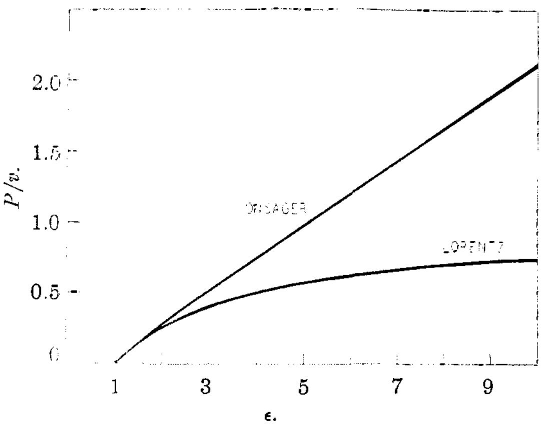
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

# Polarog :I. Description and Interpretation

.LKIRE AND JOHN M. MCGEE



In a re
observati
waves ol
in 0.1 mo
experime
extended
prehensi
tailed in
veloped i

**Apparatus.**—The instrument used was a Heyrovsky polarograph manufactured by the Sargent Co. The specially designed cells provided with this instrument were used. The potential of the mercury anode was frequently checked against the saturated calomel electrode by means of a Wolff potentiometer. In some cases the *p*H was measured by means of a quinhydrone electrode introduced into the polarographic cell immediately after the completion of the reduction wave. In other cases the *p*H was obtained by immediate transfer of a sample of solution to a Beckman *p*H meter. All waves were recorded photographically and analyzed according to standard procedures.

**Materials.**—C. P. Kahlbaum tetramethylammonium chloride and Eastman Kodak Co. white label tetramethylammonium bromide were carefully recrystallized from water–ethanol mixtures. The purity of these salts could be ascertained by means of polarograms obtained as blanks with solutions of these supporting electrolytes. The recrystallized salts and their solutions were kept in the dark. Both salts were used at the concentration 0.1 molar and it was found that the saturated calomel electrode had a potential of $-0.08$ volt with respect to the mercury anode in the case of the chloride, and of $+0.04$ volt in the case of the bromide. In other words, the absolute values of the mercury cathode–mercury anode half-wave potentials read from the polarograms were decreased by 0.08 volt in the case of the chloride and increased by 0.04 volt in the case of the bromide in order to be uniformly referred to the saturated calomel electrode. The usual accuracy of polarographic potentials seldom warrants consideration of millivolts.

All mercury used was carefully purified and distilled in vacuum.

Carbon dioxide was bubbled through the solu-

.irectly from a Pure Carbonic cylinder.
urities likely to affect the reduction waves
er detected.
temperature was in all cases close to 25°,
for the experiments specially conducted to
the influence of temperature on the half-
otential and on the half-wave slope.
ugh the use of buffers in a study of carbon
reduction might appear desirable, one im-
factor prevents it. The alkali ions or the
ium ion which would be constituents of the buffers reduce at cathode potentials in the immediate neighborhood of that of carbon dioxide itself. It is only with buffers containing salts of quaternary ammonium ions[3] that a study of carbon dioxide in buffered media would be possible. The acetate, phosphate, carbonate, citrate, etc., of these substituted ammonium ions would have to be prepared. We intend to extend our work in that direction, but the essential features of the polarographic reduction of carbon dioxide have been obtained without the use of buffers, and their interpretation is amenable to theoretical treatment without the condition of constant *p*H.[2] In a few experiments we have added tetramethylammonium hydroxide to the carbon dioxide solutions in tetramethylammonium chloride or bromide and have observed the gradual disappearance of the reduction wave, a fact proving that it is molecular carbon dioxide ($CO_2$ or possibly $H_2CO_3$), and not the bicarbonate ion $HCO_3^-$ or the carbonate ion $CO_3^=$, which reduces.

