

appear to be too low compared to ours, which is in agreement with Figurovskii's result.

Substituting $a/a_0 = 7.53$ in eq. 17 we find $x = 18 \text{ \AA}$. which can be considered as the width (*i.e.*, c dimension) of SrSO_4 nuclei. This is about 3 times the c dimension of the unit cell 6.84 \AA . (paragraph c). It can be concluded, therefore, that a nucleus consists of $3^3 = 27$ unit cells.

By similar calculations La Mer arrives at a value of 100 \AA . for the size of BaSO_4 nuclei from

their experimental results. Nevertheless, in their calculation they use Hulett's value ($1500 \text{ erg. cm.}^{-2}$) for the interfacial tension of BaSO_4 which we consider too high (*cf.* paragraph c and section 1). If we can assume that the c dimension of a BaSO_4 nucleus is also 3 times that of a unit cell, *i.e.*, 7.14 \AA ,³¹ using LaMer's value of 21.5 for the critical a/a_0 and α calculated from the unit cell dimensions,³⁴ we obtain from eq. 15 $\bar{\gamma} = 150 \text{ erg. cm.}^{-2}$ for BaSO_4 /solution mean interfacial tension.

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

Structure of the Double Layer and Electrode Processes. II. Effect of the Nature of the Electrode and Application of the Thallium-Amalgam Electrode

BY PAUL DELAHAY AND MARCOS KLEINERMAN¹

RECEIVED DECEMBER 22, 1959

The influence of the nature of the electrode in electrochemical kinetics in the absence of specific electrode effects is interpreted on the basis of a change in the double layer structure. This double layer effect, which can be quite significant, should also be considered in kinetic correlations for processes with specific electrode effects. Application is made of the dropping thallium-amalgam electrode (up to 31% Tl) for which the point of zero charge can be shifted continuously by as much as -0.4 volt with respect to this point for mercury. The following reductions are studied: bromate and iodate in alkaline solution, hexacyanochromate(III) in cyanide medium, chromate in alkaline solution and tetracyano cadmium(II) in cyanide medium. Shifts of the Tafel line for bromate and variations of the exchange current density for hexacyanochromate(III) are interpreted quantitatively. Chromate waves for the dropping thallium amalgam electrode in supporting electrolyte of low concentration exhibit a pronounced minimum which is quantitatively discussed. The maximum in the tetracyano cadmium(II) waves is ascribed to a double layer effect in agreement with other investigators, and a quantitative study is attempted for the results obtained with the dropping mercury electrode.

Introduction

The structure of the double layer at an electrode-electrolyte interface affects the kinetics of electrochemical reactions occurring on this electrode for two reasons: (a) the concentrations of ionic reactants are not the same at the reaction site as in the bulk of the solution and (b) the effective difference of potential must be corrected for the difference of potential across the diffuse double layer. These two fundamental effects were suggested by Frumkin and investigated principally by him and his school.² Much interest has been shown recently in such studies by other investigators.³⁻⁷ (For recent reviews of double layer effects in polarography see ref. 8 and 9; also ref. 3.) In general, interest has been focused on factors governed by solution composition rather than on the effect of the electrode nature. Frumkin and co-workers did study the minimum in certain current-potential curves with electrodes of different metals¹⁰ but

this is one of the rare systematic studies of the influence of electrode material on double layer effects in correlation with kinetics.

We began a study of the electrode effect by comparison of mercury and gallium electrodes but soon adopted the more versatile thallium amalgam electrode of varying composition. The point of zero charge of the latter electrode can be shifted by as much as -0.4 volt in comparison with a mercury electrode as was shown by Frumkin and Gorodetskaya.¹¹ This shift of the point of zero charge may result in a significant change in the difference of potential across the diffuse double layer (Fig. 1) and a concomitant change in the kinetics of an electrode reaction occurring on the amalgam. The thallium amalgam electrode has two advantages over the use of solid electrodes of different nature in such studies: (a) the point of zero charge can be changed continuously, and (b) spurious effects observed with solid electrodes (contamination, roughness, etc.) are minimized or eliminated by the use of a dropping amalgam electrode with a continuously renewed surface.

The following reactions were studied: (a) reduction of bromate and iodate in alkaline solution as examples of slow electrode processes without chemical complication; (b) the reduction of hexacyanochromate(III) as an example of fast reaction; (c) the reduction of chromate ion in alkaline medium as an example of a process yielding current-potential curves with a minimum when amalgam electrodes of proper concentration are

(1) Predoctoral fellow, 1957-1959.

(2) For an extensive review, see for instance A. N. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955).

(3) M. Breiter, M. Kleinerman and P. Delahay, *THIS JOURNAL*, **80**, 5111 (1958). A detailed bibliography is given.

(4) L. Gierst, "Cinétique d'approche et réactions d'électrodes irréversibles," thèse d'agrégation, University of Brussels, 1958.

(5) L. Gierst, article in "Transactions of the Symposium on Electrode Processes, Philadelphia, May 1959," E. Yeager, editor, John Wiley and Sons, Inc., New York, N. Y., in course of publication.

