth root of the product is extracted, we obtain

$$[A]^{a_u}[B]^{b_u} \ldots. [Z]^{z_u}[Y]^{y_u} \ldots = \frac{\overrightarrow{k}_u}{\overleftarrow{k}_u} \exp \left\{ - n_u \frac{FV}{RT} \right\} \quad (18)$$

The analogous equation in "v" may be obtained similarly.

From equations 10, 11, 12, 14, 17 and their analogs, the following may be derived

$$N = q_j(n_u + n_j + n_v) \quad (19)$$

$$a_0' - a_0 = q_j(a_u + a_v + a_j' - a_j) \quad (20:a)$$

$$z_j - z_u = z_j' + z_v = z \quad (21:z)$$

together with analogous expressions in "b," "y," etc. The un-subscripted symbols z, y, . . . are defined by equations (21:z), (21:y), etc.

From equations 5 and 6, the rates of the forward and backward reactions of the rate-determining pair are

$$\overrightarrow{\text{rate}}_j = \overrightarrow{k}_j[A]^{a_j}[B]^{b_j} \ldots. [Z]^{z_j}[Y]^{y_j} \ldots \exp \left\{ - n_j\alpha_j \frac{FV}{RT} \right\} \quad (22)$$

$$\overleftarrow{\text{rate}}_j = \overleftarrow{k}_j[A]^{a_j'}[B]^{b_j'} \ldots. [Z]^{z_j'}[Y]^{y_j'} \ldots \exp \left\{ n_j(1 - \alpha_j) \frac{FV}{RT} \right\} \quad (23)$$

Equation 22 may be combined with (18), and (23) with the "v" analog of (18) to give

$$\overrightarrow{\text{rate}}_j = \phi \frac{\overrightarrow{k}_j \overrightarrow{k}_u}{\overleftarrow{k}_u} [A]^{(a_j - a_u)}[B]^{(b_j - b_u)} \ldots \exp \left\{ - (n_u + n_j\alpha_j) \frac{FV}{RT} \right\} \quad (24)$$

$$\overleftarrow{\text{rate}}_j = \phi \frac{\overleftarrow{k}_j \overleftarrow{k}_v}{\overrightarrow{k}_v} [A]^{(a_j' + a_v)}[B]^{(b_j' + b_v)} \ldots \exp \left\{ (n_v + n_j - n_j\alpha_j) \frac{FV}{RT} \right\} \quad (25)$$

where

$$\phi = [Z]^z[Y]^y[X]^x \ldots.. \quad (26)$$

Henceforth it will be assumed that $\phi = 1$. The significance of this limitation is discussed in an appendix, where it is shown that the restriction is not as serious as might be imagined.

Consider the system at equilibrium with [A] = [B] = . . . = 1, *i.e.*, with the electrode at its standard potential, E_0 (*versus* some arbitrary reference electrode). Then $\overrightarrow{\text{rate}}_j = \overleftarrow{\text{rate}}_j$ and $V = 0$. Hence, from (24) and (25)

$$\frac{\overrightarrow{k_j}\,\overrightarrow{k_u}}{\overleftarrow{k_u}} = \frac{\overleftarrow{k_j}\,\overleftarrow{k_v}}{\overrightarrow{k_v}} = k \qquad (27)$$

where k is thereby defined. Now consider the system at equilibrium, but not under standard conditions. Again the two rates may be equated and utilizing (19), (20) and (27) we may derive

$$\frac{[\mathrm{A}]^{a_0'}[\mathrm{B}]^{b_0'}[\mathrm{C}]^{c_0'}\ \ldots.}{[\mathrm{A}]^{a_0}[\mathrm{B}]^{b_0}[\mathrm{C}]^{c_0}\ \ldots.} = \exp\left\{-N\frac{FV}{RT}\right\} \qquad (28)$$

To the system the familiar Nernst equation must apply and this latter on being applied to the over-all electrode reaction (8) gives a result identical with (28), except that V is replaced by $(E - E_0)$. Hence $V = (E - E_0)$ and if we conveniently choose a potential reference scale having $E_0 = 0$, then $V = E$, the actual (measurable) electrode potential.

We have now derived expressions for the rates of an opposed pair of reactions in a form independent of the activities of any Class IV substance. Thus a useful expression for the over-all net rate may now be formulated from (7), (24), (25) and the results of the last paragraph, thus

$$\begin{aligned} q_j(\text{net rate}) = {} & k[\mathrm{A}]^{(a_j - a_u)}[\mathrm{B}]^{(b_j - b_u)}\ \ldots \\ & \exp\left\{-(n_u + n_j\alpha_j)\frac{FE}{RT}\right\} \\ & - k[\mathrm{A}]^{(a_j' + a_v)}[\mathrm{B}]^{(b_j' + b_v)}\ \ldots \\ & \exp\left\{(n_v + n_j - n_j\alpha_j)\frac{FE}{RT}\right\} \qquad (29) \end{aligned}$$