## General Description of the Waves

With pure $N(CH_3)_4Cl$ or $N(CH_3)_4Br$ the waves consist of nearly horizontal lines up to cathodic potentials of the order of 2.5 volts. The reduction of the tetramethylammonium ion sets in quite abruptly and the limiting tangent potential was found to be 2.93 ± 0.03 volts *vs.* the saturated calomel electrode.[3] Usually, at the galvanometer sensitivities used, oxygen waves were negligible. The camera shutter was in general not opened until a cathodic potential of 1.60 volts had been reached. In some experiments hydrogen or nitrogen was passed through the solution beforehand. Occasionally very minute amounts of impurities were detected. If they happened to cause complications in the reduction waves of carbon dioxide the solutions were discarded. One impurity, with an apparent reduction half-wave potential at 2.61 volts *vs.* the saturated calomel electrode, was found to be particularly persistent. Its concentration had an upper limit of about 1.5% of the concentration of

---

(1) Presented as part of a paper entitled "Polarographic Studies on Carbon Dioxide and Chlorophyll," by P. Van Rysselberghe and J. M. McGee at the Pacific Northwest Regional Meeting of the American Chemical Society in Seattle, October 20, 1945.

(1a) Paper I of this series, P. Van Rysselberghe and G. J. Alkire, THIS JOURNAL, **66**, 1801 (1944).

(2) Paper II, P. Van Rysselberghe, THIS JOURNAL, **68**, 2047 (1946).

(3) P. Van Rysselberghe and J. M. McGee, THIS JOURNAL, **67**, 1039 (1945).

the supporting electrolyte (estimate established by means of the Ilkovic equation). We believe it to be some other quaternary ammonium salt, or more likely a mixture of several such salts, which, on account of exact isomorphism with the main salt, could not be eliminated by our recrystallization method. The presence of this impurity caused little inconvenience. With very small amounts of carbon dioxide present, a correction had occasionally to be made on this account. When this situation was recognized some apparent irregularities in the slopes of the waves corresponding to the reduction of carbon dioxide disappeared. Nearly all the half-wave slopes were then found to be near the lower limit 0.359 volt reported in our paper I.[1]

Close to one hundred reduction waves of carbon dioxide were recorded and most of them were analyzed in detail. It is convenient to divide them into two groups: (1) waves with diffusion currents of less than 40 microamperes; (2) waves with diffusion currents of more than 40 microamperes. A common feature of all the curves recorded in presence of carbon dioxide is the lowering and gradual removal of the oxygen reduction current. When hydrogen or nitrogen is passed through the solution beforehand carbon dioxide does not alter the residual current. The adsorption of carbon dioxide on mercury has been studied by Oliphant.[4] A detailed study of the influence of carbon dioxide on the electrocapillary curve of mercury would be of great interest.

The waves of group 1 are those recorded with the sensitivity 100 of the Sargent polarograph, those of group 2 corresponding to the sensitivities 200, 500 and 1000. (Current in microamperes = 0.0032 × sensitivity × ordinate in millimeters.) The waves of the first group (see Fig. 1) do not exhibit any maximum before the establishment of the diffusion current. They sometimes merge with the wave of the impurity mentioned above and whose diffusion current is usually about 10 microamperes, and on that account exhibit irregularities of slope at the half-wave. Whenever the interference due to this impurity was absent or whenever proper correction could be made the half-wave potential was found to be in the close neighborhood of 2.15 volts *vs.* the saturated calomel electrode. The average of fourteen determinations in this group gave the following results

$$E_{1/2} = 2.15 \pm 0.02 \text{ volts}$$

and for the slope at the half-wave (see notations in Paper II[2])

$$(\mathrm{d}E/\mathrm{d}u)_{1/2} = E'_{1/2} = 0.351 \pm 0.015 \text{ volt}$$

The individual results are given in Table I: $i_d$ in microamperes in the first column, the half-wave potential $E_{1/2}$ in volts in the second column, and the slope $E'_{1/2}$ at the half-wave in volts in the third. This slope was determined as follows: the tangent at the half-wave is drawn in pencil on the polarogram and the length of voltage abscissa $\Delta E$ corresponding to a height $i_d$ equivalent to $\Delta u = 1$ is reported as $E'_{1/2}$.