(6) R. Parsons, *ibid.*, in course of publication.

(7) W. H. Reinmuth, L. B. Rogers and L. E. I. Hummelstedt, *THIS JOURNAL*, **81**, 2947 (1959).

(8) P. Delahay, article in "Advances in Polarography," P. Zuman, editor, Interscience Publishing Co., New York, N. Y., in course of publication.

(9) P. Delahay, article in "Proceedings of the Second International Congress of Polarography," Pergamon, London, in course of publication.

(10) A. N. Frumkin, article in ref. 5; see also ref. 2.

(11) A. N. Frumkin and A. W. Gorodetskaya. *Z. physik. Chem.*, **136A**, 451 (1928). We are indebted to Dr. L. Gierst for calling this investigation to our attention.

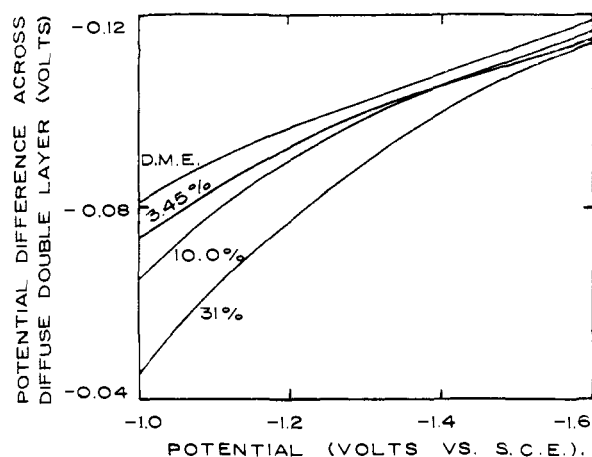


Fig. 1.—Difference of potential across the diffuse double layer (from the plane of closest approach to solution) as a function of electrode potential for the dropping mercury electrode and dropping thallium amalgam electrodes (concentration in weight per cent) in 0.1 *M* NaCN at 30°. Note that the intersection of the curves for the 3.45 and 10.0% amalgams is due to experimental errors.

utilized (no minimum is observed with a mercury electrode); (d) the discharge of tetracyanocadmium(II) as an electrode process with a preceding chemical reaction. Preliminary results on some of these reactions were summarized during discussion periods at a recent symposium.¹²

Experimental

Solutions.—Analytical grade reagents were used except for "electronic grade" (for masers possibly) potassium hexacyanochromate(III). (The latter was purchased from City Chemical Corporation, New York, N. Y.) Traces of adsorbable impurities were removed from sodium cyanide by passing a stock solution over a column of activated charcoal according to the procedure recommended by Parsons.⁶ The charcoal was purified by treatment with hydrochloric acid in a Soxhlet (no cartridge!) extractor for two weeks and, subsequently, with distilled water (frequently renewed) for one week. Potassium chloride and sodium sulfate were calcinated at 500° in an electric oven for several hours to destroy organic matter.

Amalgams.—A stock thallium amalgam was prepared by electrolysis of a saturated solution of thallosulfate at a stirred mercury electrode. A platinum foil was used as anode. Qualitative tests on the salt indicated negligible concentrations of heavy metals other than thallium. The solution was kept saturated by repeated addition of solid thallosulfate. No critical conditions were required for electrodeposition. The concentrated amalgam was kept at a potential of -0.7 v. (*vs.* s.c.e.) for several hours in a solution of 5% sulfuric acid, which was renewed about every fifteen minutes, to eliminate traces of metals less noble than thallium. Some thallium was lost in this operation, but this was not important since in all cases amalgams were analyzed for thallium before use. Three thallium amalgams of the following concentrations were prepared: $3.45 \pm 0.05\%$; $10.0 \pm 0.1\%$ and 31% .

The amalgam flowing from the capillary of the dropping electrode was analyzed as follows. Samples whose weight depended on the approximate thallium concentration were dissolved in 1:1 nitric acid and the solutions slowly evaporated until dryness. The residue was digested hot with at least five successive portions of 10–15 ml. of water. Sodium sulfate and water were then added to make 250 ml. of 0.1 *M* Na₂SO₄. After the precipitate had settled, 50 ml. of the solution were diluted to a final volume of 100 or 250 ml. with 0.1 *M* Na₂SO₄. The final solution, which also contained 0.0002% Triton X-100 as maximum suppressor, was ana-

lyzed polarographically. A 0.1 *M* Na₂SO₄ solution containing a known amount of thallosulfate was used as a comparison standard. It was ascertained that no thallium was lost in this procedure by analysis of mixtures of mercury with known amounts of thallium nitrate.

Electrode Assembly.—An all-glass apparatus was used for the dropping thallium amalgam electrodes, except for a very short piece of rubber tubing joining the amalgam reservoir column to the polarographic capillary. Tygon tubing developed a brownish color in contact with the amalgam, and its use was avoided. The bottom of the amalgam reservoir was fitted with a ground glass plunger (no grease!) which allowed one to interrupt the flow of amalgam at will. This plunger, when properly ground, was quite leak-free.