It will be noted that, apart from the factor q_j, the rate law expressed by (29) is identical with the law applicable to the single hypothetical reaction pair

$$\begin{aligned} & (a_j - a_u)\mathrm{A} + (b_j - b_u)\mathrm{B} + \ldots + (n_u + n_j\alpha_j)\mathrm{e}^- \rightleftharpoons \\ & \quad (a_j' + a_v)\mathrm{A} + (b_j' + b_v)\mathrm{B} + \ldots. - \\ & \qquad (n_v + n_j - n_j\alpha_j)\mathrm{e}^- \qquad (30) \end{aligned}$$

when both rate constants are equal to k. (30) may be termed the "equivalent reaction pair" of the mechanism, since it embodies all the kinetic properties of the sequence of reaction pairs constituting the true mechanism. It also represents the maximum information that can be gained concerning the mechanism from kinetic studies: if two different mechanisms yield the same equivalent reaction pair, they will exhibit the same kinetic properties. The foregoing remarks apply only to the range of conditions (of concentrations, potential and temperature) within which the mechanism and the rate-determining step remain unchanged.

The equivalent reaction pair may be readily deduced from the mechanistic scheme. The individual opposed pairs must first be "balanced"; the substances comprising the pairs preceding the rate-determining pair must be then grouped on the left-hand side of the equivalent pair (due regard being paid to sign), together with the left-hand side of the rate-determining pair; the remaining substances are then assigned to the right-hand side of the equivalent opposed pair. The following examples will make this procedure clear.

Example. Mercurous Ion Reduction.—Mercurous nitrate in acidic solution is reduced at a mercury electrode in accordance with the over-all reaction pair

$$\mathrm{Hg_2^{++}} + 2\mathrm{e}^- \rightleftharpoons 2\mathrm{Hg}$$

We shall consider several conceivable mechanisms for this electrode reaction, deduce the equivalent reaction pair and so derive the expression for the over-all net rate. The rate-determining pair is denoted by an asterisk.

Mechanism 1

$$\mathrm{Hg_2^{++}} \rightleftharpoons \mathrm{Hg^{++}} + \mathrm{Hg}$$
$$\mathrm{Hg^{++}} + \alpha_2\mathrm{e}^- \overset{*}{\rightleftharpoons} \mathrm{Hg^+} - (1 - \alpha_2)\mathrm{e}^-$$
$$\mathrm{Hg^+} + \alpha_3\mathrm{e}^- \rightleftharpoons \mathrm{Hg} - (1 - \alpha_3)\mathrm{e}^-$$

The equivalent reaction pair is constructed thus

$$\{\mathrm{Hg_2^{++}} - \mathrm{Hg^{++}} - \mathrm{Hg}\} + \mathrm{Hg^{++}} + \alpha_2\mathrm{e}^- \rightleftharpoons$$
$$\mathrm{Hg^+} - (1 - \alpha_2)\mathrm{e}^- + \{\mathrm{Hg} - (1 - \alpha_3)\mathrm{e}^- - \mathrm{Hg^+} - \alpha_3\mathrm{e}^-\}$$

which reduces to

$$\mathrm{Hg_2^{++}} - \mathrm{Hg} + \alpha_2\mathrm{e}^- \rightleftharpoons \mathrm{Hg} - (2 - \alpha_2)\mathrm{e}^-$$

and hence the net rate is given by

$$\text{net rate} = k[\mathrm{Hg_2^{++}}]\exp\left\{-\alpha_2\frac{FE}{RT}\right\} - k\exp\left\{(2 - \alpha_2)\frac{FE}{RT}\right\}$$

where

$$k = \overrightarrow{k_1}\overrightarrow{k_2}/\overleftarrow{k_1} = \overleftarrow{k_2}\overleftarrow{k_3}/\overrightarrow{k_3}$$

Mechanism 2

$$\mathrm{Hg_2^{++}} \rightleftharpoons 2\mathrm{Hg^+}$$
$$\mathrm{Hg^+} + \alpha_2\mathrm{e}^- \overset{*}{\rightleftharpoons} \mathrm{Hg} - (1 - \alpha_2)\mathrm{e}^-$$

Here the first pair must be divided by two to bring its stoichiometry into line with that of the rate-determining pair, thus

$$\frac{1}{2}\{\mathrm{Hg_2^{++}} - 2\mathrm{Hg^+}\} + \mathrm{Hg^+} + \alpha_2\mathrm{e}^- \rightleftharpoons \mathrm{Hg} - (1 - \alpha_2)\mathrm{e}^-$$

which reduces to the equivalent reaction pair

$$\frac{1}{2}\,\mathrm{Hg^{++}} + \alpha_2\mathrm{e}^- \leftrightharpoons \mathrm{Hg} - (1 - \alpha_2)\mathrm{e}^-$$

The net rate is given by

$$\text{net rate} = \frac{1}{2}\,k[\mathrm{Hg_2^{++}}]^{1/2}\exp\left\{-\alpha_2\frac{FE}{RT}\right\} - \frac{1}{2}\,k\exp\left\{(1 - \alpha_2)\frac{FE}{RT}\right\}$$

where the factor $^1/_2$ appears because the equivalent reaction pair represents a moiety of the stoichiometry of the over-all reaction, and where

$$k = \overrightarrow{k_2}\left(\overrightarrow{k_1}/\overleftarrow{k_1}\right)^{1/2} = \overleftarrow{k_2}$$

For the remaining mechanisms, the derivation of the net rate expressions are given in outline, only the equivalent reaction pair being given.