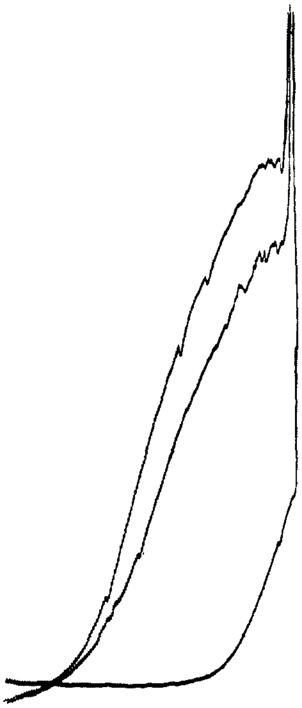


Fig. 1.—Polarographic reduction of carbon dioxide in 0.1 normal tetramethylammonium bromide: lowest curve is supporting electrolyte alone; upper curves are two slightly different concentrations of carbon dioxide, approx. 0.001 molar; sensitivity of Sargent polarograph, 100; lowest curve begins at 1.64 and finishes at 2.88 volts cathodic potential *vs.* saturated calomel electrode. Typical recordings corresponding to data in Table I. (Analysis of carbon dioxide curves necessitates referring their ordinates to corresponding ordinates of supporting electrolyte curve.)

No trend is noticeable in the data of Table I. There may be a tendency toward higher values of $E_{1/2}$ for very small diffusion currents. The somewhat smaller values of $E'_{1/2}$ at the bottom of the table do not correspond to a real decrease of $E'_{1/2}$, because with higher currents the slopes are again larger. The uncertainty of the graphic determination of $E'_{1/2}$ is somewhat larger than the average deviation ±0.015 reported above.

When the diffusion currents are larger than 40 microamperes the waves usually exhibit a maximum (see Fig. 2). The heights of these maximums and all other features of the waves are exactly reproducible. The usual maximum suppressors have no effect, except gelatin which, upon gradual addition, removes the depression of current following the peak without, however, appreciably affecting the height of the peak which is then changed into a short, flat diffusion current immediately followed by a large increase of current. The latter effect may be due to a lowering of the reduction potential of the supporting electro-

---

(4) M. L. Oliphant, *Phil. Mag.*, **6** (7th series), 422 (1928).

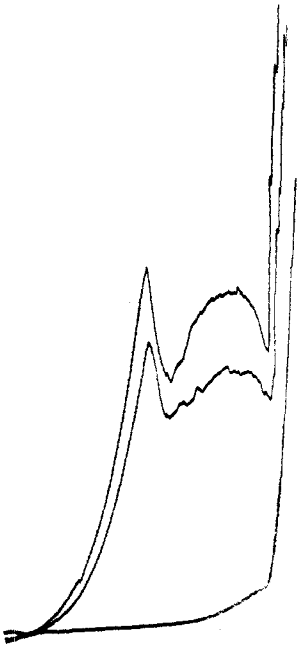


Fig. 2.—Polarographic reduction of carbon dioxide in 0.1 normal tetramethylammonium bromide: lowest curve is supporting electrolyte alone; upper curves are two slightly different concentrations of carbon dioxide, approx. 0.005 molar; sensitivity of Sargent polarograph, 500; lowest curve begins at 1.64 and finishes at 3.04 volts cathodic potential *vs.* saturated calomel electrode. Typical recordings corresponding to data in Tables II and III.

lyte by the gelatin, or to some reduction process affecting the gelatin itself. When the height of the crest is taken as the position of the diffusion current the half-wave potentials and half-wave slopes are reproducible, whether gelatin is present or not. For this reason practically all our work was carried out without the addition of gelatin. The slope of the ascending branch of the peak is not the reciprocal of the resistance of the cell, as is often the case with polarographic maxima. The slope at the half-wave, as well as at other points, is a characteristic of the reduction reaction, whether gelatin is present or not. There is a distinct indication of a very slight increase of reduction potential for the highest currents recorded. We found it convenient to divide the waves of this second group into two sub-groups: diffusion currents larger than 40 but smaller than 100 microamperes, and diffusion currents larger than 100 microamperes. Some of the data obtained are reported in Tables II and III. The averages for the fourteen waves of Table II are

$$E_{1/2} = 2.15 \pm 0.02 \text{ volts}$$
$$E'_{1/2} = 0.348 \pm 0.019 \text{ volt}$$

and for the fifteen waves of Table III

$$E_{1/2} = 2.19 \pm 0.03 \text{ volts}$$
$$E'_{1/2} = 0.357 \pm 0.010 \text{ volt}$$

