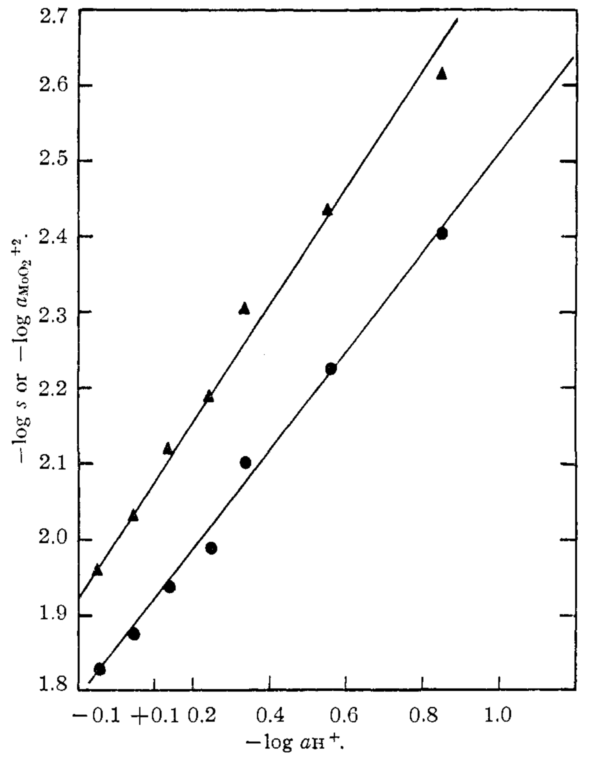

Fig. 1.—Test of the equilibrium (1): ●, log *s*; ▲, log $a_{MoO_2^{+2}}$.

perchlorate solutions.[14] If we assume that the activity coefficients of MoO_2^{+2} and UO_2^{+2} are equal at equal ionic strength, we can estimate the activity of MoO_2^{+2} in these solutions. These values are given in Table I (column five). A plot of log $a_{MoO_2^{+2}}$ *versus* log a_{H^+} is also shown in Fig. 1 and again the data do not support the equilibrium 2.

TABLE I

SOLUBILITY OF MOLYBDENUM TRIOXIDE IN PERCHLORIC ACID

$HClO_4$, *M*	Mo, *M* × 10^3	$-\log a_{H^+}$	$-\log S$	$-\log a_{MoO_2^{+2}}$
0.182	3.96	0.852	2.404	2.612
.364	5.98	.559	2.225	2.432
.546	7.99	.337	2.100	2.304
.728	10.3	.246	1.989	2.188
.910	11.7	.138	1.934	2.116
1.092	13.5	.042	1.872	2.029
1.274	15.0	−.046	1.826	1.959

There are two possible explanations for the results obtained. The first and most obvious is that the activity coefficient of the ion MoO_2^{+2} changes with ionic strength in a manner radically different from that of UO_2^{+2}. There are two reasons for objecting to this interpretation. Firstly the change in activity coefficient observed with UO_2^{+2} is fairly typical for electrolytes of this charge type in the region of ionic strength considered. Secondly, the change of activity coefficient required to make the data conform to the MoO_2^{+2} equilibrium is much greater than has yet been observed for electrolytes in this region of ionic strength and would, in itself, indicate that the molybdenum in solution was not present as a simple ion.

The alternate explanation, favored by the author, is that the molybdenum in solution is not present as simple MoO_2^{+2} ions. The fact that solutions of molybdic acid in water are complex is well established.[15,16] Molybdenum trioxide in solution has a marked tendency to form polymeric aggregates of high molecular weight (though not colloidal[17,18]). There is other evidence which supports the existence of polymers in these solutions and this is that molybdenum trioxide in 100% sulfuric acid is dimeric.[16,19] In view of the high dielectric constant of sulfuric acid it would be expected that ionization, if possible, would occur in this solvent. Although experimental evidence is quite scarce, the formation of complexes of various sorts involving MoO_3 and SO_3 has often been assumed to explain the constitution of the "molybdenyl sulfates."[5,20,21] An interpretation capable of explaining the known facts is one in which MoO_3 reacts with hydrogen ions to give complexes in solution. Equilibria of the type