Mechanism 3

$$\mathrm{Hg_2^{++}} \overset{*}{\rightleftharpoons} \mathrm{Hg^{++}} + \mathrm{Hg}$$
$$\mathrm{Hg^{++}} + 2\alpha\mathrm{e}^- \rightleftharpoons \mathrm{Hg} - 2(1 - \alpha)\mathrm{e}^-$$
$$\text{net rate} = k[\mathrm{Hg_2^{++}}] - k\exp\left\{2\frac{FE}{RT}\right\}$$

Here the forward rate is independent of potential; this is a characteristic of "kinetically controlled" reactions, since no electrons are present on the left-hand side of the equivalent reaction pair

$$\mathrm{Hg_2^{++}} \rightleftarrows \mathrm{2Hg - 2e^-}$$

Mechanism 4

$$\mathrm{Hg_2^{++}} + \alpha\mathrm{e^-} \underset{*}{\rightleftarrows} \mathrm{Hg^+ + Hg} - (1-\alpha)\mathrm{e^-}$$

$$\mathrm{2Hg^+} \rightleftarrows \mathrm{Hg_2^{++}}$$

This is a rather unlikely mechanism which results in the rates of both the forward and reverse reactions being dependent on the mercurous ion concentration, since this ion appears on both sides of the equivalent reaction pair

$$\mathrm{Hg_2^{++}} + \alpha\mathrm{e^-} \rightleftarrows \mathrm{Hg} + {}^1/_2\mathrm{Hg_2^{++}} - (1-\alpha)\mathrm{e^-}$$

$$\text{net rate} = \frac{1}{2}\,k[\mathrm{Hg^{++}}]\,\exp\left\{-\alpha\frac{FE}{RT}\right\} - \frac{1}{2}\,k[\mathrm{Hg_2^{++}}]^{1/2}\exp\left\{(1-\alpha)\frac{FE}{RT}\right\}$$

Mechanism 5.—Identical with mechanism 2, except that the first reaction pair, rather than the second, is rate determining. The equivalent reaction pair corresponding to this mechanism is identical with that of mechanism 3. Hence the law expressing the net rate is the same as that for mechanism 3 and these two mechanisms are experimentally indistinguishable, unless other data are available on the magnitude of k.

Surface Activities.—Rate laws, deduced according to the above principles, contain terms representing the activities of Class II and III substances at the electrode surface (*i.e.*, [A], [B], [C], etc.). The surface activities of all Class IIIb substances may be equated to unity (as has been done in the example above, where Hg belongs to Class IIIb). For Class IIIa substances the surface activity is equal to the bulk activity. Bulk activities will be denoted thus: $[\bar{\mathrm{A}}]$, $[\bar{\mathrm{B}}]$, $[\bar{\mathrm{C}}]$, etc.

The activity of a Class II substance at the electrode surface is determined by the net rate of the electrode reaction and by the rate of transport of the substance to or from the electrode. If substance A of electrode reaction (8) is a Class II substance, steady-state considerations require that

$$(a_0 - a_0')(\text{net rate}) = \text{rate of transport of A} \quad (31)$$

where the rate of transport is considered positive if transport is toward the electrode and the other terms are as previously defined.

Since we are considering only systems containing excess inert electrolyte, ionic migration cannot contribute to transport and we need consider only diffusion and convection. In practice it is found that stable steady-state conditions exist only for systems in which transport is by the combined effect of both diffusion and convection.[3] The steady state is most reproducible if artificial convection is applied,[6] by stirring the solution, for example, or by rotating the electrode. A strict mathematical derivation of the rate of transport to such electrodes is very difficult, even in the case of idealized conditions.[7] However, the "boundary layer" concept[8] has proved useful in interpreting the results of steady-state experiments. According to this concept

$$\text{rate of transport of A} = tD_{\mathrm{A}}^{\beta}\left\{\frac{[\bar{\mathrm{A}}]}{\bar{\gamma}} - \frac{[\mathrm{A}]}{\gamma}\right\} \quad (32)$$

where D_{A} is the diffusion coefficient of A and t is a constant for a given system that is dependent on the magnitude of the transport forces. The exponent β takes values between zero and unity, being determined by the nature of the transport forces. Thus $\beta = 0$ for pure convection,[3] whereas $\beta = 1$ in unstirred solutions.[9] The terms γ and $\bar{\gamma}$ are activity coefficients and, assuming them to be equal, we can combine equations (31) and (32) to give

$$\text{net rate} = \frac{k_t[\bar{\mathrm{A}}] - k_t[\mathrm{A}]}{a_0 - a_0'} \quad (33)$$

where k_t is a constant for a given set of conditions having the same dimensions, moles cm.$^{-2}$ sec.$^{-1}$, as a rate constant.

