

DC/i , where \bar{A} is average area of electrode, D diffusion coefficient of metal ion, n its valence, C concentration and i limiting current¹¹ of a typical D.M.E. with those of a typical R.D.M.E., shows that \bar{A} and δ are of the order of 0.02 cm.² and 0.058 mm. for the D.M.E. and 0.05 cm.² and 0.016 mm. for the R.D.M.E. (210 r.p.m.). Thus the average area of a drop at a R.D.M.E. is about three times as large as that at the D.M.E. while the "thickness of the diffusion layer" is about 1/3.6 of that at the D.M.E. These two factors give the R.D.M.E. in the presence of a suppressor a sensitivity of the order of ten times as large as that of a D.M.E. In the unrotated state \bar{A}_0 and δ_0 of the above electrode were found to be 0.06 cm.² and 0.05 mm., respectively, indicating that the higher limiting currents at the unrotated electrode are almost entirely due to the larger surface of its drops.

(11) J. A. V. Butler, "Electrical Phenomena at Interfaces," The Macmillan Co., New York, N. Y., 1951, Chap. VIII.

From the analytical viewpoint limiting currents generally should be measured in the presence of a suitable surface active agent which suppresses the stirring completely. For analytical purposes it would be very risky not to suppress the stirring, because traces of surface active agents often are found in solutions. Moreover, the electro-active compound or its reaction product at the electrode may be surface active and thus cause complications in the interpretation of the limiting currents.

If used as an indicator electrode in amperometric titrations, addition of maximum suppressors is not required, the limiting current being proportional to the concentration of electroactive species at a given potential.

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Mercury Exchange between Mercuric Chloride and *p*-Chloromercuribenzoic Acid

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It has been possible to produce ²⁰³Hg-labeled *p*-chloromercuribenzoic acid using an exchange reaction between mercuric chloride and *p*-chloromercuribenzoic acid. The velocity constant k_2 for the mercury exchange reaction was found to be of second order and had a value of 1.09 ± 0.03 . The activation energy was found to be 12.0 ± 0.6 kcal./mole.

It has been possible to produce ²⁰³Hg-labeled *p*-chloromercuribenzoic acid using an exchange reaction between mercuric chloride and *p*-chloromercuribenzoic acid. This reaction was accomplished by mixing solutions of radioactive mercuric chloride and inactive *p*-chloromercuribenzoic acid in a thermostat and separating the components after a suitable period for analysis. By establishing the quantity of mercuric chloride and *p*-chloromercuribenzoic acid present and measuring the radioactivity of both fractions, the specific activity could be determined. The velocity constant k_2 for the mercury exchange reaction

$^{203}\text{HgCl}_2 + \text{ClHgC}_6\text{H}_4\text{CO}_2\text{H} \rightleftharpoons \text{HgCl}_2 + \text{Cl}^{203}\text{HgC}_6\text{H}_4\text{CO}_2\text{H}$
was calculated from

$$k_2 = -\frac{2.303}{(a+b)t} \log \left(1 - \frac{b_t^*}{b_{t\infty}^*} \right)$$

where

k_2 = velocity constant in l. mole⁻¹ sec.⁻¹
 a = concn. of HgCl₂ in mole/l. at $t = 0$
 b = concn. of ClHgC₆H₄CO₂H in mole/l. at $t = 0$
 t = reaction time in sec.
 $b_t^*/b_{t\infty}^*$ = ratio of spec. activity of ClHgC₆H₄CO₂H at t and t_{∞}

The reaction was of second order as k_2 was found to be independent of the concentrations of *p*-chloromercuribenzoic acid and mercuric chloride. Concentration variation of HgCl₂ (0.85×10^{-3} — 3.94×10^{-3} mole/l.) and *p*-ClHgC₆H₄CO₂H (0.32×10^{-3} — 2.78×10^{-3} mole/l.) gave at 5.0° a constant k_2 of 1.09 ± 0.03 . The exchange experiments were carried out at four different tempera-

tures and the second-order velocity constants calculated. The results are summarized in Table I.