The following procedure was used to fill the electrode assembly: the reservoir was evacuated and pure mercury was sucked into the capillary up to a very small section of the connecting glass tube. The amalgam was then quickly vacuum-pumped into the reservoir from the top.

The oxidation of the amalgam by air in the reservoir was prevented by making it the cathode of an electrolytic cell in 0.1 *M* H₂SO₄, the anode being a piece of platinum foil. The cell voltage was adjusted to maintain a slow continuous evolution of hydrogen.

A polarographic H-cell was used as electrolysis vessel, the solution under study being in both arms of the cell. The amalgam electrode entered one arm while the other arm was connected to a saturated calomel electrode through a salt bridge. Thus, contamination of the solution in the electrolysis compartment by potassium chloride was avoided. For a.c. impedance measurements a third electrode, *i.e.*, a platinum cylinder of about 1.5 cm. diameter coaxial with the capillary of the dropping amalgam was inserted in the cell.

Capillaries were not ground to a conic tip for double layer and faradaic impedance measurements to avoid danger of plugging. It was realized that this resulted in frequency dispersion¹³ but this effect was quite minor in comparison with other sources of errors (uncertainty on points of zero charge, etc.).

Capillary characteristics in polarographic studies were as follows. In the reduction of chromate, $m = 1.23$ mg. sec.⁻¹, $\tau = 5.7$ sec. at $E = -1.10$ v. (*vs.* s.c.e.) for d.m.e.; $m = 2.65$, $\tau = 3.15$ at $E = -1.10$ v. for 3.45% Tl; $m = 1.22$, $\tau = 6.3$ at $E = -1.10$ v. for 10% Tl. For the tetracyano cadmium(II) reduction, $m = 1.23$, 2.70, 1.13, 1.18 mg. sec.⁻¹ and $\tau = 5.4$, 3.1, 6.1, 6.8 sec. at $E = -1.30$ v. (*vs.* s.c.e.) for the same sequence of electrodes and the 31% Tl electrode. Densities of amalgam (needed in computation of the numerical coefficient in the Ilkovic equation): 13.5 (3.45% Tl), 13.3 (10.0% Tl), 12.9 (31% Tl).

Determination of Points of Zero Charge.—The drop time method was applied for thallium amalgams in 0.1 *M* Na₂SO₄ but the determination of the apex of the electrocapillary curves was quite uncertain. Points of zero charge were finally estimated from the shift of the tail electrocapillary curves with respect to the curve of pure mercury. This procedure is open to question since an increase in thallium concentration in the amalgam not only shifted the electrocapillary curve but also altered somewhat its shape. Results are compared in Table I with those Frumkin and Gorodetskaya¹¹ obtained by the inherently more precise method of the Lippmann electrometer.

Recording of Current-Potential Curves.—A Sargent polarograph model XXI was used, the pen-and-ink recorder of which had been replaced by a faster recorder (1.2 seconds full-scale deflection). Currents were measured at the end of drop life.

Bridge.—Alternating current measurements followed conventional practice.^{13,14} The amplitude of the alternating bridge voltage never exceeded 5 mv. The bridge was balanced at the end of drop life.

Exchange Current and Transfer Coefficient Measurements.—The following method was adopted to avoid the preparation of the highly unstable potassium hexacyanochromate(II). A polarogram¹⁵ was taken of the 5×10^{-3} *M* solution of potassium hexacyanochromate(III) in 0.2 *M* sodium cyanide and the half-wave potential was carefully

(13) D. C. Grahame, *THIS JOURNAL*, **68**, 301 (1946).

(14) D. C. Grahame, *ibid.*, **71**, 2975 (1949).

(15) For polarographic studies, see D. N. Hume and I. M. Kolthoff, *ibid.*, **65**, 1897 (1943).

(12) P. Delahay in discussion of the papers by A. N. Frumkin and L. Gierst in ref. 5.

measured. The dropping (mercury or amalgam) electrode was kept at the half-wave potential while the faradaic impedance was measured at several frequencies. The chromium(III) and (II) complexes thus had the same concentration of $2.5 \times 10^{-3} M$ at the electrode surface since their diffusion coefficients should be nearly the same. The exchange current density I_0 was calculated from the polarization resistance R_s (series or parallel circuit) extrapolated to infinite frequency by

$$R_s = \frac{RT}{nFA} \frac{1}{I_0} \quad (1)$$

where A is the electrode area.

This method of preparation of one reactant *in situ* under polarographic conditions is satisfactory when the standard rate constant is not too low ($> 10^{-3}$ cm. sec.⁻¹ perhaps). The effect of the curvature in the concentration profile near the electrode is then quite small.

The transfer coefficient was determined from variations of I_0 with the ratio of concentrations of chromium(II) to chromium(III) complexes at the electrode surface. From the relation between exchange current density and standard rate constant one can show that $\log [I_0/C_{Cr(III)}]$ varies linearly with $\log [C_{Cr(II)}/C_{Cr(III)}]$, the proportionality constant being the cathodic transfer coefficient α .¹⁶

The ratio $C_{Cr(II)}/C_{Cr(III)}$ was varied by change of the potential at which the faradaic impedance was measured, and the ratio of concentrations was calculated from polarographic theory.