$$x\mathrm{MoO_3} + 2\mathrm{H^+} \rightleftarrows [(\mathrm{MoO_2})(\mathrm{MoO_3})_{x-1}]^{+2} + \mathrm{H_2O} \quad (5)$$

are capable of explaining the known experimental facts. The formation of MoO_2SO_4 in the presence of SO_3 would be the result of a competition between MoO_3 and SO_3, the solubility would not be proportional to the square of the hydrogen ion activity,[22] and the high molecular weight of the species in solution is readily understood.

(14) Reference 10, p. 83.

(15) Reference 12, p. 435.

(16) A. Mazzucchelli and G. Zangrilli, *Gazz. chim. ital.*, **40**, II, 66, 72 (1910).

(17) L. Wohler and W. Engels, *Kolloidchem. Beihefte*, **1**, 454 (1909–1910).

(18) Reference 12, p. 431.

(19) E. Beckmann, *Z. physik. Chem.*, **53**, 133 (1905).

(20) R. F. Weinland and H. Kühl, *Z. anorg. Chem.*, **54**, 259 (1907).

(21) L. Forsen, *Compt. rend.*, **172**, 681 (1921).

(22) Although a combination of equilibria of the type (5) leads to the relationship $S = (\mathrm{H^+})^2 \sum_{x=1}^{x=\infty} (x+1) K_x$ among the solubility, the hydrogen ion concentration, and the equilibrium constants, this is obtained only by ignoring activity coefficients. When the activity coefficients are taken into account, and they would be very important for species of the type postulated, no such simple relationship is found.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

On the Analysis of Irreversible Polarographic Waves

BY DAVID M. H. KERN

RECEIVED APRIL 8, 1954

The general system of polarographic processes involving reversible electrode reactions and one chemical reaction in solution has been solved for the plane electrode by Koutecky.[1,2] A special case of this system, that in which the product of a reversible electrode reaction is converted by a chemical reaction to an inactive form, was solved independently by the author in a recent article.[3] The resulting equation for the half-wave potential ($E_{1/2}$) of the instantaneous current as a function

(1) Proceedings of the International Polarographic Congress, Vol. I, p. 826 (1951).

(2) J. Koutecky, *Collection Czech. Chem. Communs.*, **18**, 183 (1953).

(3) D. Kern, THIS JOURNAL, **76**, 1011 (1954).

of the drop time and rate constant is identical with that obtained earlier by Koutecky.[1] The equation for the instantaneous current ratio can be written[3]

$$i/i_d = \sqrt{\pi}\beta e^{\beta^2}(1 - \text{erf}\,\beta) \qquad (1)$$

in which β is defined below. This equation differs only by the definition of β from the equation for a slow electrode reaction (the reverse reactions having been neglected in both cases) which in turn has been shown to be[4] similarly related to the equation for the limiting current of kinetic waves.[5]

The relationship of these waves to one another can be clarified by resorting to a general scheme somewhat more restricted than that proposed by Koutecky, namely,

$$A_b \xrightarrow{\text{diffusion}} A_0 \xrightarrow[\text{reaction}]{k} B \qquad (2)$$

where A_b and A_0 are, respectively, the bulk and surface concentrations of the substance engaged in mass transfer to the electrode surface and k is a heterogeneous rate constant which, multiplied by A_0, gives the rate of production of B. All three reaction types mentioned above are represented by this scheme, as also the reversible electrode reaction followed by an irreversible electrode reaction treated recently by Berzins and Delahay.[6] The actual reacting species may be an intermediate in equilibrium with A at the surface, and present in vanishingly small amounts. Such a situation is indistinguishable from the above scheme provided that the rate of diffusion of the intermediate is insignificant compared with its rate of reaction, and that its concentration remains proportional to A_0.

