

zene has been investigated. The results of this investigation are as follows:

The freezing points of pure *p*-dichlorobenzene, *p*-chlorobromobenzene and *p*-dibromobenzene were redetermined as 53.08, 64.58 and 87.30°, respectively. It was confirmed that pure *p*-dichlorobenzene exists in at least two forms under atmospheric pressure, the reversible transformation occurring at 39.6°.

p-Dibromobenzene and *p*-chlorobromobenzene are miscible in all proportions in both liquid and solid states; the freezing points of all solutions lie between the freezing points of the pure components. The binary system *p*-dichlorobenzene-*p*-dibromobenzene exhibits a minimum freezing temperature of 52.90° at a concentration of 1.22

mole per cent. dibromobenzene. The components are miscible in all proportions in both liquid and solid states. The binary system *p*-dichlorobenzene-*p*-chlorobromobenzene exhibits a minimum freezing temperature of 52.96° at a concentration of 2.57 mole per cent. chlorobromobenzene. The components are miscible in all proportions in both liquid and solid states.

The ternary system *p*-dichlorobenzene-*p*-chlorobromobenzene-*p*-dibromobenzene exhibits miscibility in all proportions in both liquid and solid states. No ternary solution of minimum freezing point exists; neither is there any temperature at which the compositions of liquid and solid solutions coincide.

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[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE UNIVERSITY OF AKRON, GOVERNMENT LABORATORIES]

Potentiometric Determination of Oxygen Using the Dropping Mercury Electrode¹

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A dropping mercury electrode in a solution free of capillary-active substances or electro-reducible or oxidizable substances assumes a potential corresponding to the electrocapillary zero potential of mercury. Under these conditions, the electrokinetic potential of mercury, with respect to the solution, is zero. To maintain the dropping electrode at any other potential, it is necessary to supply electrons or to remove electrons from the reservoir of mercury connected to the capillary from which the mercury is dropping. Thus, it is necessary to maintain a continuous flow of electrons to charge electrically the double layer existing between the mercury and the solution because the double layer is continually being formed. The polarographic charging or condenser current is a familiar manifestation of this phenomenon. The charging current as shown in Fig. 1 is negative in sign (corresponding to an anodic process at the dropping electrode) at potentials more positive than the electrocapillary maximum, at which point the charging current changes sign and increases in positive value as the potential is made more negative.

Any substance, such as oxygen, which is reducible on the positive side of the electrocapillary maximum, will yield a polarographic diffusion current which is positive in sign and hence opposed in direction to the charging current. For very small concentrations of oxygen, it is evident that at some value of the potential the diffusion and charging currents will be equal in magnitude but opposite in direction and hence will cancel. Since

the instantaneous value of the diffusion current varies with the one-sixth power of the time and is independent of the potential while the charging current at a constant potential varies with the two-thirds power of the time,² it is evident that the null potential must vary with time in such a way that the instantaneous current will be zero at all times.

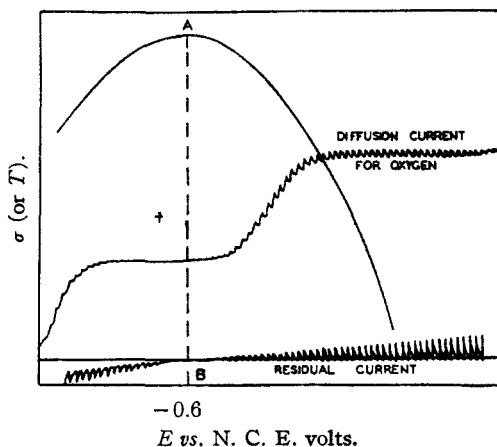


Fig. 1.—Electrocapillary curve.

To calculate the magnitude of the effect, it is convenient to equate the total charge, $(q_c)_t$, held by the drop at any time, t , with the number of coulombs, $(q_d)_t$, lost by the drop through the electro-reduction of oxygen molecules from the beginning of the drop formation to time, t , or

$$(q_c)_t = (q_d)_t \quad (1)$$

(1) This investigation was sponsored by the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the government synthetic rubber program.

(1a) Noyes Chemical Laboratory, University of Illinois.