Description and Discussion of Results

Reduction of Bromate in Alkaline Solution.—This reaction was selected for the following reasons: (a) its polarography is well-known,¹⁷ (b) its kinetics is pH-independent for pH > 12; (c) it occurs at polarographic current densities at potentials at which oxidation of thallium amalgam is negligible; (d) there is no specific adsorption of reactants at the markedly negative potentials at which this reaction occurs.

Tafel lines in the absence of concentration polarization (foot of the wave) are plotted in Fig. 2. The change of overvoltage $\Delta\eta$ at constant current density with the difference of potential across the diffuse double layer, $\phi_H - \phi_S$ from the Helmholtz plane to solution is (see eq. 3, ref. 3)

$$\Delta\eta = \frac{\alpha n_a - z}{\alpha n_a} \Delta(\phi_H - \phi_S) \quad (2)$$

where α is the transfer coefficient, n_a the number of electrons in the activation step and z the valence of bromate ion with its sign ($z = -1$). Furthermore, one deduces from the slope of the Tafel line¹³ $\alpha n_a = 0.50$. The values of $\phi_H - \phi_S$ needed for application of eq. 2 were calculated from the point of zero charge and differential capacities for the electrolyte alone. In this case, the point of zero charge in the absence of specific adsorption must be used since bromate ion is not adsorbed in the range of potentials being covered (≈ -1.6 v. vs. s.c.e.). The following values of the integral

(16) This is variation of the classical method of determining α from a plot of $\log I_0$ with the logarithm of one varying concentration. This modified method was reported by H. A. Laitinen, R. P. Tischer and D. K. Roe; see discussion section in ref. 5. See also ref. 6.

(17) E. F. Orleman and I. M. Kolthoff, THIS JOURNAL, 64, 1970 (1942). For double layer effects with the dropping mercury electrode see Gierst.⁵

(18) This procedure yields an apparent value αn_a because the value of α determined in this fashion is affected by the variations of $\phi_H - \phi_S$ over the interval of potential being considered. This point was already discussed.⁵ The corrected value of αn_a should be a little larger than 0.50 but the error ought to be quite small because of the narrow interval of potentials and the rather flat $\phi_H - \phi_S$ vs. E curve at -1.6 volts (vs. s.c.e.). Corrected values of αn_a can be obtained by the graphical method of Gierst.⁶

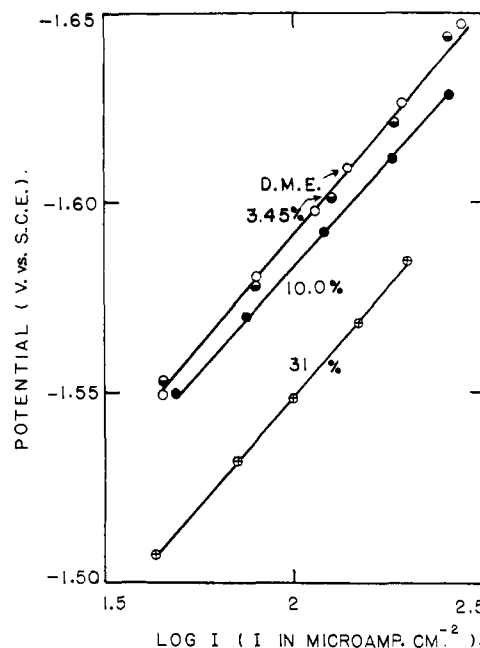


Fig. 2.—Tafel lines for the reduction of $5 \times 10^{-3} M$ $NaBrO_3$ in $0.05 M$ $NaOH$ and $0.1 M$ $NaCl$ on mercury and thallium amalgam dropping electrodes of varying composition at 30° .

capacity at -1.6 v. (vs. s.c.e.) were used: 18.0 microfarads cm^{-2} (d.m.e.), 19.9 (3.45% Tl), 21.3 (10.0% Tl) and 25 (31% Tl).

Experimental and calculated values of $\Delta\eta$ are listed in Table II for the points of zero charge of Table I. Points of zero charge determined in this

TABLE I
POINTS OF ZERO CHARGE FOR THALLIUM AMALGAMS IN 0.1 M Na_2SO_4

Tl concentration, %	E_z , volts vs. s.c.e.
0	-0.45
3.35	-.69 ^a
3.45	-.57 ^b
10.0	-.68 ^b
10.35	-.76 ^a
31	-.85 ^b
33.9	-.88 ^a

^a Ref. 11. ^b This work.

TABLE II
DATA FOR THE REDUCTION OF BROMATE (FIG. 2) AT -1.6 VOLTS (vs. S.C.E.)