Comparison of (33) with equations 7 shows that the same result, *i.e.*, equation 33, would have been obtained had we included the opposed pair

$$\bar{\mathrm{A}} \rightleftarrows \mathrm{A} \quad (34)$$

in our original mechanistic scheme of opposed reaction pairs, treating $\bar{\mathrm{A}}$ and A as if they were different substances. Such an opposed pair could have been carried through the complete derivation of the equivalent reaction pair, treating $\bar{\mathrm{A}}$ as a Class IIIa substance and A as a Class IV substance. This procedure is possible because the law governing transport takes exactly the same form as the rate law governing a simple equilibrium having an equilibrium constant of unity and opposed unimolecular rate constants, each equal to k_t.[10]

The analogy may be carried further. A "transport pair," such as (34), may be rate determining in the same sense that a reaction pair is. If a transport pair is taken to be rate determining, an equivalent reaction pair may be derived and the corresponding expression for the net rate includes all the properties associated with a "transport limited" electrode reaction. On the other hand, a transport pair may not be at all rate determining. In this case, the transport pair is in true equilibrium and $[\mathrm{A}] = [\bar{\mathrm{A}}]$, *i.e.*, the Class II substance behaves as a Class IIIa substance. A further possibility is that the transport pair may be partially rate determining. A later section will deal with mixed rate determination by two or more pairs; the results of that section are equally applicable whether or not

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[3] Transport to the "convection electrodes" described by Kolthoff, Jordan and Prager[4,5] appears to be purely convective. In this case the rate of transport is independent of diffusion coefficients.

[4] I. M. Kolthoff and J. Jordan, THIS JOURNAL, **76**, 3843 (1954).

[5] I. M. Kolthoff, J. Jordan and S. Prager, *ibid.*, **76**, 5221 (1954).

[6] If the natural convection that results from density gradients is relied upon, the convective force is not a constant but a function of the concentration gradient. This introduces an undesirable dependence of the "constant," t, on $[\bar{\mathrm{A}}] - [\mathrm{A}]$ in equation 32.

[7] B. Levich, *Acta Physicochim. U.R.S.S.*, **17**, 257 (1942).

[8] This is an extension of the "diffusion layer" approach of Nernst and is discussed by Kolthoff and Jordan.[4]

[9] H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1061, 1079 (1941).

[10] A similar device has been extensively employed in analyses of polarographic data, enabling useful interpretations to be made,[11] even though steady-state conditions are not realized at dropping electrodes.[12]

[11] See, for example, P. Kivalo, THIS JOURNAL, **75**, 3286 (1953); *Acta Chim. Scand.*, in press (1955).

[12] N. S. Hush and K. B. Oldham, *Trans. Faraday Soc.*, in press (1955).

one of the partially rate-determining pairs is a transport pair.

If more than one Class II substance is involved in the electrode reaction, a transport pair may be set up for each. The equivalent reaction pair corresponding to any rate-determining pair (transport or otherwise) may be derived; thereby an expression for the net rate may be set up which will be perfectly valid. It may be pointed out here that an alternative method is available for the deduction of a rate law from any postulated mechanism. This method involves the setting-up and the solution of a series of simultaneous equations. This method need not involve the treatment of transport as a kinetic process, but, in cases when the simultaneous equations can actually be solved, it yields results identical with the "equivalent reaction pair" approach.

Mixed Rate Determination.—It has been demonstrated how the rate law may be readily deduced from any postulated mechanism of an electrode reaction assuming that one reaction pair is wholly rate determining. However, the possibility exists that two or more opposed pairs (reaction pairs or transport pairs) may each possess a measure of the property we have termed "rate determination." We shall now consider this problem of mixed rate determination, which will shed light on the significance of the property.

If a scheme of opposed pairs is set up, two of which, say the *g*th and the *j*th, are taken to be rate determining, the rest being in equilibrium, then the following result may be derived[13]

$$\frac{1}{\text{net rate}} = \frac{1}{(\text{net rate})_g} + \frac{1}{(\text{net rate})_j} \quad (35)$$

where $(\text{net rate})_g$ is the expression for the net rate if only the *g*th pair was rate determining and $(\text{net rate})_j$ has similar significance. The derivation of (35) involves again the assumption $\phi = 1$ for both rate-determining pairs.

Equation 35 is quantitatively correct only if $q_g = q_j = 1$, *i.e.*, if both rate-determining pairs express the same stoichiometry as the over-all electrode reaction. If this condition is not fulfilled (35) is only approximate. In all cases the qualitative implications of (35) are true: net rate is most nearly equal to the smaller of the two terms $(\text{net rate})_j$ and $(\text{net rate})_g$, never being larger than it and approaching it when the larger term is much larger than the smaller term.

The principle may be extended to cover cases where three or more pairs are considered as rate determining. Again, the actual net rate is related to the net rate expressions derived by considering each pair, in turn, to be wholly rate determining in the same fashion as the over-all resistance of a parallel network is related to the resistances of the individual elements. In view of this, we can attach a more precise significance to the concept of rate determination. Let us say that a certain electrode reaction mechanism is composed of *m* opposed pairs (a transport pair corresponding to each Class II substance, the remainder being reaction pairs). Then we may treat each pair in turn as being wholly rate determining, derive the corresponding equivalent reaction pair and so formulate *m* expressions for the net rate, thus: $(\text{net rate})_1$, $(\text{net rate})_2$, . . . $(\text{net rate})_m$. The degree of rate determination of any pair, say the *j*th, is then inversely proportional to the corresponding expression, *i.e.*, to $(\text{net rate})_j$.

