[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE, DEPARTMENT OF HEALTH, EDUCATION AND WELFARE]

Polarography of the Noble Metals

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In order to show that strong complexation of a noble metal is not required for successful polarography, the mechanism is discussed and polarograms are presented indicating that reaction of a noble metal with the mercury drop is not a deterrent to the polarographic determination of the metal. It is shown that gold may be determined in acetate, chloride or other electrolytes. The diffusion current may be too small, however, if the noble metal is in the form of a difficultly reducible complex or hydroxide, as is illustrated by Pd, Ir, Ru and Rh.

Although several papers have shown that noble metals such as silver,[1] gold[2] and platinum[3,4] may be determined polarographically without the addition of complexing agents, others[5-9] have fostered the impression that the noble metal must be complexed strongly so as to prevent the noble metal ion from reacting spontaneously with the mercury drop. Consideration of the mechanism of reduction shows, however, that reaction of the metal ion with the mercury drop should not be a deterrent to the polarographic determination. Our experiments with the noble metals in several electrolytes indicate that reasonable diffusion coefficients may be obtained, provided only that the metal is sufficiently reactive.

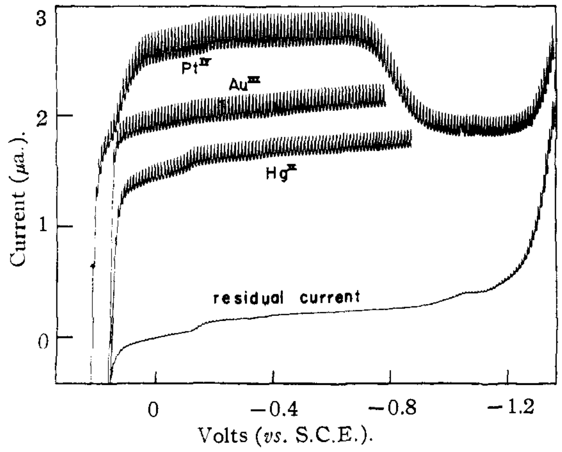

Fig. 1.—Polarograms of 2.0 × 10^{-4} *M* Hg(II), Au(III) and Pt(IV) in the *p*H 5 acetate buffer + the following maximum suppressors or complexing agents: Pt(IV), approx. 10^{-5} *M* methyl red; Au(III), approx. 0.05 *M* KCl; Hg(II), approx. 10^{-5} *M* methyl red + approx. 0.05 *M* KCl; residual current, approx. 10^{-5} *N* methyl red + approx. 0.05 *M* KCl. No methyl red was added to the gold solution since methyl red reduces gold, and since no maximum suppressor was found necessary. The slight waves in the other curves at approximately −0.1 v. are due to the polarographic reduction of methyl red.

Experimental

The stock solutions were made up from dried Fisher Scientific Co. C.P. salts and the concentrations calculated from these. The palladium, however, was determined by precipitation with dimethylglyoxime in acid solution since this reaction is so specific. A gold solution was also made by dissolving pure gold in aqua regia.

The solutions for polarographic analysis were made by diluting the stock solutions with an arbitrarily chosen *p*H 5 acetate buffer to a final ionic strength 0.1. Essentially the same results were obtained with supporting electrolytes of nitrate, chloride or perchlorate, except that more irregularities in the polarograms occurred with these solutions than with buffered solutions.

Deoxygenation was carried out in the absence of mercury. The polarograms were run soon after the dropping mercury electrode had been inserted, and bulk exchange of the noble metal ion with the mercury in the pool at the bottom of the half cell was prevented by avoidance of bubbling. A saturated calomel electrode was used as reference electrode.

The rate of flow of mercury was 1.62 mg. per sec. and the drop time was nearly four seconds. The temperature was maintained at 25.0°. A Sargent Model XXI polarograph was used.

Results and Discussion

In Fig. 1 are polarograms of 2 × 10^{-4} *M* Hg(II), Au(III) and Pt(IV).