Tl concn., %	$\phi_H - \phi_S$, v.	$\Delta(\phi_H - \phi_S)$, mv.	$\Delta\eta$ calcd., mv.	$\Delta\eta$ exp., mv.
0	-0.113
3.45	-.105	8	18	0 ^b
	-.111	2	5	
10.0	-.104	9	20	8
	-.109	4	9	
31	-.103	10	23	41
	-.105	8	18	

^a Upper values calculated by using points of zero charge of Frumkin and Gorodetzskaya; lower values from points of zero charge determined in this work. ^b Smaller than experimental errors.

work seem to give better agreement than the values of Frumkin and Gorodetzskaya but even so $\Delta\eta$

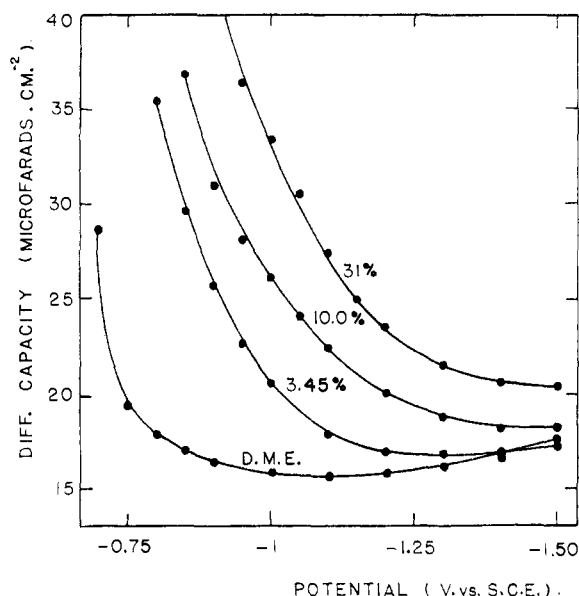


Fig. 3.—Differential capacity for mercury and thallium amalgam dropping electrodes in 0.2 *M* NaCN at 30°.

calculated is markedly too low for the 31% Tl amalgam. The shift of Tafel line is in the right direction and in semi-quantitative agreement with theory. Shifts being quite small, there is no doubt that experimental errors account in part for discrepancies. Uncertainty on the integral capacity, particularly for the 31% Tl electrode, is an other source of error.

Reduction of Iodate in Alkaline Solution.—Double layer effects in kinetics can be conveniently studied for the reduction of iodate in alkaline solution ($pH > 12$), and indeed relatively large shifts were observed with thallium amalgam electrodes of varying composition. Thus, in the reduction of $5 \times 10^{-3} M$ NaIO₃ in $5 \times 10^{-2} M$ NaOH and 0.1 *M* NaCl, $\Delta\eta = 12$ and 41 mv. with respect to the dropping mercury electrode for the 3.45 and 10.0% Tl electrodes. Quantitative interpretation was too uncertain because of specific adsorption of the reaction product, iodide, on the thallium amalgam (especially for the 10% Tl electrode) in the range of potentials in which iodate reduction was studied (≈ -1.05 v. vs. s.c.e.).

Reduction of Hexacyanochromate(III).—The apparent exchange current density for the couple $Cr(CN)_6^{-3} + e = Cr(CN)_6^{-4}$ strongly depends on double layer effects because of the highly negative charge of the ions and the very negative standard potential for this couple (≈ -1.4 v. vs. s.c.e.). Randles and Somerton¹⁹ indeed reported a marked effect of supporting electrolyte concentration on the standard rate constant, and preliminary quantitative results on this double layer effect were obtained in this Laboratory.¹² Unexpectedly, the exchange current density in 0.2 *M* NaCN at 30° hardly varied for mercury and thallium-amalgam electrodes: 3.9×10^{-3} amp.cm.⁻² for the d.m.e., 3.45 and 10% Tl electrodes and 4.8×10^{-3} amp. cm.⁻² for the 31% Tl electrode. The trans-

fer coefficient was 0.67 for the d.m.e. and 0.73 for the 31% Tl electrode. Since the apparent exchange current density is proportional³ to $\exp[(\alpha n - z)F(\phi_H - \phi_S)/RT]$ (z valence of hexacyanochromate(III); $n = 1$), the foregoing results indicate that $\phi_H - \phi_S$ hardly varied for the different electrodes. Now, $\phi_H - \phi_S$ is the solution of (see eq. 5, ref. 3)

$$K_i[(E - E_z) - (\phi_H - \phi_S)] = \pm \frac{RT\epsilon}{2\pi} \sum C_i \left[\exp\left(-\frac{z_i F(\phi_H - \phi_S)}{RT}\right) - 1 \right]^{1/2} \quad (3)$$

where K_i is the integral capacity of the Helmholtz double layer, E_z the potential at the point of zero charge, ϵ the dielectric constant (assumed to be constant in the double layer) and C_i the concentration of ion i and valence z_i . The plus and minus signs correspond to $E \geq E_z$, respectively. It follows from eq. 3 that $|\phi_H - \phi_S|$ decreases with $|E - E_z|$ for a given K_i . In this case, however, the decrease of $|E - E_z|$ at a given E is almost compensated by an increase in K_i (see differential capacity-potential curves of Fig. 3) at the potentials (≈ -1.4 v. vs. s.c.e.) at which the reduction of hexacyanochromate(III) was studied (Fig. 1).²⁰ Further, some specific adsorption of cyanide may have complicated matters. This example shows the danger of rash conclusions about the effect of shifts in the point of zero charge on electrode kinetics.