Current–Voltage Relationships

Let us consider a certain electrode reaction that can be represented by a mechanistic scheme of opposed pairs, of which the *j*th is wholly rate determining. Then if the equivalent reaction pair is

$$aA + bB + cC + \ldots. + ne^- \rightleftarrows a'A + b'B + c'C + \ldots - n'e^- \quad (36)$$

where A, B, C, . . . are Class II or III substances and *a*, *b*, *c*, *a′*, *b′*, etc., are numbers expressing the molecularities of these substances, the current, in amperes, is given by

$$i = NSF(\text{net rate}) = \frac{NSF}{q_j}(\overrightarrow{\text{rate}} - \overleftarrow{\text{rate}}) \quad (37)$$

where the current is considered positive if cathodic. *S* is the area of the electrode surface in cm.², $\overrightarrow{\text{rate}}$ and $\overleftarrow{\text{rate}}$ are the forward and reverse rates of the equivalent reaction pair as written, and other terms are as previously defined. Applying the results of the preceding discussion, we can write

$$i = (n + n')SFk\left[[\bar{A}]^a[\bar{B}]^b \ldots \exp\left\{-n\frac{FE}{RT}\right\} - [\bar{A}]^{a'}[\bar{B}]^{b'} \ldots \exp\left\{n'\frac{FE}{RT}\right\}\right] \quad (38)$$

Equation 38 relates current and potential; it will be obeyed at all values of potential and concentration, provided (36) remains the equivalent reaction pair. Equation 38 shows that the current represents the difference between two terms which are equal at the null-potential. As the potential is made more negative, the first term increases, whereas the second decreases. At sufficiently negative potentials, the second term becomes insignificant and the current, which may then be termed the "cathodically controlled current," i_c, varies exponentially with potential. In this cathodically controlled current region, a graph of log *i versus E* will yield a straight line, since, taking Briggsian logarithms of (38)

$$\log i_c = \log(n + n')SFk + a\log[\bar{A}] + b\log[\bar{B}] + \ldots - \frac{nF\log e}{RT}E \quad (39)$$

Similarly, at potentials sufficiently more positive than the null-potential, an anodically controlled current region exists where

$$\log(-i_a) = \log(n + n')SFk + a'\log[\bar{A}] + b'\log[\bar{B}] + \ldots + \frac{n'F\log e}{RT}E \quad (40)$$

so that a graph of $\log(-i)$ *versus E* will here give a straight line.

The Experimental Determination of Mechanism.—An experimental current–voltage curve of an electrode reaction may be readily obtained over a certain range of potentials (limited by the range

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[13] The derivation, which is too lengthy to be conveniently presented here, is straightforward and involves only algebraic manipulations similar to those in the section "The Equivalent Reaction Pair." No assumptions are involved other than those noted in the text.

of stability of the solvent and the "inert" electrolyte). The effect of changes in the bulk activity of Class II and IIIa substances on the current–voltage curve may also be readily studied. We will assume that such curves have been recorded for a certain electrode reaction (suitably corrected for "residual current," and "*i***R** drop," and expressed on a potential scale having the standard potential as its zero), and analyze what information may thereby be gathered concerning the mechanism.

The determination of the equivalent reaction pair(s) must be the goal of such a procedure, the actual mechanism being then inferred, since we have seen that the latter is not directly determinable. Equations 39 and 40 suggest a very simple method of determining the equivalent reaction pair from current–voltage curves (Bockris[2] discusses some other methods). If log i (or log $-i$ for anodic current) is plotted as a function of E, n and n' can readily be calculated from the gradients of the straight-line portions of the graphs. Also, a, b, a', b', etc., can be determined from the changes in the intercepts of the linear portions with changes in the bulk activities $[\overline{\text{A}}]$, $[\overline{\text{B}}]$, etc. Once the coefficients n, n', a, a', b, etc., are known, the complete equivalent reaction pair (36) is determined. The terms a, a', b, etc., and also the sum $(n + n')$ must be whole numbers or simple fractions; however, this is not necessarily true of the individual terms n and n', since these may contain irrational "α" terms. The composite rate constant, k, can also be found. A useful check on the constancy of the equivalent reaction pair is provided by a comparison of the k value obtained from the anodically controlled current region with that from the cathodic region: they should be identical.

It is necessary to study both the cathodically- and anodically-controlled current regions, if the equivalent reaction pair is to be completely established.[14] Study of the cathodically controlled region enables the left-hand side of the equivalent reaction pair to be constructed: the anodically controlled region provides data for the right-hand side. The equivalent reaction pair when constructed should be consistent with the over-all stoichiometry. If it is not, it may be inferred that the mechanism of the electrode reaction has not remained constant over the potential span separating the cathodically- and anodically-controlled regions.

Limitations of the Method.—One obvious difficulty that may be encountered in following the above procedure is that the log ± i *versus* E plots may not assume linearity below impracticably large current magnitudes. This will be the case if k in (38) is very large. Results obtained at too great a current density may be invalid for any of a number of reasons, including the following.

(i) A substance that can be justifiably classified into Class III at low current densities may now behave as a Class II substance.

(ii) The "*i***R** drop" may become too large for accurate correction to be made.

(iii) The reference electrode may exhibit polarization.

