[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Millicoulometry. I. Construction and Operation of an Apparatus for the Determination of Polarographic *n*-Values

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The design and calibration of a millicoulometer incorporating a Weston integrating relay and accessory electronic circuits are described. When this instrument is used to integrate the current flowing through a polarographic circuit under such conditions that a considerable decrease in the concentration of reducible or oxidizable material takes place during the electrolysis, data are secured from which the value of n, the number of faradays per mole of electrode reaction, can be computed. The application of the method is illustrated by data on some representative inorganic reductions.

Introduction

Due, primarily, to the excellent researches of Lingane and co-workers,[1-5] there has recently developed a considerable interest in methods for the determination of the number of electrons involved in a unit of reaction at the dropping mercury electrode. Using a hydrogen-oxygen volume coulometer, Lingane[3] developed a technique by which the current consumed during a quantitative electrolysis at a large stirred mercury cathode, whose potential was controlled by a potentiostat[1] at a value previously determined from polarographic experiments, was integrated and compared with the number of moles of the reducible material known to have been present initially. This technique has been applied with outstanding success to the interpretation of the polarographic waves secured with the various oxidation states of molybdenum[4] and wolfram,[5] and very recently it has succeeded in casting valuable light on the electrode processes occurring during the electrolysis of perrhenate solutions.[6]

Nevertheless, the suspicion remains that, especially in the case of a rate-controlled reaction, as so many organic reductions may be, the final reduction products from an electrolysis at a well-stirred large cathode may not be identical with those produced by electrolysis at a dropping electrode. To overcome this doubt, many attempts have been made to integrate directly the current flowing during a prolonged electrolysis under polarographic conditions. These have generally been done by measuring the diffusion current at periodic intervals and integrating the current-time curve thus secured. But during an exhaustive electrolysis with a dropping electrode, the portion of the solution around the capillary tip becomes depleted, and this leads to extraneous stirring effects which, in turn, produce erratic fluctuations in the current which may not be detected by occasional measurements.[7]

It is apparent that, if an accurate integration of the current-time curve could be secured, these difficulties would vanish, and with them the need for the frequently elaborate apparatus necessary in large-scale electrolyses because of the variation of the back e.m.f. with concentration and because of the generally poorer definition of a wave at a large stirred electrode.

The present communication describes an instrument which performs this integration, and its application to electrolyses at a dropping electrode of conventional design.

Apparatus

Polarographic measurements were made with the manual instrument previously described,[8] using a micro H-cell[9] thermostatted at 25.00 ± 0.02°.[10]

A schematic diagram of the millicoulometer is shown in Fig. 1. The voltage developed across a precision resistor by the current to be integrated is applied, through the contacts of a double-pole, double-throw relay, S2, to the coil of an integrating relay.[11] This relay is essentially a d.-c. motor whose armature turns at a rate proportional to the voltage applied to it, but which is constrained by periodic reversal of the sign of this voltage to an oscillatory motion instead of a continuous rotation. The armature carries a contacting arm by which these reversals in voltage are automatically initiated.

Tubes V2B and V3B (B sections have pin numbers 6, 7 and 8) constitute a conventional Eccles-Jordan circuit. Tubes V2A and V3A are buffer tubes which serve to minimize any current flow through the contacts of the integrating relay at the instant of reversal. The grids of V2A and V3A are normally held below cut-off by the flow of current through V2B or V3B and their common cathode resistors.

Let us suppose that V2B is carrying current and V3B is cut off, so that the relay S2 is energized. This means that the positive side of the voltage across the 10K precision resistor is applied to the positive terminal of the integrating relay, causing its contacting arm to move toward the right-hand contact. When contact is made, the grid of V3A is momentarily raised above cut-off. This causes the plate potential of V3B to drop as a result of flow of current through the 33K resistor and the coil of relay S3 in its plate circuit. The drop in potential of the plate of V3B is transmitted to the grid of V2B, thus producing a corresponding rise in the plate potential of this tube. This rise is transmitted to the grid of V3B, thus helping further to reduce the plate potential of V3B. In this way a very rapid switch of plate current from V2B to V3B is brought about. The 330K-240K resistor combination between the plate of one tube in the Eccles-Jordan circuit and the grid of the other tube is selected so that the grid of the tube not carrying current is held well below cut-off until the switching action is initiated by the integrating relay.