Reduction of Chromate in Alkaline Solution.—Large double layer effects are observed for the reduction of chromate in alkaline solution (see eq. 2; $z = -2$) on the dropping mercury electrode as was shown by Gierst.⁵ A marked shift of the chromate wave was observed with thallium amalgam electrodes of increasing thallium concentration, and waves exhibited a minimum at low supporting electrolyte concentrations (Fig. 4). Minima were particularly pronounced for the 3.45% Tl amalgam. No minimum was observed for mercury.

These minima recall those studied by Frumkin and his school^{2,10} and others for a number of anions. According to Frumkin's views, the decrease in current is due to a decrease in concentration of chromate ions at the reaction site because of electrostatic repulsion; and the increase of current beyond the minimum is observed because the increase of the rate constant for charge transfer, as the potential becomes more negative, more than compensates the decrease in chromate concentration at the reaction site. The chromate concentration C^* in the plane of closest approach (identified with the reaction site) is (see eq. 2, ref. 3)

$$C^* = C_s \exp[-zF(\phi_H - \phi_S)/RT] \quad (4)$$

where C_s is the concentration outside the diffuse layer and $z = -2$. One has $C^* < C_s$ for $\phi_H - \phi_S < 0$, i.e. for $E < E_z$, E_z being the point of zero charge. A decrease in current is observed provided that the rate constant for charge transfer is not too large for potentials at which $C^* < C_s$. The difference between the 3.45 and 10% Tl amalgams

(20) Figure 1 pertains to the tetracyanocadmium(II) study in 0.1 *M* NaCN whereas hexacyanochromate(III) was studied in 0.2 *M* NaCN. Values of $\phi_H - \phi_S$ are of course slightly different for these two concentrations but the $(\phi_H - \phi_S)$'s are nearly the same at -1.4 volts versus s.c.e. for the two solutions.

(19) J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 957 (1952).

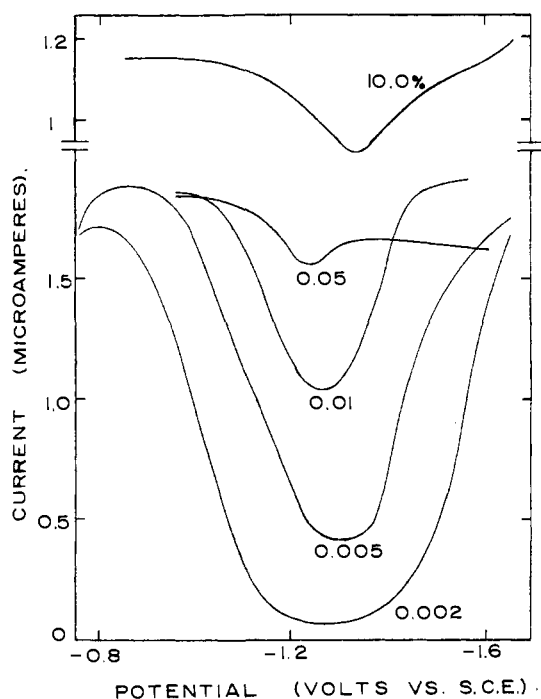


Fig. 4.—Tracings of current-potential curves for the reduction of $10^{-4} M$ Na_2CrO_4 in NaOH of varying molar concentration on thallium amalgam dropping electrodes at 30° . Upper curve for 10.0% Tl amalgam and 0.01 M NaOH ; the others for 3.45% Tl and a varying molar concentration of NaOH . Curves are corrected for the residual current.

is now understood. Thus, E_z is more negative for the 10% Tl amalgam than the 3.45% Tl amalgam, and $(\phi_H - \phi_S)_{3.45} < (\phi_H - \phi_S)_{10.0}$ at a given potential for $E < E_z$. Hence, $C_{3.45}^* < C_{10.0}^*$ at a given E and the minimum is less pronounced for the 10% amalgam. Conversely, chromate waves on mercury are observed at potentials at which $\phi_H - \phi_S$ does not vary rapidly enough²¹ with E to cause a minimum in the current-potential curves.

Quantitative analysis²⁵ rests on the equation for the current density (neglecting the backward reaction)

$$I = nFk^0C_s \exp \left\{ -\frac{\alpha n_a FE}{RT} + \frac{(\alpha n_a - z)F(\phi_H - \phi_S)}{RT} \right\} \quad (5)$$

where $n = 3$ here, F is the faraday, k^0 a constant and n_a is the number of electrons in the single (presumably) rate-determining step of the electrode reaction. The concentration C_s just outside the diffuse double layer is corrected for concentration polarization either by rather rigorous polarographic theory or by the simple, but more approximate, equation²²

$$C_s = C^0 \left(1 - \frac{I}{I_d} \right) \quad (6)$$

where C^0 is the bulk concentration of chromate and I_d is the diffusion current density. It follows from eq. 5 and 6 that a plot of $\log [I/(I_d - I)]$ at constant E against $\phi_H - \phi_S$ has the slope $(\alpha n_a -$

(21) See Fig. 2, ref. 3 for a plot of $\phi_H - \phi_S$ with E for instance; see also Fig. 1 of this paper.