In the simplest system, the slow electrode reaction, the reaction is the electron transfer itself and k can be identified with the potential-dependent rate constant k_e for the electron transfer. It is well known[4] that equation 1 describes this system when $\beta = k_e\sqrt{t/D}$. It follows that equation 1 is the general solution for the above scheme if $\beta = k\sqrt{t/D}$. One obtains the solution for the other three wave types by substituting the appropriate expression for k into this last equation.

For the kinetic wave the reaction is the chemical reaction which produces the depolarizer at the electrode surface. The electron transfer following it is so rapid that the over-all rate is governed by that of the chemical reaction. According to Wiesner's concept of the reaction volume[7,8] the heterogeneous rate constant k in equation 2 is obtained by multiplying the homogeneous rate constant k_1 for the reaction by the reaction volume thickness $\mu = \sqrt{D/k_2}$, where k_2 is the rate of the reverse reaction.[9] Thus

$$k = k_1\sqrt{D/k_2} \text{ and } \beta = k_1\sqrt{t/k_2}$$

In the case treated recently by Delahay, a reversible electrode reaction intervenes before the rate-determining electrode reaction. The concentration of the intermediate is related to A_0 by the equation $A^* = A_0/c = A_0 \exp{(E_0 - E)nF/RT}$ (for a reduction), where E_0 is the standard potential of the reversible couple. Therefore $k = k_e/c$, and $\beta = k_e\sqrt{t}/c\sqrt{D}$. The value for the instantaneous current ratio obtained from Delahay's equation 13, ref. 6, agrees with this simple analysis, provided only that c (for which he uses the symbol θ) is sufficiently large, as is required by the conditions for the applicability of our scheme.

For the ascorbic acid or post-kinetic case, a reversible electrode reaction again intervenes before the rate-determining reaction. Thus $k = (k_3\mu)/c$, where k_3 is the homogeneous rate constant for the conversion of the intermediate to B, $\mu = \sqrt{D/k_3}$,[8] and c has the same meaning as above. It follows that $\beta = \sqrt{k_3 t}/c$, as was shown earlier.[3]

Recently Koutecky has solved the kinetic wave and slow electrode reaction problems for an expanding electrode surface.[10] The inaccuracies introduced by the non-rigorous adaptation of the plane electrode solution to the dropping mercury electrode heretofore employed in the study of such problems have in these cases been overcome. For both wave-types mentioned the solution was found to be approximated very accurately by the simple expression

$$\bar{\imath}/\bar{\imath}_d = 0.87\beta/(1 + 0.87\beta) \qquad (3)$$

$\bar{\imath}$ being the limiting kinetic current in one case and the current at a given potential in the other, and β being the same function as in equation 1, except that the drop time τ is used instead of t.

Now by the same arguments that have been put forth above for the plane electrode solution, equation 3 can clearly be extended to the ascorbic acid case and the one described by Berzins and Delahay. Equation 3 differs considerably from the plane electrode solution. In particular it follows that

$$\log \bar{\imath}/(\bar{\imath}_d - \bar{\imath}) = \log 0.87\beta \qquad (4)$$

For a slow electrode reaction $\beta \sim k_e$, and according to the absolute rate theory

$$k_e = \text{const.} \times \exp{(-\alpha nFE/RT)} \text{ (for a reduction)}$$

Hence a plot of a $\log \bar{\imath}/(\bar{\imath}_d - \bar{\imath})$ *vs.* E should give a straight line with slope $\alpha n/0.059$ at 25°. This relationship has been known empirically for years.[11]

For an irreversible reaction following upon a reversible one, $\beta \sim k_e/c$ where $c = \exp{(E - E_0)}\cdot nF/RT$. Thus the log plot should be linear with a slope of $(n_1 + \alpha n_2)/0.059$, where n_1 refers to the number of electrons in the reversible step and n_2 to the number in the succeeding irreversible one. Delahay, however, from his plane electrode calculation predicted a non-linear slope under all conditions.

Finally for the ascorbic acid case $\beta \sim 1/c$. Thus equation 3 predicts a straight log plot with

---

(4) M. Smutek, *Collection Czech. Chem. Communs.*, **18**, 171 (1953); P. Delahay and J. Strassner, THIS JOURNAL, **73**, 5219 (1951).