When the plate current switches from V2B to V3B as described above, the relay S2 is de-energized and the voltage

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[1] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 147 (1944).

[2] J. J. Lingane, C. G. Swain and M. Fields, THIS JOURNAL, **65**, 1348 (1943).

[3] J. J. Lingane, *ibid.*, **67**, 1916 (1945).

[4] D. C. Carritt, Ph.D. Thesis, Harvard University, 1947.

[5] J. J. Lingane and L. A. Small, THIS JOURNAL, **71**, 973 (1949).

[6] C. L. Rulfs and P. J. Elving, *ibid.*, in press.

[7] B. A. Loveridge and J. J. Lingane, private communication.

[8] L. Meites and T. Meites, THIS JOURNAL, **72**, 3686 (1950).

[9] T. Meites and L. Meites, *Anal. Chem.*, in press.

[10] This cell has been used in the present work solely as a matter of convenience. Loveridge and Lingane,[7] working with chloride solutions, used a silver wire wound around the capillary as an anode, and their cell consisted essentially of a micro test-tube. Such an arrangement complicates the stirring problem somewhat, but may be decidedly advantageous, especially when neutral or alkaline solutions are used, so that oxygen can be removed by sulfite. Cells with mercury pool anodes may not be used because it is impossible to prevent cyclic re-solution of the deposited metal from the anodic pool. With extremely rare exceptions, re-solution of metal from the mercury which collects on the bottom of a cell with an external or silver wire anode is impossible. The exceptions (caused by the presence in the solution of a substance whose reduction at the potential of electrolysis is possible but is too slow to contribute to the diffusion current) are easily treated by the addition of a few drops of chloroform to the cell.

[11] R. W. Gilbert, *Rev. Sci. Instruments*, **18**, 328 (1947).