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

The charge held by the drop at any time, t , is given by

$$(q_0)_t = A_t k (E - E_{\max.})_t \quad (2)$$

where A_t is the area of the drop at time, t , k is the capacity of the double layer per unit area (microfarads per square centimeter), $E_{\max.}$ is the potential corresponding to the electrocapillary maximum and E is the potential of the dropping mercury electrode in volts. From geometric considerations

$$A_t = 4\pi^{1/2} (3/4d)^{2/3} m^2 / t^{2/3} \quad (3)$$

if the spherical drops grow at a uniform rate of m/d cubic centimeter per second where m is the mass of mercury flowing per second and d is the density of mercury. Substituting (3) in (2)

$$(q_0)_t = 4\pi^{1/2} (3/4d)^{2/3} k (E - E_{\max.}) t^{2/3} m^2 / t^{2/3} \quad (4)$$

The charge lost because of reaction of oxygen at the drop surface can be obtained by integrating the Ilkovic equation³ (where i_t is the diffusion current at time, t)

$$(q_a)_t = \int i_t dt = \frac{4}{7} (7/3)^{1/2} (3/4d)^{2/3} \pi^{-1/2} n F D^{1/2} C m^2 / t^{1/2} dt \\ = 6/7 \cdot 4 (7/3)^{1/2} (3/4d)^{2/3} \pi^{-1/2} n F D^{1/2} C m^2 / t^{1/2} \quad (5)$$

Substituting (4) and (5) into (1) and solving for $(E - E_{\max.})_t$

$$(E - E_{\max.})_t = \frac{6}{\sqrt{21}\pi} \frac{n F C D^{1/2} t^{1/2}}{k} = \\ 7.128 \times 10^4 \frac{n C D^{1/2} t^{1/2}}{k} \quad (6)$$

where nF is the number of coulombs of electricity involved per mole, D is the diffusion coefficient in square centimeters per second and C is the concentration of reducible substance in millimoles per liter.

To evaluate the final expression for the specific case of oxygen, $n = 2$, $D = 2.6 \times 10^{-5}$, from the polarographic measurements of Kolthoff and Miller⁴ and $k = 42.2$ microfarads per square centimeter (0.1 N KCl), the value of Ilkovic.⁵

Since the latter value was determined by Ilkovic from the slope of the polarographic residual current curve, 42.2 was used rather than the value of 48.8 microfarads per square centimeter reported by Philpot.⁶ The final expression (6) becomes

$$E - E_{\max.} = 17.2 C t^{1/2} \quad (7)$$

where the potential shift is measured in volts, the concentration in millimoles per liter and the drop time in seconds.

According to equation (7), the potential difference is zero at the beginning of the drop formation and increases as the square root of the time until the drop breaks. This variation is brought about by the fact that the instantaneous diffusion current is independent of the potential, while the

(3) D. Ilkovic, *Collection Czechoslovak Chem. Commun.*, **6**, 498 (1934); *J. chim. phys.*, **35**, 129 (1938).

(4) I. M. Kolthoff and C. S. Miller, *THIS JOURNAL*, **63**, 1013 (1941).

(5) D. Ilkovic, *Collection Czechoslovak Chem. Commun.*, **8**, 170 (1936).

(6) St. L. Philpot, *Phil. Mag.*, [7] **13**, 775 (1932).

charging current is proportional to the potential difference ($E - E_{\max.}$). Thus, for the observed current to be zero at every instant, the potential difference must fluctuate with time. The voltage fluctuation should be directly proportional to the oxygen content of the electrolyte, but independent of the rate of flow of mercury (m).

If a high capacity condenser is inserted into the circuit to lower the voltage fluctuation to a negligible value, the observed potential will correspond to the maximum potential difference of the undamped system just before the drop breaks. This relationship can readily be derived by equating the total number of coulombs of electricity due to the diffusion current during the life-time of the drop with that due to the charging current at a constant potential. Since the charging current at any instant is determined by the diffusion current, the magnitude of the former is unaffected by the presence or absence of damping condensers. At the time of the drop break, the final charge (equation 2) and therefore the final potential difference is the same in the damped and undamped systems.

Equation (7) relates the potential of the system with the concentration of oxygen actually dissolved in the electrolyte. To determine the actual oxygen content of any non-reducible gas it is necessary only to bring the electrolyte into equilibrium with the gas before measuring the potential.

In such case, equation (7) would take the form

$$\text{Percentage oxygen in gas} = \frac{(E - E_{\max.})}{\frac{10\alpha}{22.4} 17.2 t^{1/2}} \quad (8)$$

where α is the absorption coefficient of oxygen in the electrolyte expressed in cubic centimeters per liter and the total gas pressure is one atmosphere.