The general averages for the forty-three waves of the three Tables are

$$E_{1/2} = 2.16 \pm 0.03 \text{ volts}$$
$$E'_{1/2} = 0.352 \pm 0.015 \text{ volt}$$

The data summarized in Paper I[1] had been obtained with currents close to the highest reported in the present paper. The somewhat lower potentials observed in presence of hydrogen were due to lower concentrations of carbon dioxide, the effect of hydrogen itself on the reduction potential being probably negligible.

TABLE I

HALF-WAVE POTENTIALS AND SLOPES OF REDUCTION WAVES OF CARBON DIOXIDE

($i_d$ < 40 microamperes)

| $i_d$ microamp. | $E_{1/2}$ volts | $E'_{1/2}$ volts |
|---|---|---|
| 2.08 | 2.20 | 0.367 |
| 6.56 | 2.19 | .358 |
| 9.28 | 2.17 | .358 |
| 13.8 | 2.14 | .358 |
| 16.6 | 2.15 | .357 |
| 18.4 | 2.13 | .376 |
| 19.4 | 2.14 | .366 |
| 20.5 | 2.16 | .354 |
| 22.7 | 2.15 | .362 |
| 25.9 | 2.10 | .344 |
| 27.2 | 2.16 | .357 |
| 28.5 | 2.14 | .321 |
| 30.4 | 2.16 | .312 |
| 34.6 | 2.14 | .325 |
| Average | 2.15 | .351 |

(maximum *Ri* drop at half-wave, 0.003 volt)

TABLE II

HALF-WAVE POTENTIALS AND SLOPES OF REDUCTION WAVES OF CARBON DIOXIDE

(40 < $i_d$ < 100 microamperes)

| $i_d$ microamp. | $E_{1/2}$ volts | $E'_{1/2}$ volts |
|---|---|---|
| 42.6 | 2.13 | 0.294 |
| 43.2 | 2.11 | .322 |
| 44.5 | 2.16 | .357 |
| 45.4 | 2.12 | .341 |
| 48.0 | 2.12 | .340 |
| 49.3 | 2.16 | .376 |
| 50.6 | 2.12 | .348 |
| 56.0 | 2.12 | .367 |
| 62.4 | 2.13 | .321 |
| 67.2 | 2.17 | .386 |
| 75.2 | 2.15 | .340 |
| 83.2 | 2.22 | .358 |
| 89.6 | 2.17 | .367 |
| 99.2 | 2.16 | .355 |
| Average | 2.15 | .348 |

(maximum *Ri* drop at half-wave, 0.010 volt)

TABLE III

HALF-WAVE POTENTIALS AND SLOPES OF REDUCTION WAVES OF CARBON DIOXIDE

($i_d > 100$ microamperes)

| $i_d$ microamp. | $E_{1/2}$ volts | $E'_{1/2}$ volts |
|---|---|---|
| 106 | 2.18 | 0.330 |
| 107 | 2.14 | .368 |
| 113 | 2.19 | .349 |
| 115 | 2.15 | .359 |
| 116 | 2.18 | .358 |
| 118 | 2.16 | .367 |
| 128 | 2.13 | .348 |
| 131 | 2.19 | .358 |
| 133 | 2.21 | .335 |
| 144 | 2.17 | .350 |
| 162 | 2.23 | .351 |
| 189 | 2.19 | .385 |
| 197 | 2.24 | .376 |
| 200 | 2.19 | .358 |
| 358 | 2.25 | .358 |
| Average | 2.19 | .357 |