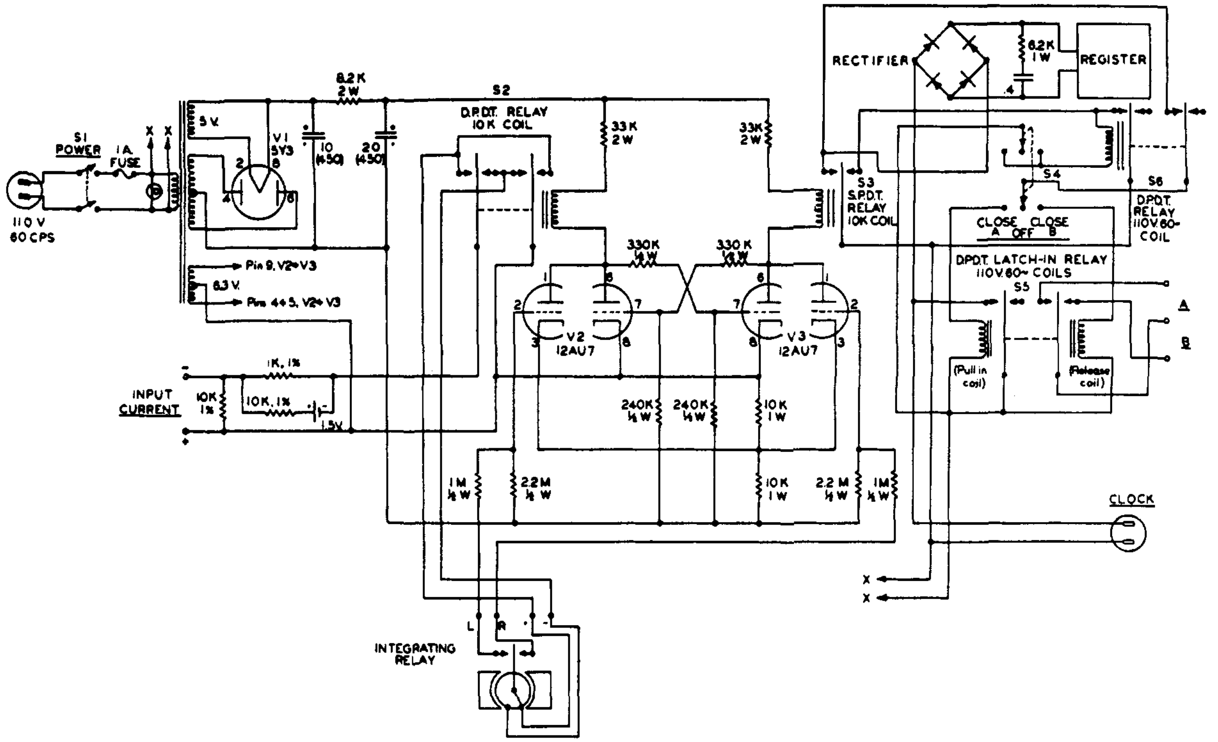

Fig. 1.—Schematic diagram of millicoulometer: all resistors 10% tolerance except as noted; capacitances in microfarads; transformer, Thordarson T70R78 or equivalent; rectifier, selenium full-wave rectifier, rated at 110 v. a.c., approximately 50 ma.; register, "Mercury" electromagnetic register, Production Instrument Co., Chicago, Ill.; integrating relay, Model 806, Type 5, Weston Electrical Instrument Corp., Newark, N. J.

applied to the armature of the integrating relay is reversed. A similar series of events, involving switch of plate current from V3B back to V2B, occurs, when the contacting arm meets the left-hand contact. The switching operation requires about 8 milliseconds, most of which is, of course, due to relay lag.

To secure integration, it is merely necessary to count the oscillations of the integrating relay. This is conveniently done by another relay, S3, in the plate circuit of V3B, which actuates an electromechanical register once for each complete cycle of the integrating relay. The particular register we have used requires too large a current to be actuated directly by the plate current of one half of a 12AU7, so that a full-wave selenium rectifier is used to enable its operation from the 100 v. a.-c. line. The 6.2K–0.4 μF network is selected to make the register appear like a resistive load, in order to avoid unwanted tripping of the Eccles–Jordan circuit by transients.

The manual switch S4, and the relays S5 and S6, the former being of the mechanical latch-in, electrical reset type, are convenient in the present application of the integrator. With S4 in the "Close A" position, the next energization of S3 starts the actuation of the register, closes external circuit A, and applies current to an electric stop-clock connected to the indicated outlet. After this sequence of operations, S4 is returned to the "Off" position. If S4 is at a later time put in the position "Close B," the next energization of S3 will stop the register and the clock, and open the external circuit A. In the present application, the polarographic circuit comprises circuit A (the millicoulometer is connected between S4 and S5 in our polarographic circuit: *cf.* ref. 8, Fig. 1), so that in this way the period of integration is rigidly synchronized with the period of electrolysis at the dropping electrode, and always corresponds to an integral number of oscillations of the integrating relay, so that interpolation errors are avoided.

The effects of friction in the integrating relay seriously interfere with its accuracy at very slow rates of motion. A bias battery giving about 0.15 v. is therefore placed in series with the input voltage so that a suitably fast rate of motion is obtained even at zero input current. This battery should be connected for several hours prior to use of the instrument. Because of this introduction of a "background" counting rate, it is necessary to time accurately any interval during which integration is performed. This is the reason for including provision for automatically starting and stopping an external electric stop-clock.

A conventional power supply, with R-C filtering, is included for the Eccles–Jordan circuit.

Figure 2 gives a calibration curve obtained by applying known input currents to the instrument. The currents were evaluated by measuring with a Rubicon precision potentiometer the voltage drop across a 1K standard resistor in series with the source of current and the millicoulometer. It is seen that the calibration is linear within about 1% between 0 and 70 microamperes, and within this range one count corresponds to 43.8 microcoulombs: this figure may vary among relays, so that each instrument must be calibrated before use. Although the calibration curve falls off about 3% as the input current is further increased to 100 microamperes, this does not constitute a serious limitation of the use of the instrument, for the value of $m^{2/3}t^{1/6}$ may easily be adjusted by varying the height of the mercury column in the stand tube so that the maximum current during the life of the drop does not exceed 70 microamperes (i_d approximately 60 microamperes).

Experimental

Solutions of thallium(I) chloride in 0.2 *F* potassium chloride and of lead(II) nitrate in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid were prepared from recrystallized salts. Other materials used were ordinary reagent grade.