If the noble metal ion is not strongly complexed, equilibrium favors the right-hand side of

$$2Au^{+++} + 6Hg \rightleftarrows 2Au + 3Hg_2^{++} \qquad (1)$$

At potentials too positive for mercury to be reduced, the above reaction proceeds at the surface of the electrode, but no net reduction occurs. At potentials more negative than the mercury wave any mercurous ions produced by reaction 1 are reduced

$$3Hg_2^{++} + 6e^- \longrightarrow 6Hg \qquad (2)$$

and the net result is

$$Au^{+++} + 3e^- \longrightarrow Au \qquad (3)$$

whether it occurs by the mechanism of reactions 1 + 2 or directly by reaction 3. Thus the noble metal wave occurs at the same voltage as the mercury wave.

The effect of complexing agents is readily predicted. Most anions complex with mercury as well as the noble metal, and the right-hand side of (1) is still favored. Thus the wave of the noble metal is shifted along with the mercury wave to a more negative potential. In the polarograms of Fig. 1 the effect of chloride as a complexing agent was employed to shift the gold, mercury and residual current curves so that they would not overlap the platinum curve.

The calculated diffusion coefficients, which are nearly independent of concentration, are recorded in Table I. Those for Hg, Au and Pt are similar and are large enough to show that the fundamenta

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[7] I. M. Kolthoff and J. J. Lingane, ref. 1, pp. 489, 501.

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[9] J. B. Willis, *ibid.*, **67**, 547 (1945).

assumption of the Ilkovic equation for the limiting current is obeyed, *i.e.*, that all of the metal ion diffusing to the mercury drop is rapidly reduced.

TABLE I

Metal	Polarographic soln. prepared by diln. from	Appar. diff. curr. const.	Apparent calcd. diff. coeff.[a] (cm.^{2} × sec.$^{-1}$ × 10^{-5})
Hg(II)	Fresh $HgCl_2$ stock soln.	3.9	1.05
Au(III)	Fresh $HAuCl_4$ stock soln.	5.8	1.04
Au(III)	Year-old stock soln.	5.8	1.02
Pt(IV) A	Fresh stock soln. prepared by dissolving K_2PtCl_6 in aqua regia or H_2PtCl_6 in water	7.6	0.98
Pt(IV) B	Year-old H_2PtCl_6 stock soln.	0.8	0.01
Pt(IV) C	Year-old H_2PtCl_6 stock soln. treated with aqua regia	6.8	0.80
Pt(IV) D	Year-old H_2PtCl_6 stock soln. treated with HCl	6.1	0.64
Pt(II)	Fresh K_2PtCl_4 stock soln.	4.0	1.09
	Year-old K_2PtCl_4 stock soln.	4.0	1.08
Pd(II)	Fresh, clear stock soln. 0.06 *M* in NaCl. Final dilution to 0.1 *M* acetate and 0.003 *M* chloride	2.5	0.4
Pd(II)	Same stock soln., but final soln. was made 0.1 *M* in acetate and 0.01 *M* in chloride	3.0	0.6
Pd(II)	Same stock soln., but final soln. was made 0.1 *M* in acetate and 0.1 *M* in chloride	3.5	.8
Ir(III)	Fresh $IrCl_3$ stock soln.	0.8	.02
Ru(III)	Fresh $RuCl_3$ stock soln.	.8	.02
Rh(III)	One fresh $RhCl_3$ stock soln.	.30	.29
Rh(III)	Another fresh $RhCl_3$ stock soln.	.33	.33
Rh(III)	Same stock soln., but diluted after one hour	.34	.34
Rh(III)	Same stock soln., but diluted after five hours	.36	.39
Rh(III)	Same stock soln., but diluted after one day	.37	.42
Rh(III)	Same stock soln., but diluted after three days	.38	.45
Rh(III)	Same stock soln., but diluted after nine days	.40	.49
Rh(III)	Same stock soln., but diluted after one year	.41	.50

[a] Calculated from diffusion current (after subtraction of residual current) by means of Ilkovic equation, on the assumption that the ion is reduced to the free metal. The stock solutions (usually 5 millimolar) were diluted with *p*H 5 acetate buffer.

Difficulty arises in determining noble metals polarographically when, in fact, the noble metal in solution *does not* react quickly at the surface of the mercury drop.