(maximum *Ri* drop at half-wave, 0.036 volt)

## Theoretical Treatment of Experimental Data[5]

The polarographic reduction of carbon dioxide in unbuffered solutions corresponds to sub-case b of case II in the theoretical treatment presented in paper II[2] of this series. Neglecting the very small variation of $E_{1/2}$ with concentration, and on the basis of the fact that the half-wave is, as far as can be ascertained with the usual accuracy of polarographic recordings, a point of inflection, we have $z = x + 1$, and, therefore, in accordance with formula (33) of paper II[2]

$$x + 1 = 0.352/0.051$$

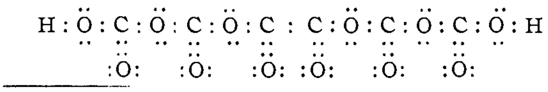
The closest integer is 7, and hence $x = 6$. The reaction is therefore

$$6CO_2 + 2H^+ + 2e^- \longrightarrow (CO_2)_6H_2$$

or

$$6CO_2 + H_2 \longrightarrow (CO_2)_6H_2 \qquad (1)$$

A possible structure for the reduction product is the following



$$\mathrm{H:\ddot{O}:\underset{:\ddot{O}:}{C}:\ddot{O}:\underset{:\ddot{O}:}{C}:\ddot{O}:\underset{:\ddot{O}:}{C}\ :\ \underset{:\ddot{O}:}{C}:\ddot{O}:\underset{:\ddot{O}:}{C}:\ddot{O}:\underset{:\ddot{O}:}{C}:\ddot{O}:H}$$

The free energy of formation of such a compound from the elements can be estimated as follows from the data of Parks and Huffman[6]: $\Delta F^\circ$ for oxalic acid = $-166$ kilocalories, insertion of four groups —CO—O— = $-70 \times 4 = -280$ kcal. Total free energy of formation for $(CO_2)_6H_2$

$$\Delta F^\circ_{(CO_2)_6H_2} = -446 \text{ kcal.}$$

The free energy of formation of carbon dioxide in solution is obtained from that of $H_2CO_3$ and that of $H_2O$[7]: $-149.17 + 56.69 = -92.48$ kcal. For $6CO_2$ we have

$$\Delta F^\circ_{6CO_2} = -555 \text{ kcal.}$$

For reaction (1) above we thus have

$$\Delta F^\circ = -446 - (-555) = 109 \text{ kcal.}$$

The half-wave potential of 2.16 volts *vs.* the saturated calomel electrode corresponds to 1.91 volts *vs.* the standard hydrogen electrode. We have

$$2FE_{1/2} = 2 \times 23.1 \times 1.91 = 88.2 \text{ kcal.}$$

and therefore, on the basis of formula (41) of paper II[2]

$$-RT \ln K/K_a = \Delta F^\circ - 2FE_{1/2} = 109 - 88.2 = 20.8 \text{ kcal.}$$

At 25° the first ionization constant of carbonic acid[8] is $4.31 \times 10^{-7}$. We have

$$RT \ln K_a = -8.7 \text{ kcal.}$$

and

$$-RT \ln K = 20.8 + 8.7 = 29.5 \text{ kcal.}$$
$$\log K = -21.7$$

The Freundlich isotherm for the adsorption equilibrium of the reduction product $(CO_2)_6H_2$ or X is thus (see formula (11) of paper II[2])

$$C_X = 10^{-21.7}\, C^7_{X_s}$$

in which $C_X$ is the concentration in the solution, $C_{X_s}$ the surface concentration. The concentration of the reduced product in solution thus appears to be infinitesimally small. It is quite possible that, at potentials in the neighborhood of those at which $(CO_2)_6H_2$ is formed, further reduction occurs, but there is no possibility of obtaining direct evidence to that effect as long as the first reduction product cannot be isolated in sufficient amounts. For each $H_2$ available at the potential 1.91 volt there are 88.2 kcal. of free energy provided. Several successive reductions are therefore theoretically possible, and they may actually occur in the surface phase of the mercury drops. Moreover, the gradual removal of the oxygen bridges between carbon pairs appears to be spontaneous. For instance