To begin an electrolysis, the cell was thoroughly washed with water and acetone, dried with a stream of air, and filled to just below the lower gas inlet tube with pure mercury. In electrolyses of materials which can oxidize mercury, a few drops of chloroform should be added as a protective layer. About 0.3 g. of a solution of the reducible material in the supporting electrolyte to be used was then weighed in, the stopper, covered with a very thin film of silicone grease to prevent any possible collection on its surface of small drops of solution entrained in the gas stream, was inserted, and the solution was deaerated by the passage of a very slow stream of hydrogen for a few minutes. With such small volumes of solution, it is obvious that care should be taken to avoid mechanical loss due to the use of too rapid a

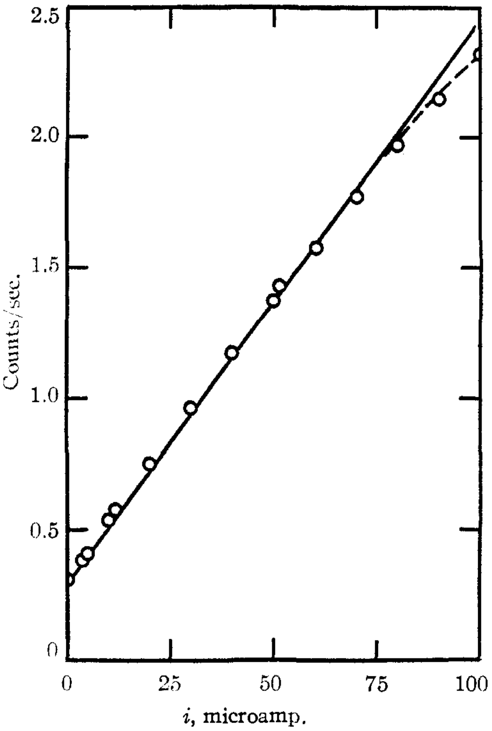

Fig. 2.—Calibration curve for millicoulometer.

gas stream. Evaporation from or condensation into the solution may be prevented by the use of a presaturator in the gas stream. This may consist of a gas washing bottle filled with the supporting electrolyte used and immersed in the thermostat.

Meanwhile the blank counting rate of the millicoulometer was determined, usually as the average of four or five measurements whose mean deviation rarely exceeded 0.1%: this is necessary because of the slow deterioration of the bias battery. When deaeration was judged to be complete, the capillary was inserted, and the electrolysis was begun as described above. The initial diffusion current, which is needed in the calculations, must be measured as soon as possible after the circuit is closed.

Ordinarily the electrolysis will be allowed to proceed uninterrupted until an hour or two has elapsed, when the solution is stirred mechanically or by hydrogen for a few seconds to eliminate concentration gradients around the capillary tip, and the diffusion current is again measured. The circuit is immediately opened by throwing S4 of the millicoulometer to the "Close B" position, and the register and stop-clock are read. From the ratio between the initial and final diffusion currents and the number of moles of substance known to have been present initially, the number of moles reduced during the electrolysis can readily be computed. This, on division into the number of faradays used in the electrolysis, calculated from the initial and final register readings and the previously determined calibration curve, gives n directly.

In order to secure more information about the behavior of the instrument and the precision to be expected in its use, we have modified this procedure slightly by stirring the solution and recording the diffusion current, register reading, and clock reading at intervals of a few hundred seconds during the course of a run. The data thus secured in the electrolysis of a solution of cadmium(II) in 0.1 F potassium nitrate are shown in Table I.

In a typical experiment with 0.987 micromole of thallium(I) in 0.53 ml. of 0.1 F potassium chloride, i_d decreased from 4.94 to 3.92 microamperes in 4000 seconds: thus 0.204 micromole was reduced. Meanwhile the millicoulometer indicated the passage of 0.201 microfaraday, giving n = 0.99. It is apparent that the instrument can be successfully applied even when i_d is relatively low.