The converse limitation may be encountered if k is too small. The current may then be either immeasurably small or of a magnitude too comparable with the residual current for accurate measurement.

Probably the most serious limitation, however, arises from the possibility that the equivalent reaction pair may not remain constant over a sufficient potential range to permit the investigation of the cathodically- and anodically-controlled current regions. Several zones will then exist, in each of which a particular equivalent reaction pair will apply, separated by regions of mixed rate determination. Frequently extensive regions will exist which correspond to "trivial" equivalent reaction pairs, such as one resulting from a transport pair being rate determining.

To illustrate these three limitations, let us consider the over-all electrode reaction

$$\text{II} + \text{e}^- \rightleftarrows \text{III} \qquad (41)$$

where II is a Class II substance and III belongs to Class III. We will consider the mechanism to consist of two pairs, a transport pair

$$\overline{\text{II}} \rightleftarrows \text{II} \qquad (42)$$

and a reaction pair

$$\text{II} + \alpha\text{e}^- \rightleftarrows \text{III} - (1 - \alpha)\text{e}^- \qquad (43)$$

either of which may be rate determining. If (42) is rate determining, the equivalent reaction pair is

$$\overline{\text{II}} \rightleftarrows \text{III} - \text{e}^- \qquad (44)$$

and hence the current will be given by

$$i_1 = SFk_t\left([\overline{\text{II}}] - [\overline{\text{III}}]\exp\left\{\frac{FE}{RT}\right\}\right) \qquad (45)$$

On the other hand, if (43) is rate determining, (46) is the equivalent reaction pair and (47) is the corresponding current–voltage expression.

$$\overline{\text{II}} + \alpha\text{e}^- \rightleftarrows \text{III} - (1 - \alpha)\text{e}^- \qquad (46)$$

$$i_2 = SFk_2\left([\overline{\text{II}}]\exp\left\{-\alpha\frac{FE}{RT}\right\} - [\overline{\text{III}}]\exp\left\{(1 - \alpha)\frac{FE}{RT}\right\}\right) \qquad (47)$$

Which of the expressions (45) or (47) is the true expression for the current, i, will depend on the relative magnitudes of i_1 and i_2. If $i_1 << i_2$, then $i = i_1$, whereas if $i_1 >> i_2$, $i = i_2$. If i_1 and i_2 are of comparable magnitude, then

$$1/i = 1/i_1 + 1/i_2$$

Figure 1 illustrates these relationships if $k_2 = 5 \times 10^{-6}$. In drawing Figs. 1, 2 and 3 the following constant values were assumed: $S = 1.04 \times 10^{-2}$ cm.^{2}, $k_t = 10^{-3}$ moles cm.$^{-2}$ sec.$^{-1}$, $[\overline{\text{II}}] = 10^{-3}$, $[\overline{\text{III}}] = 1$, $\alpha = 0.6$ and $T = 29.4°$.

Figure 2 shows the dependence of the current–voltage curve upon the magnitude of the rate constant k_2, and Fig. 3 presents the same data on a graph with a logarithmic current axis. Figure 3 shows the linear portions of the logarithmic plots which correspond to the cathodically- and anodically-controlled regions. The curve marked "$-\infty$" corresponds to an infinite value of k_2, and hence the transport pair is wholly rate determining. Two

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[14] Compare mechanisms 1 and 4 in the mercurous ion reduction example, where the i_c's are identical, yet the equivalent reaction pairs are completely dissimilar.

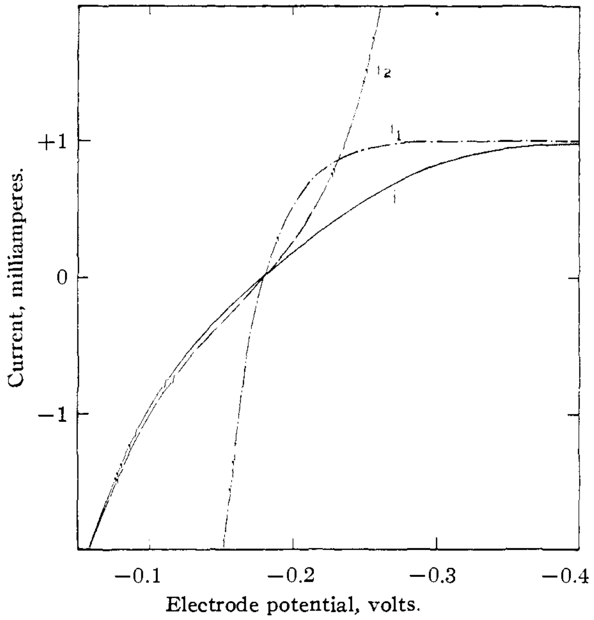

Fig. 1.—Illustrating the relationship $1/i = 1/i_1 + 1/i_2$ for the electrode reaction $\text{II} + e^- \rightleftarrows \text{III}$. The actual current is represented by i, i_1 is the current assuming the transport pair to be wholly rate determining, and i_2 is the current assuming the reaction pair to be wholly rate determining.