(5) The ratio of *average* currents $\bar{\imath}/\bar{\imath}_d$ also can be expressed for all these wave types as a function of the single parameter β. This fact was overlooked by the author in his treatment of the ascorbic acid case, in which $\bar{\imath}/\bar{\imath}_d$ was expressed less neatly as a function of β and τ.

(6) T. Berzins and G. Delahay, THIS JOURNAL, **75**, 5716 (1953).

(7) K. Wiesner, *Chem. Listy*, **41**, 6 (1947).

(8) The conditions under which this concept is valid have been discussed by D. Kern, THIS JOURNAL, **75**, 2473 (1953).

(9) This result is in agreement with the original derivation of J. Koutecky and R. Brdicka, *Collection Czech. Chem. Communs.*, **12**, 387 (1947).

(10) J. Koutecky, *Collection Czech. Chem. Communs.*, **18**, 597 (1953).

(11) This feature of the new solution for the slow electrode reaction has been pointed out by Koutecky, see ref. 2.

slope $n/0.059$, just as for a reversible wave. The ascorbic acid wave does in fact satisfy this requirement.[3] The agreement is particularly gratifying in that on the basis of the plane electrode theory, which predicted a non-linear plot, the reversible slope appeared to be a troubling anomaly. The new equation for the $E_{1/2}$ of the *average* current becomes $E_{1/2} = E_0 - (RT/2nF)\ln k - (RT/nF)\ln 0.87$. In the previous equation based on plane electrode calculations,[3] the last term was RT/nF ln 0.65.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

Purification of Germanium Tetrachloride by Solvent Extraction

BY GEORGE H. MORRISON, E. G. DORFMAN AND JAMES F. COSGROVE

RECEIVED FEBRUARY 18, 1954

Introduction.—Liquid–liquid solvent extraction methods have provided a valuable tool for the separation of impurities from many materials.[1] Since germanium tetrachloride and concentrated hydrochloric acid solutions form an immiscible extraction system,[2] a series of experiments was performed to determine the distribution ratios of a number of elements between these two phases for the purpose of developing a chemical method of purification of germanium. Other chemical methods of separation used in the past have involved the distillation of germanium tetrachloride.[3]

It is well known that traces of various impurities have a great effect upon the electrical properties of germanium metal used in semiconductor devices. In some instances it is necessary to control the significant impurities in germanium single crystals to within one part in 10 billion.[4] Consequently, it was of particular interest to study the behavior of very small amounts of impurity elements in this investigation. Radiochemical tracer techniques were used, wherever possible, in the present study, since these provided the double advantage of simplicity and sensitivity. Among the impurities known or suspected of producing an effect upon the electrical behavior of germanium, the elements antimony, arsenic, boron and copper were examined by this extraction technique.

Experimental

Batch Extractions.—Fifteen-ml. portions of germanium tetrachloride, purified by distillation (b.p. 83.1°) were placed in 30-ml. glass stoppered graduated weighing burets. No attempt was made to remove hydrogen chloride from the product since it was to be used in experiments in which it would be shaken with hydrochloric acid. The hydrochloric acid phase consisted of 15 ml. of either 6 or 12 *N* hydrochloric acid (reagent grade) containing the appropriate amount of impurity element. The fact that the values obtained with arsenic by adding the impurity element to either phase prior to equilibration result in the proper relation is an indication that the initial location of the impurity in the system is not significant. If the hydrochloric acid concentration is much less than 6 *N*, hydrolysis of germanium tetrachloride will result. Various extractions were performed at equilibration times of 5, 30 and 60 minutes. A series of extractions was performed at 0 and 25 ± 0.2° to determine the effect of temperature on the distribution. The extractors were mechanically shaken in a constant temperature water-bath for the appropriate time. To maintain a temperature of 0° the extractors were mounted in a Dewar flask containing crushed ice and the Dewar flask was mechanically shaken. Changes of phase volumes were measured and in all cases the phases were permitted to settle for 10 minutes prior to sampling.