TABLE I

ELECTROLYSIS OF CADMIUM(II)

1.540 micromole of cadmium was initially present in 0.309 ml. of solution in 0.1 F potassium nitrate. $E_{d.e.} = -1.00$ v. *vs.* S.C.E. $m^{2/3}t^{1/6}$ = *ca.* 1.0; t = *ca.* 4 sec. The blank counting rate of the millicoulometer was 0.2998 count/sec. The residual current corresponded to a galvanometer deflection (1 cm. = *ca.* 0.75 μamp.) of 0.23 cm. and to a counting rate of 0.0070 count/sec.

Time, sec.	Register	Counts	Counts, cor.	Millicoulombs	d, cm.	Micromole reduced	n
0	31090	0	0	0	23.44	0	..
430	31468	378	246	10.8	22.61	0.055	2.03
1126	32068	978	632	27.7	21.30	.142	2.02
1920	32739	1649	1060	46.4	19.67	.250	1.92
2432	33160	2070	1324	58.0	18.90	.301	2.00
2720	33393	2303	1469	64.3	18.36	.337	1.98
2944	33572	2482	1578	69.1	18.16	.350	2.05
3214	33784	2694	1707	74.8	17.56	.390	1.99
3415	33941	2851	1802	78.9	17.38	.402	2.03
3579	34067	2977	1879	82.3	16.95	.431	1.98
3751	34198	3108	1957	85.7	16.67	.449	1.98
4233	34561	3471	2173	95.2	16.08	.488	2.02
4442	34713	3623	2260	99.0	15.63	.518	1.98

$\bar{n} = 2.00 \pm 0.02_6$ (mean deviation)

Both the current measurements and the millicoulometer readings must be corrected for the residual current. Theoretically, the residual current should, in the absence of oxidizable or reducible impurities from the supporting electrolyte, be entirely due to the necessity of charging the electrical double layer around the drop. That is, the "diffusion current" term k_1 in the expression for the residual current[12]

$$i_r/m^{2/3}t^{1/6} = k_1 + k_2/t^{1/2}$$

should be zero. It has been shown[13] that in 0.1 F potassium chloride, 0.1 F potassium nitrate or 0.1 F potassium chloride–0.1 F hydrochloric acid at $E_{d.e.} = -1.00$ v. *vs.* S.C.E., and in 0.1 F potassium chloride at -1.50 v. *vs.* S. C. E., the value of k_1 is 0.030 ± 0.003. Accordingly, one would expect that the residual current would be substantially independent of the time of electrolysis, and this is actually found to be the case. For example, after 6200 seconds electrolysis at -1.00 v. *vs.* S.C.E. the residual current in 0.29 ml. of 0.2 F potassium chloride was 0.25 microampere, compared with 0.23 microampere in the fresh solution. Hence it is sufficiently accurate to determine the residual current of a freshly deaerated portion of the supporting electrolyte under the conditions used and apply this correction directly to each of the current readings during the electrolysis. Furthermore, the corresponding correction to be applied to the millicoulometer readings is simply secured by multiplying the initial residual current by the time of electrolysis to secure the number of millicoulombs required by the residual current.

Because of the necessity of correcting for the residual current and for the background counting rate

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[12] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., pp. 108-110.

[13] L. Meites, THIS JOURNAL, in press.

of the millicoulometer, it is evident that more accurate values of n are available when the diffusion current is relatively high, and the fact that the number of moles of material reduced is found from the difference between two current measurements means that the electrolysis should be allowed to proceed for as long a period of time as is convenient. From these considerations it can be deduced that the volume of solution should be very small and that the value of $m^{2/3}t^{1/6}$ should be fairly high. Increasing the concentration of the solution improves the accuracy of the millicoulometric measurements, but it correspondingly increases the time required for the deposition of a given fraction of the reducible material.

It can readily be shown that the diffusion current at the end of an electrolysis lasting for T seconds should be given by the equation

$$\log i_d = \log i_d^0 - \frac{4.403 \times 10^{-6}\, Im^{2/3}t^{1/6}\, T}{Vn} \qquad (1)$$

where i_d^0 is the diffusion current at the beginning of the electrolysis, V is the volume of the solution (ml.) and the other symbols have their ordinary polarographic significance. This relation is implicitly inherent in methods for the determination of n by the graphical integration of the current–time curve.