TABLE I
MERCURY EXCHANGE BETWEEN MERCURIC CHLORIDE AND
p-CHLOROMERCURIBENZOIC ACID

Temp., °C.	k_2 , l. mole ⁻¹ sec. ⁻¹
5.0	1.09 ± 0.03
17.0	2.70 ± 0.04
25.0	5.4 ± 0.2
49.5	26.0 ± 1.6

The activation energy was calculated from an Arrhenius plot of these velocity constants and found to be 12.0 ± 0.6 kcal./mole.

Experimental

Materials.—The *p*-chloromercuribenzoic acid was obtained from Bios Laboratories, Inc., New York, N. Y. As Hg tracer was used a mixture of ¹⁹⁷Hg and ²⁰³Hg, obtained by irradiating 2 g. of HgO for a week in a neutron beam with a flux of 5×10^{11} n/cm.² sec. in the Joint Establishment Experimental Pile at Kjeller, Norway. The γ -decay curve showed two components with half-lives of 49.0 days and 66.5 hr., corresponding to the values reported for ¹⁹⁷Hg and ²⁰³Hg.¹

Counting Equipment.—All measurements were performed with a hollow anode γ -counter (Philips Nr. 18.508), inside of which glass tubes containing the test solutions could be introduced.

Analytical Procedure.—Mercuric chloride was assessed by a colorimetric method, described by Sandell² using dithizone.

(1) J. M. Cork, D. W. Martin, J. M. Leblanc and C. E. Branyan, *Phys. Rev.*, **85**, 386 (1952).

(2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 1944, p. 321.

From a HgCl_2 solution of 10^{-5} mole/l. in 1 N H_2SO_4 a volume corresponding to 10–20 μg . of Hg was mixed with 5.0 ml. of a ± 0.006 g./l. dithizone carbon tetrachloride solution. After one minute shaking the density was measured at λ 510 and 620 $m\mu$ in a Beckman spectrophotometer Model DU and the corresponding quantity of Hg estimated by means of a calibration curve. *p*-Chloromercuribenzoic acid also gives a stable dithizone complex under the circumstances described above. *p*-Chloromercuribenzoic acid was determined on the basis of its ultraviolet absorption. Characteristics are given in Table II.

TABLE II
CHARACTERISTICS FOR THE AROMATIC ABSORPTION OF *p*-CHLOROMERCURIBENZOIC ACID

ρH	$\lambda_{\text{max}}, m\mu$	$E\lambda_{\text{max}}, \text{l. mole}^{-1} \text{ cm.}^{-1}$
<2.0	238	15900
>6.5	233	12700

p-Chloromercuribenzoic acid was estimated in a dilution of 10^{-5} mole/l. with a $\rho\text{H} > 9.0$ at λ 233 $m\mu$.

Procedure.—**Solution A.**— ± 0.5 g. of radioactive mercuric oxide was dissolved in 3.0 ml. of 2.5 N HCl ; 2 N NaOH (± 1.0 ml.) was added to ρH 6.6 and the solution made up to 250 ml. (10^{-2} mole/l.).

Solution B.— ± 0.30 g. of *p*-chloromercuribenzoic acid was dissolved in 0.1 ml. of 2 N NaOH ; 0.1 N HCl (± 0.5 ml.) was added to ρH 9.0 and the solution made up to 100 ml. (10^{-2} mole/l.).

1.0 ml. of solution A, 8.0 ml. of H_2O and 1.0 ml. of solution B were mixed in centrifuge tubes. After the desired time 1.0 ml. of 1 N H_2SO_4 was added and the insoluble *p*-chloromercuribenzoic acid centrifuged. The clear solution (HgCl_2 fraction) was removed and a sample of 10.0 ml. was counted. The precipitate was washed with 9.0 ml. of H_2O in 1.0 ml. of 1 N H_2SO_4 and once more centrifuged. The clear supernatant was removed; to the precipitate two drops 2 N NaOH were added and the solution was made up to 15.0 ml. ($\text{ClHgC}_6\text{H}_4\text{CO}_2\text{H}$ fraction); a sample of 10.0 ml. of this solution was counted. Every experiment was carried out in duplicate. At each temperature the experimental conditions for $t = 0$ were realized by adding 1.0 ml. of solution B to a mixture of 1.0 ml. of solution A, 8.0 ml. of H_2O and 1.0 ml. of 1 N H_2SO_4 .