(22) G. M. Florianovich and A. N. Frumkin, *Zhur. fiz. Khim.*, **29**, 1827 (1955).

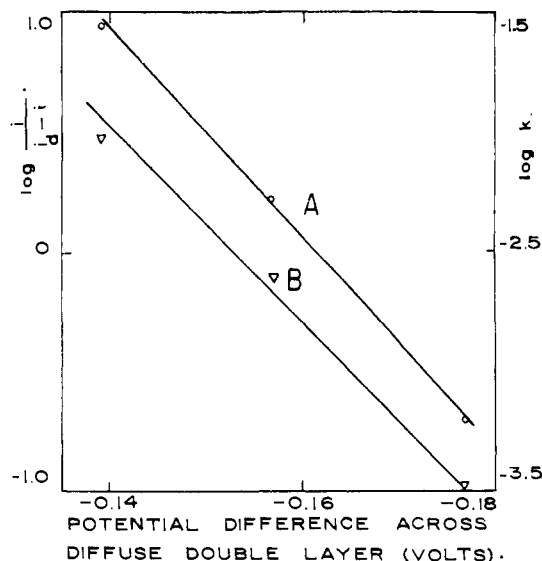


Fig. 5.—Plot of $\log [I/(I_d - I)]$ (line A) and $\log k$ (line B) against $\phi_H - \phi_S$ for the reduction of chromate at -1.10 v. (vs. s.c.e.) on the 3.45% Tl electrode (Fig. 4).

$z)F/2.3RT$. Such a linear plot was indeed obtained for the current measured at -1.1 v. vs. s.c.e. with the 3.45% Tl electrode (Fig. 5). The experimental slope yields $\alpha n_a - z = 2.56$, i.e. $\alpha n_a = 0.56$ for $z = -2$. Direct analysis of the chromate wave obtained with a dropping mercury electrode (the wave for Tl(Hg) could not be analyzed because of thallium oxidation) yielded $\alpha n_a = 0.42$. Agreement between the two values of αn_a is good in view of the various sources of experimental errors and the sensitivity of αn_a to a small error on $\alpha n_a - z$. Values of the integral capacity K_i used in the computation of $\phi_H - \phi_S$ were for the 3.45% Tl electrode at -1.1 v. vs. s.c.e.: 24.7 microfarads. cm^{-2} (0.002 M NaOH), 25.0 (0.005 M) and 24.1 (0.01 M).

In a more rigorous polarographic analysis one calculates from experimental values of I/I_d at constant potential, by application of Koutecky's treatment,²³ the parameter $k\tau^{1/2}/D^{1/2}$ where τ is the drop time, D the diffusion coefficient of chromate ion and k is (see eq. 5)

$$k = k^0 \exp \left\{ -\frac{\alpha n_a FE}{RT} + \frac{(\alpha n_a - z)F(\phi_H - \phi_S)}{RT} \right\} \quad (7)$$

Hence a plot of $\log k$ against $\phi_H - \phi_S$ at constant E has the slope $(\alpha n_a - z)F/2.3 RT$ (Fig. 5, line B). One deduces from Fig. 5 $\alpha n_a - z = 2.30$ in good agreement (experimental errors!) for $z = -2$ with the independently determined value $\alpha n_a = 0.42$ (see above).

Reduction of Tetracyanocadmium(II).—This complex is reduced²⁴ on the dropping mercury electrode *via* a preceding chemical transformation into $\text{Cd}(\text{CN})_3^-$. Reduction *via* $\text{Cd}(\text{CN})_2$ must also be considered, especially at low cyanide concentrations. The kinetics of the $\text{Cd}(\text{CN})_4^{2-} = \text{Cd}$

(23) J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **18**, 597 (1953). See P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishing Co., New York, N. Y., 1954, p. 79.

(24) For bibliography see ref. 3 and 5. Also J. Koryta, *Z. Elektrochem.*, **64**, 23 (1960); H. Gerischer, *ibid.*, **64**, 29 (1960).

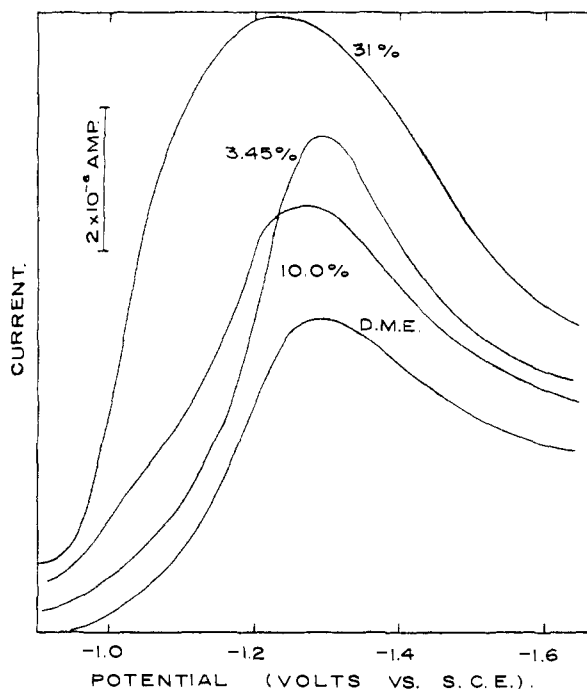


Fig. 6.—Tracings of current-potential curves for the reduction of $10^{-3} M$ Cd(II) in $0.1 M$ NaCN at 30° for different electrodes. Curves are shifted upward for clarity and are corrected for the residual current.