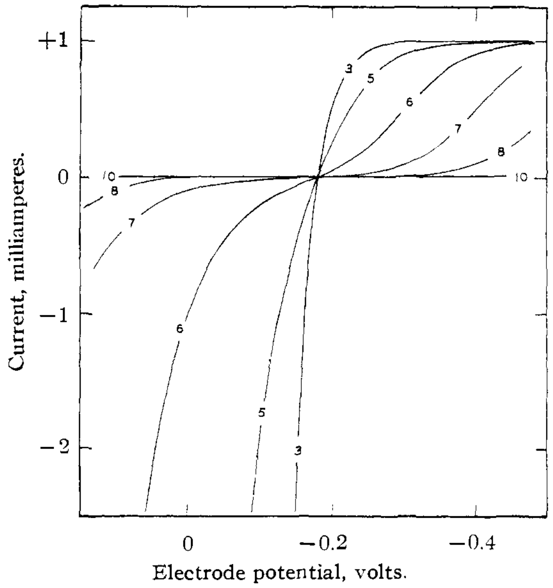

Fig. 2.—Shape of the current-voltage curve as a function of the magnitude of the rate constant k_2: curve 3, $k_2 \geqslant 10^{-3}$ mole cm.$^{-2}$ sec.$^{-1}$; curve 5, $k_2 = 10^{-5}$; curve 6, $k_2 = 10^{-6}$; curve 7, $k_2 = 10^{-7}$; curve 8, $k_2 = 10^{-8}$; curve 10, $k_2 \leqslant 10^{-10}$.

linear portions are seen on this curve; one is horizontal and is the cathodically-controlled current corresponding to the equivalent reaction pair (44); an anodically-controlled region exists at the most positive potentials on this curve. Most of the linear sections in Fig. 3, however, correspond to the two limiting regions of (46). It will be seen that no cathodically-controlled region exists corresponding to (46) if $k_2 > 10^{-7}$.

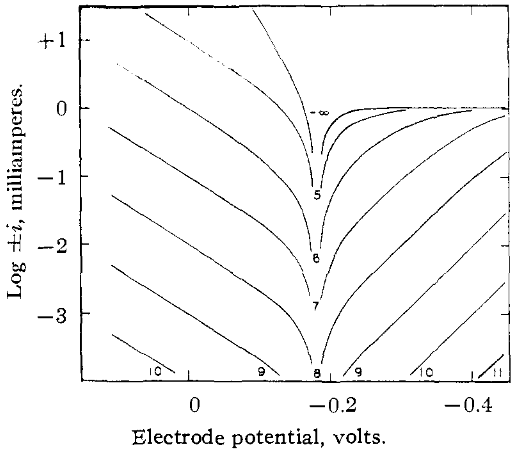

Fig. 3.—Logarithmic representation of current-voltage curves showing the regions of specific control. The number associated with each curve is $-\log k_2$.

Let us suppose that accurate current measurement can be made only for currents between one microampere and ten milliamperes. Then it is clear that conditions for the determination of the equivalent reaction pair are optimum when k_2 has a value in the neighborhood of 10^{-8}. In fact, if the potential range is restricted to that shown in the figure, complete evaluation of the equivalent reaction pair is possible only if $10^{-7} \geq k_2 \geq 10^{-9}$, a very limited range indeed. Smaller values of k_2 can be covered if data are recorded over a wider potential span; however, as the potential range separating the cathodically- and anodically-controlled regions is increased, the danger that a different mechanism may become operative is also increased. The right-hand side of the equivalent reaction pair may be determined for k_2 values as high as 10^{-5}, since the transport pair is not very competitive in the anodic branch of the current–voltage curves, as Figs. 1 and 2 clearly demonstrate.

We have here considered a very simple electrode reaction, but diagrams similar to Figs. 2 and 3 may be constructed for most mechanisms of any electrode reaction. The same conclusion will always be reached: that determination of the mechanism by analysis of cathodically- and anodically-controlled current regions is possible only if the rate constant of the equivalent reaction pair falls within a restricted range. This range can be somewhat extended, however, by suitable changes in experimental conditions, such as changes in k_t, S, or concentration variables.

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Appendix 1

Parallel Reaction Paths.—In developing the treatment for the reduction of a complex electrode reaction mechanism to a simple equivalent reaction pair, it was assumed that only "series" combinations of reaction pairs need be considered. However, the possibility of "parallel" reaction paths must also be considered.

Consider the over-all electrode reaction $A + e^-$

$\rightleftarrows$ C. Let us assume that two paths for this reaction are possible: the direct reduction of A; and the reduction of B to C, where B is an isomer of A. We may depict this mechanism thus

$$\begin{tikzcd}
A + \alpha_2 e^- \arrow[r, shift left, "k_2"] \arrow[d, shift left] & C - (1 - \alpha_2)e^- \arrow[l, shift left] \\
B + \alpha_3 e^- \arrow[r, shift left, "k_3"] \arrow[u, shift left, "k_1"] & C - (1 - \alpha_3)e^- \arrow[l, shift left]
\end{tikzcd}$$