The concentrations of HgCl_2 and $\text{ClHgC}_6\text{H}_4\text{CO}_2\text{H}$ were varied by mixing different volumes of solution A (1.0–4.0 ml.), solution B (0.5–4.0 ml.) and water to a total volume of 10.0 ml.

The concentrations of solution A, the HgCl_2 fraction, solution B and the $\text{ClHgC}_6\text{H}_4\text{CO}_2\text{H}$ fraction were determined by the above-described methods.

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Electrochemical Behavior in Anhydrous Formic Acid. I. The Quinhydrone–Formic Acid Electrode as Polarographic Anode

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The polarographic investigation of anhydrous formic acid solutions was preceded by examination of the quinhydrone electrode in that solvent. The electrode was found to be reversible, reproducible and non-polarizable irrespective of whether nitrogen was used to agitate the solution or not. The electrode potential was found to be independent of the quality or concentration of quinhydrone used, to have an inappreciable salt effect and to be little influenced by the addition of small quantities of water. The formic acid analog of the saturated calomel electrode also was prepared. The potential of the quinhydrone–formic acid electrode against the saturated calomel–formic acid electrode was found to be $+0.5384 \pm 0.0005$ volt at $25.00 \pm 0.01^\circ$.

In an investigation of polarography in anhydrous formic acid in order to compare the measured half-wave potentials of the electro-reducible species, it was desirable to have an electrode of constant potential for use as anode. A quinhydrone–formic acid electrode was investigated for this purpose. A quinhydrone electrode has only once previously been reported as a polarographic anode.¹ This was in aqueous solution, and was found to undergo polarization, which was somewhat reduced by bubbling nitrogen through the solution. Because of it the electrode was discarded as unsatisfactory.

Because anhydrous formic acid slowly absorbs moisture, the non-polarizable electrode has to be one capable of rapid preparation, able to attain a reproducible potential instantaneously and able to maintain this value for at least a half-hour, the duration of an experiment. The electrode should not be significantly affected by traces of moisture, or small concentration of salts, and, furthermore, it should be such that liquid-junction potentials are minimized without the introduction of gel-salt bridges.

The quinhydrone–formic acid electrode was found to fulfil all these requirements. As formic acid ex-

hibits reducing properties, a possibility exists that it may reduce quinone to hydroquinone, thereby altering the potential and vitiating its use as a reproducible electrode. If this were so, the potential should have depended markedly on the concentration of quinhydrone present, and such was not found to be the case. The quinhydrone electrode has been used in formic acid on two occasions in potentiometric studies of acid–base titrations^{2,3}; Hammett and Dietz² stated that in the sodium formate solutions used, there was no evidence of any reaction between the formic acid and the quinhydrone. They maintained, however, that platinum electrodes were unsatisfactory, often showing differences of several millivolts in the same solution and recommended the use of gold electrodes. We have found, however, that platinum electrodes are entirely satisfactory. In a wide range of solutions, with divergent concentration of quinhydrone and supporting electrolyte, the maximum difference of potential observed between any two electrodes was 0.2 millivolt.

In aqueous polarography, the standard practice is to refer the half-wave potentials to the saturated

(1) J. P. Baumberger and K. Bardwell, *Ind. Eng. Chem., Anal. Ed.*, **15**, 629 (1943).

(2) L. P. Hammett and R. N. Dietz, *THIS JOURNAL*, **52**, 4729 (1930).

(3) O. Tomicek and P. Vidner, *Chem. Listy*, **47**, 516 (1953).