$(\text{CN})_3 + \text{CN}^-$ reaction is strongly dependent on double layer structure as was shown independently by Gierst⁵ and by us.³ Current-potential curves exhibit a maximum which has been explained on the basis of double layer effect.⁵

A maximum is also observed with thallium amalgam electrodes, and the height of the maximum current increases with thallium concentration in the amalgam (Fig. 6). The drop in current beyond the maximum is caused by a decrease in the velocity of dissociation of $\text{Cd}(\text{CN})_4^-$ as a result of the increasingly negative potential, $\phi_H - \phi_S$, and the concomitant change in reactant concentrations (see analysis in refs. 3 and 5). Electrostatic repulsion is less pronounced and the maximum current increases accordingly, when the amalgam becomes richer in thallium because of the decrease of $\phi_H - \phi_S$ (shift of E_z).

Quantitative treatments of this double layer effects were developed by Gierst and Hurwitz^{5,25} and, in this Laboratory, by Matsuda.²⁶ According to the latter author one has

$$\log \frac{I_d - I}{I} + \frac{1}{2} \log \tau = \log G + \text{constant} \quad (8)$$

where I_d is the diffusion current density that would be obtained if $\text{Cd}(\text{CN})_4^-$ were reduced directly without a chemical reaction preceding charge

(25) L. Gierst and H. Hurwitz, *Z. Elektrochem.*, **64**, 36 (1960).

(26) H. Matsuda, *J. Phys. Chem.*, **64**, 336 (1960).

transfer, τ is the drop time and G is a complicated function of $\phi_H - \phi_S$. Values of G were computed by Matsuda for dissociation of $\text{Cd}(\text{CN})_4^-$ into $\text{Cd}(\text{CN})_3^-$. Analysis of the data of Fig. 6 for the dropping mercury electrode yielded essentially a straight line (values of $\phi_H - \phi_S$ needed were taken from Fig. 1) with a slope $\log G_1/[F(\phi_H - \phi_S)/2 \times 2.3RT] = 2.60$ (the upper limit is 3 in this case) for the interval $F(\phi_H - \phi_S)/2 \times 2.3RT = -0.83$ to -0.99 ($T = 303^\circ \text{K}$). The diffusion current for $10^{-3} M$ Cd(II) in $0.1 M$ NaCl was used in the computation of $[(I_d - I)/I]$. This value of I_d was probably too high since the diffusion coefficient for the cyano complex is expected to be smaller than for the chloro complex. However, it was ascertained that a change of $\pm 10\%$ in the value of I_d hardly affected the reaction layer thickness calculated below. It was deduced by comparison with Matsuda's results that the above slope corresponds to $1/\kappa\mu \approx 100$ where κ is Debye's reciprocal length for the double layer and μ the reaction layer thickness. One has approximately $1/\kappa \approx 10^{-7}$ cm., and $\mu \approx 10^{-9}$ cm. This value of μ is too low by more than one order of magnitude. Simplification in the theoretical analysis and experimental errors can be invoked, and indeed the shape of current-potential curves is very sensitive to traces of adsorbed impurities. However, the abnormally low value of μ probably results from kinetic complications, namely the simultaneous discharge via $\text{Cd}(\text{CN})_3^-$ and $\text{Cd}(\text{CN})_2$. Only a single chemical reaction was considered in the analysis. Discharge via $\text{Cd}(\text{CN})_2$ was conclusively proven by Koryta²⁴ by interpretation of the double wave in the ascending branch of current-potential curves obtained with the dropping mercury electrode. Such a double wave is not readily apparent in Fig. 6 for the mercury electrode but is detected in the curves for the thallium amalgam electrodes.

Conclusion

Even in the absence of any specific electrode effects, a change in the nature of the electrode affects electrode kinetics because of the modification of double layer structure. The influence of the electrode nature can be quite pronounced for metals with markedly different points of zero charge, especially in the vicinity of the points of zero charge, and the correction of the exchange current density then can be of a few orders of magnitude. This correction should not be overlooked in the comparison of kinetics on different electrodes in the case of specific electrode effects, as for instance in hydrogen overvoltage studies.

Quantitative interpretation is similar to that for the double layer effect resulting from a change of electrolyte composition. Experimental difficulties with the thallium amalgam electrode, however, limit somewhat applications.

Acknowledgment.—This work was supported by the Office of Naval Research.