Typical diffusion current data for the electrolysis of a solution of 2.57 micromoles of lead(II) in 0.1 F potassium chloride 0.1 F hydrochloric acid are shown in Fig. 3. Under these conditions equation (1) becomes

$$\log i_d = 1.2711 - 2.009 \times 10^{-5}T \qquad (2)$$

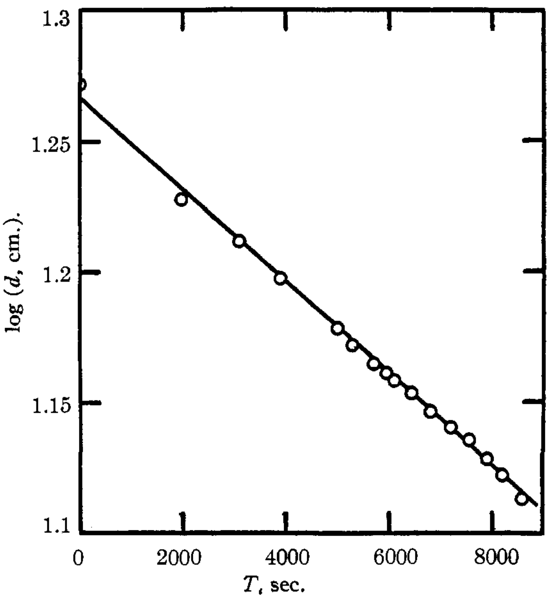

Fig. 3.—Current–time curve for the electrolysis of lead (II); see text for experimental details. Diffusion currents are in arbitrary units of galvanometer deflection, and have been corrected for the residual current.

In agreement with equation (2), the points are seen to fall very well on a straight line, but the slope of this line is found to be 1.82×10^{-5}. This gives a value of 2.21 for n, which is not in very good agreement with the theoretical $n = 2.00$ for the reduction of lead ion. The discrepancy is comparable with the errors found by Loveridge and Lingane[7] in their attempts to integrate the current–time curve, and it is directly attributable to the depletion of the solution around the capillary tip during the electrolysis.

From a number of electrolyses of solutions of thallium(I), cadmium(II) and lead(II), the average accuracy and precision to be expected from the method here described appears to be about 3%.

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The Heats of Formation of TiO, Ti_2O_3, Ti_3O_5 and TiO_2 from Combustion Calorimetry[1]

BY GEORGE L. HUMPHREY

A precise combustion calorimeter has been constructed to measure the heats of combustion of inorganic substances. Calculations from measured heats of combustion for titanium, titanium monoxide, titanium sesquioxide and titanium tritapentoxide have yielded the following values for the standard heats of formation ($-\Delta H_f^0$) in kcal./mole: TiO, $123.9_1 \pm 0.2_8$; Ti_2O_3, $362.9_3 \pm 0.4_8$; Ti_3O_5, $586.9_1 \pm 0.6_9$; TiO_2, $225.5_2 \pm 0.2_3$. Free energies of formation also are presented.

The facilities of this Laboratory for obtaining thermodynamic data for inorganic substances have been extended by the development of a precise combustion calorimeter. This calorimeter makes possible the determination of heats of formation of many substances that are not susceptible to the methods of solution calorimetry, either because of slow reaction rates or because of difficulties in obtaining unequivocal final solution states.

The heats of formation of the titanium oxides are important thermodynamic quantities in various metallurgical calculations of both research and industry. A survey of the literature shows large deviations among the existing values, or else the values are missing entirely. The only direct determination is the heat of formation of TiO_2 by combustion measurements, which yield values[2] ranging from 218.0 to 225.3 kcal. per mole for $-\Delta H_f^0$.

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(1) Article not copyrighted.

(2) (a) W. G. Mixter, *Z. anorg. Chem.*, **74**, 122 (1912); (b) W. A. Roth and G. Becker, *Z. physik. Chem.*, Ergänzungsband (1931) Bodenstein Festband; (c) A. Sieverts and A. Gotta, *Z. anorg. Chem.*, **199**, 384 (1931); (d) B. Neumann, C. Kröger, and H. Kunz, *ibid.*, **218**, 379 (1934); (e) W. A. Roth and U. Wolf, *Rec. trav. chim.*, **59**, 511 (1940).