This may be due to the formation of unreactive complexes[10–12] or of colloidal aggregates of the metallic hydroxides which do not quickly establish equilibrium with the mercury.

F. L. English[3] noted a decrease in diffusion current of Pt(IV) on standing in a *p*H 7 buffer and ascribed it to formation of Pt(II). It seems more likely that the decrease in current is due to formation of the colloidal precipitate (presumably platinum hydroxide) which may be observed in such solutions, since we found by titration with Ce(IV) no significant amount of Pt(II) in such solutions.[13]

The presence of unreactive complexes may also cause an abnormally small diffusion current, as is indicated by the following experiments with Pt(IV). An aliquot of 2×10^{-3} *M* H_2PtCl_6, after standing for a year, showed no visible precipitate and no significant reduction of Ce(IV), but had a low diffusion current (soln. B). Another aliquot of this year-old solution, evaporated to dryness, boiled with aqua regia, and then diluted so as to reach nearly the same acidity and electrolyte concentration as solution B, yielded a diffusion current (soln. C) nearly equal to that of freshly made H_2PtCl_6 (soln. A). A similar treatment but with HCl rather than aqua regia also restored most of the diffusion current (soln. D). We interpret the decrease in diffusion current as the formation of an "inert" complex, probably by the demonstrably[14] slow replacement of chlorine by hydroxyl. The acid treatment of the old Pt(IV) solution apparently converts the "inert" Pt complex to a more easily reducible one.

In Fig. 2 are typical polarograms of 2×10^{-4} $RuCl_3$, $IrCl_3$, $Pd(NO_3)_2$ and $RhCl_3$. It may be seen from the slopes of the waves and/or the unreasonably small calculated diffusion coefficients (Table I) that complete reduction does not take place at the voltage at which mercury is reduced. The noble metal must therefore be in the form of an unreactive complex.

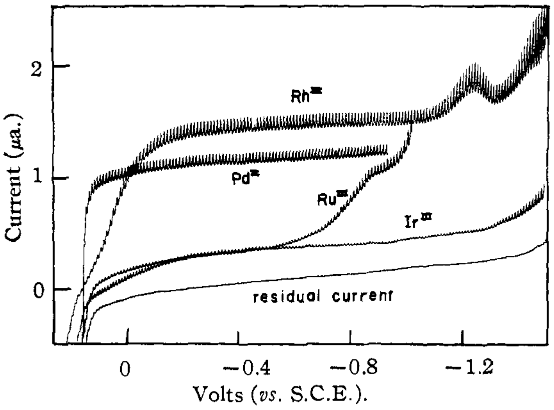

Fig. 2.—Polarograms of 2.0×10^{-4} *M* $RhCl_3$, $Pd(NO_3)_2$, $RuCl_3$ and $IrCl_3$ in 0.1 *M* acetate buffer: Rh(III), run immediately after dilution (with acetate buffer) of month-old $RhCl_3$ stock solution; $Pd(NO_3)_2$, $RuCl_3$ and $IrCl_3$, run after dilutions (with acetate buffer) of stock solutions 0.06 *M* in HCl.

Solutions of $Pd(NO_3)_2$, $IrCl_3$ or of $RuCl_3$ in distilled water turn darker on standing, and the diffusion current (measured after addition of electrolyte) decreases. Colloidal precipitates gradually appear.

Although 0.1 *N* HCl or HNO_3 might be expected

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(10) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(11) R. E. Hamm and C. M. Shull, Jr., THIS JOURNAL, **73**, 1240 (1951).

(12) P. Wehner and J. C. Hindman, *ibid.*, **72**, 3911 (1950).

(13) That this was not due to a slow rate of reaction of any Pt(II) present was shown by the rapid reduction of Ce(IV) with a known solution of K_2PtCl_4.

(14) Reference 9, p. 116.

to dissolve metallic hydroxides, noble metals whose diffusion currents are low in *p*H 5 buffer also show low diffusion currents in 0.1 N acid.

The formation of a precipitate in the palladium solution may be prevented by the addition of chloride. The diffusion current increases with the chloride ion concentration (Table I). Uncontrolled factors apparently also have an effect, for we obtained somewhat different diffusion coefficients for several palladium solutions with the same chloride ion concentration.