$$(CO_2)_6H_2 + H_2 \longrightarrow C_6O_{11}H_2 + H_2O$$

involves a free energy change

$$\Delta F^\circ = -405 - 57 - (-446) = -16 \text{ kcal.}$$

---

(5) It has been suggested by Referees that the observed waves are due to the reduction of hydrogen ion and not to that of carbon dioxide. A comparison of the characteristics of the waves described in the present paper with those corresponding to the reduction of hydrogen ion shows fundamental differences. While the slope at the half-wave has been found to be 0.35 for carbon dioxide that of hydrogen ion has been found to be 0.22 in six out of nine acids (weak and strong) and to be less than 0.25 in the other cases. The potential at the half-wave is 2.16 volts for carbon dioxide while it is close to 1.65 volt for all strong acids. It is somewhat larger for weak acids. The geometrical properties of the carbon dioxide and hydrogen ion waves are also quite different; the point of inflection of the carbon dioxide waves is practically at the half-wave while that of the hydrogen ion waves is at about 65% of the diffusion current. Moreover the hydrogen ion waves never show the peak exhibited by carbon dioxide waves above a certain concentration. Extensive studies on the polarographic reduction of hydrogen ion have been carried out in this Laboratory by R. D. Williams. They will be reported in a later communication.

(6) G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," Chemical Catalog Co., New York, N. Y., 1932, see Table 27, p. 134, and Table 40, pp. 210–211.

(7) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, see Table 22, p. 119.

(8) D. A. MacInnes and D. Belcher, THIS JOURNAL, **55**, 2630 (1933); T. Shedlovsky and D. A. MacInnes, *ibid.*, **57**, 1705 (1935).

with equal ΔF° changes for the next three steps, ending with

HOCO—CO—CO—CO—CO—COOH

which has an estimated ΔF° of formation of −282 kcal. The transformation of this compound into HOCO-(CHOH)$_4$-COOH would be spontaneous with a ΔF° of −28 kcal. (−310 − (−282) = −28 kcal.). The further reduction to glucose or some other similar carbohydrate would require ΔF° = −216 − (−310) = 104 kcal., while the direct formation of carbohydrate from HOCO-(CO)$_4$ − COOH by the reaction

$$\mathrm{HOCO{-}(CO)_4{-}COOH} + 5\mathrm{H_2} \longrightarrow \mathrm{C_6H_{12}O_6} + 4\mathrm{O_2}$$

would require ΔF° = −216 − (−282) = 66 kcal. The preceding considerations, beyond the formation of $(CO_2)_6H_2$, are in the nature of speculations, but they give a clue toward possible mechanisms of formation of carbohydrates or carbohydrate-precursors by reduction of carbon dioxide. We believe that the primary condition for the formation of carbon chains from carbon dioxide is the adsorption and subsequent surface-phase reduction of carbon dioxide. The conditions existing at the surface of the mercury drops in the polarograph may have significant points of similarity with conditions in plant leaves.

## Influence of Temperature

As indicated in paper II[2] it is advisable to examine the effect of temperature on the half-wave potential, as well as on the half-wave slope. The results obtained for a few temperatures are reported in Table IV. It is apparent that, below 50°, the half-wave potential is not affected by temperature. The gradual lowering above 50°, as well as the possibly smaller slope at the highest temperature, are probably due to changes in the conditions of adsorption. We conclude that, certainly below 50°, and possibly also above, the reduction reaction is not affected by rate complications, and is therefore properly treated by the theory of electrochemical equilibrium.