To the system in equilibrium we can apply the "principle of microscopic reversibility"[15] to obtain

$$\overrightarrow{\text{rate}_1} - \overleftarrow{\text{rate}_1} = \overrightarrow{\text{rate}_2} - \overleftarrow{\text{rate}_2} = \overrightarrow{\text{rate}_3} - \overleftarrow{\text{rate}_3} = 0$$

where the nomenclature is self-evident. Substituting into these three equations the kinetic expressions for the rates, we can obtain the relationship $\overrightarrow{k_2}/\overrightarrow{k_3} = K(\overleftarrow{k_2}/\overleftarrow{k_3})$, where K is the equilibrium constant $(= \overrightarrow{k_1}/\overleftarrow{k_1})$ for the isomerization. This result is valid at all potentials. Now, if for the reaction path (1 + 3), reaction pair (1) is rate determining, we may derive the relationship: $\overrightarrow{\text{rate}_1}/\overrightarrow{\text{rate}_2} = \overleftarrow{\text{rate}_1}/\overleftarrow{\text{rate}_2}$. Or, should reaction pair (3) be the rate-determining member, we have: $\overrightarrow{\text{rate}_3}/\overrightarrow{\text{rate}_2} = \overleftarrow{\text{rate}_3}/\overleftarrow{\text{rate}_2}$. That is, in either case, if one path contributes a certain fraction to the total forward rate, then the reverse rate of that path contributes the same fraction to the total reverse rate.

The same conclusion holds for the majority of such parallel schemes. It means that an electrode reaction at any constant potential cannot proceed by a certain forward path coupled with a different reverse path. The possibility of different forward and reverse paths at different potentials is not, of course, precluded. Systems of parallel reaction paths may therefore be treated as the additive effect of the individual paths.

Appendix 2

The Condition $\phi = 1$.—The derivation of the equivalent reaction pair required the condition $\phi = [Z]^z[Y]^y[X]^x \ldots = 1$. We will now analyze the significance of this limitation. The condition will not be satisfied, except fortuitously, unless $z = y = x = \ldots = 0$. Equation 21 define these terms and shows that for the condition to be satisfied, no Class IV substance produced prior to the rate-determining pair must be consumed subsequent to it, or *vice versa*. This simply means that an equivalent reaction pair can be written in a form that involves no Class IV substance. An equivalent reaction pair containing a Class IV substance would, in any case, be valueless.

Actually. most mechanistic schemes that can be envisaged do not involve this limitation. The following is a scheme that does

$$Fe(CN)_6^{---} \rightleftarrows Fe(CN)_5^{--} + CN^-$$
$$Fe(CN)_5^{--} + \alpha e^- \underset{*}{\rightleftarrows} Fe(CN)_5^{---} - (1 - \alpha)e^-$$
$$CN^- + Fe(CN)_5^{---} \rightleftarrows Fe(CN)_6^{----}$$

In attempting to construct an equivalent reaction pair from this mechanism, it is found to be impossible to eliminate the CN^- ion. Therefore, unless cyanide ion is present in the bulk, this reaction scheme is not amenable to the equivalent reaction pair treatment.

URBANA, ILLINOIS

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[15] See, for example, E. D. Eastman and G. K. Rollefson, "Physical Chemistry," McGraw-Hill Book Co., New York, N. Y., 1947, p. 396.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The System UO_2CrO_4–H_2O

BY FRANK J. LOPREST, WILLIAM L. MARSHALL AND C. H. SECOY

RECEIVED MARCH 14, 1955

Phase equilibria in the system uranyl chromate-water have been studied from 0° to the ice eutectic at −0.145° and to temperatures at which hydrolytic precipitation of an uncharacterized solid phase occurs. The solubility of $UO_2CrO_4 \cdot 5^1/_2H_2O$ exhibits a marked increase with temperature from 3.11 weight per cent. of uranyl chromate at 0° to 70.4 at 66°. A transition between the $5^1/_2H_2O$ hydrate and a lower hydrate (probably $1H_2O$) occurs at 66.3°. The solubility of the latter solid exhibits practically no variation with temperature.

The preparation of uranyl chromate has been described by Formánek[1] and by Orlow[2] but very few data on the solubility of this salt have been reported in the literature. Orlow gives the solubility at 15° as 7.52 parts of the trihydrate per 100 parts of water. Formánek reports the existence of $UO_2CrO_4 \cdot 5^1/_2H_2O$, but gives no quantitative solubility data. This study confirms Formánek's identification of the solid and presents solubility data over a wide temperature range.

Experimental

Uranyl chromate was prepared by dissolving at 50° a stoichiometric amount (from 50–100 g.) of pre-washed Mallinckrodt uranium trioxide, of nitrate content less than 0.1 p.p.m., in a weighed amount of a standardized 1 to 2 molar aqueous solution of Baker and Adamson C.P. chromic trioxide and crystallizing the uranyl chromate at 0°. The solid phase appeared as very small light yellow-orange needle crystals. The remaining liquid was removed from the solid by suction filtration and the solid was washed with several portions of cold water, redissolved and recrystallized. Several different batches of the solid were prepared. Determinations of the UO_3/CrO_3 ratio in samples taken from two of the batches yielded values of 0.99 and 1.00, the precision of the analysis being of the order of ±0.5%. In-

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[1] J. Formánek, *Ann. Chem.* (*Liebig*), **257**, 102 (1890).

[2] N. A. Orlow, *Chem. Z.*, **31**, 375 (1907).