The addition of chloride to iridium or ruthenium solutions does not prevent precipitation, and therefore the diffusion current remains small.

On standing without added salt, solutions of rhodium(III) chloride show a slow change in color from red to yellow accompanied by an increase in diffusion current (Table I). Evidently the yellow complex, in which the chlorines have been replaced by hydroxyls or water,[15,16] is more easily reducible than the red complex.

When rhodium chloride is allowed to stand in acetate buffer, still another complex is formed, for the slope of the wave in such solutions decreases, *i.e.*, the reduction becomes more irreversible.

Laitinen and Onstott[4] investigated the polarographic reduction of chloroplatinite and showed that the current measured at -0.7 volt obeys the Ilkovic equation. Nevertheless, they interpreted the wave between 0 and -0.8 volt as an "adsorption wave," and their work has been cited in a review[17] as "a very convincing demonstration of the part which adsorption may play in polarographic reductions."

Except for the dip at -0.8 v., platinum waves exhibit the characteristics of a normal diffusion controlled wave, including the voltage at which they appear. We therefore think that the cause for the dip would bear further investigation. We have noted that the dip is less pronounced in an old solution than in a freshly dissolved one. Measurement of the current through the same voltage range using a rotating platinum electrode would be of interest to see whether the dip in current occurs with a different polarographic method.

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[15] Reference 9, p. 112.

[16] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 2, Univ. Press, Oxford, 1951, p. 1518.

[17] C. Tanford and S. Wawzonek, "Annual Review of Physical Chemistry," Vol. 3, Annual Reviews, Inc., Stanford, Calif., 1952, p. 255.

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Exchange of Radioiridium between Hexachloroiridate(III) and Hexachloroiridate(IV) Ions[1a]

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Exchange of radioiridium between $IrCl_6^{-2}$ and $IrCl_6^{-3}$ ions in 1 f hydrochloric acid at complex ion concentrations ranging from 0.1 to 0.0001 f has been found to be complete in exchange times of the order of one minute at 1 and 50° in the dark. Although the same results were obtained with three different chemical separation methods, the possibility of an induced exchange cannot be excluded. If it be assumed that the exchange is not separation-induced and that a rate law first order in each of the reactant iridium complexes is followed, the specific rate at 1° is greater than 290 liter mole^{-1} sec.$^{-1}$. Precautions in the isotopic labeling of substitution-inert complexes are discussed.

At the time when this investigation was started only two anion–anion systems had been examined for isotopic exchange *via* a possible electron-transfer mechanism, namely, the permanganate–manganate[2–5] and hexacyanoferrate(II)-hexacyanoferrate(III)[6–11] systems. Complete exchange in the time required for mixing and separating the reactants was reported[12] in both cases. More recently both systems have been shown to have measurable exchange rates, the former[13] with half-times of several seconds at 1° and reactant concentrations of $\sim 10^{-4}$ m, and the latter[14] with a half-time of ~ 0.3 second at 4° and reactant concentrations of 0.002 m. In addition, the octacyanomolybdate(IV)–octacyanomolybdate(V) system was later reported[15] to exhibit complete exchange at similar low concentrations and exchange times of the order of several seconds at 2°, and the hexacyanomanganate(II)–hexacyanomanganate(III) exchange has been tentatively reported[16] as immeasurably rapid.

The hexachloro complexes of iridium(IV) and iridium(III) in acid solution offer another opportunity to examine an anion–anion system for pos-

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[1] (a) This work was supported in part under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University of California. (b) Chemistry Division, Argonne National Laboratory, Lemont, Illinois.

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[11] L. Eimer and R. W. Dodson, Brookhaven National Laboratory Quarterly Progress Report, BNL 93 (S-8), 1950, p. 69.

[12] Ref. 6 reported incomplete exchange, but this was apparently an error arising from a faulty separation method; see ref. 7.

[13] J. C. Sheppard and A. C. Wahl, THIS JOURNAL, **75**, 5133 (1953).

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[16] A. W. Adamson, *J. Phys. Chem.*, **56**, 858 (1952).