TABLE IV

INFLUENCE OF TEMPERATURE ON HALF-WAVE POTENTIALS AND SLOPES OF CARBON DIOXIDE WAVES

| Temp., °C. | $E_{1/2}$ volts | $E'_{1/2}$ volts |
|---|---|---|
| 25 | 2.16 | 0.352 |
| 38.5 | 2.10 | .330 |
| 42 | 2.23 | .353 |
| 44.5 | 2.15 | .376 |
| 44.5 | 2.22 | .348 |
| 45.5 | 2.16 | .349 |
| 46 | 2.18 | .357 |
| 46.5 | 2.16 | .362 |
| 48.5 | 2.16 | .345 |
| 51 | 2.05 | .344 |
| 52.5 | 2.02 | .362 |
| 54.5 | 2.02 | .344 |
| 58.5 | 2.01 | .326 |
| 63 | 1.90 | .385 |
| 68.5 | 1.92 | .349 |
| 77 | 1.89 | .294 |

Since hydrogen ions are consumed in the reduction at the rate of two for every six molecules of carbon dioxide the slowness of the hydration of carbon dioxide and therefore that of the liberation of hydrogen ions[9] do not introduce, with the conditions holding here, a slow step causing irreversibility. The assumption of immediate regulation of the ionization equilibrium of carbonic acid, postulated in the foregoing considerations, is justified by the nature of the reduction reaction and proved by the study of the temperature effect.

## Application of the Ilkovic Equation

When the diffusion current $i_d$ is expressed in microamperes and the concentration $C$ of the reducible substance is expressed in moles per liter the Ilkovic equation is[10]

$$i_d = 6.05 \times 10^5 \times n \times D^{1/2} \times m^{2/3} \times t^{1/6} \times C$$

in which $n$ is the number of electrons involved in the reduction of one molecule, $D$ is the diffusion coefficient of the substance reduced in cm.$^2$ sec.$^{-1}$, $m$ is the mass of mercury dropping in mg. sec.$^{-1}$, $t$ is the drop time in seconds. In the range of potentials corresponding to the carbon dioxide waves the rate of dropping of the mercury increases appreciably (*i.e.*, the number of drops per second) and, at very large cathodic potentials, streaming finally occurs. Nevertheless, we have verified that over the range of potential $\Delta E$ corresponding to $\Delta u = 1$ the product $m^{2/3} \times t^{1/6}$ stays fairly constant, its value in most of our experiments being close to an average of 2.50. Taking the I.C.T. value for the diffusion coefficient of carbon dioxide we get $D^{1/2} = 4.21 \times 10^{-3}$. Hence

$$i_d = 6.37 \times 10^3 \times n \times C$$

Since in most of our experiments the solutions were actually supersaturated with respect to carbon dioxide for the partial pressures existing in the gas phase over the solution, the exact determination of the concentration of carbon dioxide proved to be a complicated problem. Although the amount of carbon dioxide does not vary during the time required to take a polarogram (between potentials 1.6 and 2.8 volts the time elapsed is about three minutes) or even during the time required for consecutive duplicate runs, any handling of the solution for any type of analytical determination of carbon dioxide results in a variation of the concentration. The introduction of some quinhydrone and of a platinum electrode immediately after the establishment of the diffusion current, using the mercury anode as reference electrode, involves a minimum of manipulation, but the *p*H values so obtained were often not reliable. Immediate transfer of a sample to the glass cup of a Beckman *p*H meter proved to be a more

---

(9) G. N. Lewis and G. T. Seaborg, This Journal, **61**, 1886 (1939).

(10) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., **1941**, p. 55.

satisfactory method. The problem of obtaining exact concentrations of carbon dioxide and the resulting establishment of a reliable polarographic method of determining carbon dioxide will require further investigation. However, if the value $x = 6$ for the coefficient of carbon dioxide in the reduction reaction corresponding to two electrons is introduced in the Ilkovic equation we get, with $n = 1/3$

$$i_d = 2.12 \times 10^3 \times C$$

That this formula is essentially correct (for $m^{2/3} \times t^{1/6} = 2.50$) we have been able to verify in a few cases. For instance, for the concentration of carbon dioxide giving $i_d = 128$ microamperes, we found $p\text{H} = 3.80$ by means of the Beckman $p$H meter. We then have $a_{\text{H}^+} = 1.6 \times 10^{-4}$ and[8]

$$C = a^2_{\text{H}^+}/4.31 \times 10^{-7} = 0.0594 \text{ mole per liter}$$

and $i_d = 126$ microamperes, in good agreement with the observed 128 microamperes. If the reaction had been the simpler one

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$

for instance, we would have had $n = 2$ instead of 1/3 and the current would have been six times larger. In other words, the use of the Ilkovic equation, as far as we have carried it out, verifies the result obtained from the half-wave slope, namely, that with a pair of hydrogen ions and a pair of electrons, six molecules of carbon dioxide are involved in the reduction process.