Impurity Elements.—Of particular interest in this study was the behavior of very small amounts of impurity elements in the parts per million concentration range and lower. Consequently, whenever possible high specific activity or carrier-free radioisotopes were used as impurity elements.

Arsenic.—A standard solution of 100-ml. volume was prepared from 0.25 millicurie of processed carrier-free As^{73-74} produced by cyclotron bombardment of germanium with deuterons.[5] The chemical form of the tracer was arsenic trichloride in 12 *N* hydrochloric acid. Appropriate aliquots of tracer solution were used in the respective extractions to permit quantitative measurement of activity.

Antimony.—Fifteen millicuries of processed high specific activity (1751 mc./g.) Sb^{124} as antimony trichloride[5] was used to prepare a 25-ml. standard solution of antimony in 12 *N* hydrochloric acid. An aliquot of this solution was oxidized with $KBrO_3$ to produce pentavalent antimony.

Copper.—Ninety-five millicuries of Cu^{64} produced by irradiating 50 mg. of copper powder with neutrons in the Brookhaven pile was used to prepare a standard solution of copper chloride in 12 *N* hydrochloric acid (4.5 mg./ml. Cu).

Boron.—0.2858 g. of recrystallized boric acid (C.P.) was dissolved in 500 ml. of distilled water (0.1 mg./ml. B).

Radioactivity Measurements.—At least two aliquots of each phase were placed in 5-ml. screw cap vials and the γ activity was measured by means of a liquid scintillation counting technique. In the case of copper and antimony a liquid phosphor, diphenylbenzene, was used as detector. A well type thallium activated sodium iodide crystal was employed in the measurement of arsenic activity. An RCA 5819 photomultiplier tube was used in a General Electric scintillation counter. A Nuclear Instruments Model 172 scaler was used to record the counts. A sufficient number of counts was taken on each sample to give a statistical fluctuation of less than 1% from the true average rate.[6]

This arrangement permitted counting at a high geometric efficiency. No difficult sample preparation is involved and the counting rate is independent of the density of the solvent under the conditions employed.

Colorimetric Measurements.—Since the radioactive isotope of boron has an extremely short half-life, boron was determined by means of a colorimetric procedure employing carminic acid.[7] Wherever possible platinum or polyethylene apparatus was used to avoid boron contamination. A color change from bright red in the absence of boron to bluish red or blue in the presence of boron is produced. The percentage transmission was measured at 600 mμ using a Beckman Model DU spectrophotometer. Beer's Law is followed over the range from 0 to 20 μg. of boron. There is no interference from small amounts of germanium.

Miscibility of Germanium Tetrachloride in Hydrochloric Acid.—The miscibility of germanium tetrachloride in 6 and 12 *N* hydrochloric acid solutions was determined in order to ascertain the loss of germanium during extraction. Solutions of both 6 and 12 *N* hydrochloric acid were shaken with excess germanium tetrachloride for 5 minutes at 0 and 25 ± 0.2°. The germanium content of the hydrochloric acid phases was analyzed by means of a gravimetric procedure involving precipitation as the sulfide and subsequent ignition and weighing of the oxide.[8] The results of the analyses are given in Table I.

---

(1) G. H. Morrison, *Anal. Chem.*, **22**, 1388 (1950).

(2) E. R. Allison and J. H. Muller, THIS JOURNAL, **54**, 2833 (1932).

(3) L. M. Dennis and E. B. Johnson, *ibid.*, **45**, 1380 (1923).

(4) W. Shockley, "Electrons and Holes in Semiconductors," D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 12.

(5) Isotopes obtained from the Isotopes Division, U. S. Atomic Energy Commission.

(6) A. A. Jarrett, "Statistical Methods Used in the Measurement of Radioactivity," U. S. Atomic Energy Report AECU-262, June 17, 1946.

(7) J. T. Hatcher and L. V. Wilcox, *Anal. Chem.*, **22**, 547 (1950).

(8) W. F. Hillebrand and G. E. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 299.