**Acknowledgment.**—Part of the equipment and of the materials used in this work was obtained through grants from the General Research Council of the Oregon State System of Higher Education, to which the authors express their gratitude.

## Summary

1. Polarographic reduction waves obtained with solutions of carbon dioxide in 0.1 molar tetramethylammonium chloride and bromide are described.

2. The half-wave potential is 2.16 volts *vs.* the saturated calomel electrode.[11] The half-wave slope is 0.352 volt.

3. Theoretical considerations previously developed are applied to the data. It is concluded that the reduction reaction is

$$6CO_2 + H_2 \longrightarrow (CO_2)_6H_2$$

Free energy changes are calculated and discussed.

4. The influence of temperature on the half-wave potential and on the half-wave slope is reported and discussed.

5. The use of the Ilkovic equation also leads to the coefficient six for carbon dioxide in the reduction reaction.

---

[11] Added in proof: After careful recalibration of the slidewire of the polarograph and the adoption of an improved method for the determination of applied potentials on the photographic records a few additional polarograms were taken. These lead us to favor the lower limit for the average half-wave potential 2.16 ± 0.03 volts.

EUGENE, OREGON RECEIVED NOVEMBER 13, 1945

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# A New Magnetic Effect Applied to the Structure of Catalytically Active Solids[1]

BY P. W. SELWOOD, FRED N. HILL AND HAROLD BOARDMAN

Applications of magnetism to catalysis have recently been reviewed by the senior author.[2] The purpose of the present work was to apply magnetic susceptibility measurements to catalytically active solids such as copper–chromium oxide and related substances. It was hoped that magnetic measurements would indicate oxidation states and structural properties in these substances. During the course of the work it became evident that the magnetic suceptibility of a supported transition group oxide is described by a hitherto unrecognized principle. This principle promises to be of value in determining structure and structural changes in solid catalysts containing elements such as chromium, molybdenum, nickel and copper. The method is expected to be particularly valuable in finding the effective dispersion of the active agent in supported catalysts.

## Experimental Procedures

**Magnetic Measurements.**—Susceptibilities were measured by the Gouy method as previously described.[3]

**Preparation of Materials.**—Of the approximately twenty different substances investigated, a considerable number were prepared in this Laboratory. Others were obtained elsewhere.

1. $\gamma$-$Al_2O_3$.—Samples of commercially available alumina show marked differences in magnetic susceptibilities, owing largely to differences in iron content. Susceptibilities have been found ranging from $-0.3 \times 10^{-6}$ to $+6.8 \times 10^{-6}$. It was found that Harshaw gamma alumina was satisfactory for the work described here. Samples of gamma alumina were also prepared in this Laboratory by the usual methods. The susceptibility found for the best samples ($-0.3 \times 10^{-6}$) was independent of field strength, and almost independent of temperature.

2. $Cr_2O_3$.—C. P. chromic acid anhydride was reduced in hydrogen at 350°. The susceptibility was independent of field strength, indicating absence of ferromagnetic impurities. On the other hand, C. P. chromic oxide was, in general, unsatisfactory.

3. **$Cr_2O_3$-$Al_2O_3$ Catalyst.**—The usual method of impregnation was followed. $\gamma$-Aluminum oxide was im-

---

[1] Presented at the Atlantic City Meeting of the American Chemical Society, April 10, 1946.

[2] Selwood, *Chem. Rev.*, **38**, 41 (1946).

[3] Selwood, THIS JOURNAL, **61**, 3168 (1939).