At 25°, $\alpha = 28.3^{6a}$ and the equation reduces to

$$\text{Percentage oxygen} = \frac{(E - E_{\max.})}{217 t^{1/2}} \quad (9)$$

where $(E - E_{\max.})$ is expressed in millivolts.

The object of the present investigation was to determine the effects of the factors "C" and "t" in equation (6) and to determine whether the potential is independent of the rate of flow of mercury.

Apparatus

Design of Cell for Continuous Measurements.

—A cell suitable for the present investigation had to fulfill the following requirements: (1) Arrangements had to be made to bring the electrolyte rapidly in equilibrium, with respect to its oxygen content, with the sample gas. (2) The dropping electrode had to be shielded from any turbulence caused by flow of gas through the solution. (3) The reference electrode had to have constant reversible potential and possess relatively low resistance. It had to be placed so that the re-

(6a) The value of 28.3 holds only for pure water. When an appreciable amount of electrolyte is present the value is, of course, lower.

ducible products, if any, of the electrode could not affect the dropping electrode. (4) The mercury from the dropping electrode had to be removed in a manner to minimize contact with the electrolyte. Any mercurous chloride formed through interaction of the mercury with the electrolyte might affect the dropping electrode potential. (5) To permit continuous operation, it was advisable to construct the cell in such a manner as to permit cautious partial replacement of the electrolyte. This prevented accumulation of contaminants over a long period of time.

A schematic diagram of the apparatus which was employed in this study is shown in Fig. 2. The apparatus was designed to meet the conditions previously set forth.

Operation of the Unit.—The electrolyte in a 1-liter stoppered flask (Reservoir A) in Fig. 2 was maintained at constant head in the scrubbing vessel B. The solution was allowed to flow at a predetermined rate of 1.1 ml. per minute through capillary tube C into the dropping mercury electrode cell D, past the silver-silver chloride reference electrode E, to the outlet F.

The gas sample was first saturated with water vapor from the electrolyte solution in vessel G and then part of the gas stream was forced through the fritted glass disc H into the scrubbing vessel B where the electrolyte received a preliminary scrubbing with the gas sample. The final solubility equilibrium between the oxygen in the sample and the electrolyte solution was obtained by passing another portion of the gas stream through the fritted disc I into the dropping mercury electrode cell. The gas was allowed to escape through two spray trap bulbs, J and K, on either side of the cell.

Mercury from reservoir L was forced through the dropping mercury electrode capillary M. The funnel-shaped shield, surrounding the tip of the capillary, served to protect the slowly forming mercury drops from agitation of the rising gas bubbles, and also to direct the mercury drops into the siphon, thus removing them from the cell.

An important feature of the design of the equipment was the continuous removal of any reducible materials such as mercurous chloride and silver chloride which would form at the electrodes in small concentrations in a stationary system. The flow of electrolyte was in such a direction as to prevent the accumulation of calomel around the dropping electrode. For the same reason, the reference electrode was situated in the outflowing stream of electrolyte.

Operational Characteristics of Cell Assembly.—To determine the rate of approach to solubility equilibrium, the rate of change of the potential difference was determined using purified nitrogen as the gas sample. Starting with an air-saturated 0.1 *N* potassium chloride solution throughout the reservoirs and the cell, a thousand-fold decrease in oxygen concentration was observed in one minute.

To check the possible interference from back-diffusion of oxygen, the nitrogen stream was shut off after reaching a constant potential reading. No noticeable change in potential (less than 1 millivolt) was observed after 5 minutes of standing.

Potential Measurements.—A Beckman Research Model G pH meter, operated as a millivoltmeter, was used for the measurement of the cell e. m. f. This instrument was found to be particularly suitable because of its sensitivity and rapid response. In an undamped system, the meter was permitted to remain continuously in the circuit, and the maximum e. m. f. developed during the formation of each drop was determined by balancing the slide wire so that the galvanometer showed zero deflection at the end of the drop formation.

To determine whether the e. m. f. in a damped system

corresponds to the maximum e. m. f., a condenser of 16 m. f. d. capacitance was connected across the dropping electrode system. The observed non-fluctuating e. m. f. was found to be identical (within 2 millivolts) with the maximum e. m. f. observed in the undamped system, as was expected from the theoretical considerations. Since it was found that a time lag of two to three minutes was introduced by the necessity of charging the condenser, it proved to be more convenient to measure the maximum e. m. f. in the undamped system. However, a damped system would probably be more practicable in a continuously recording apparatus.

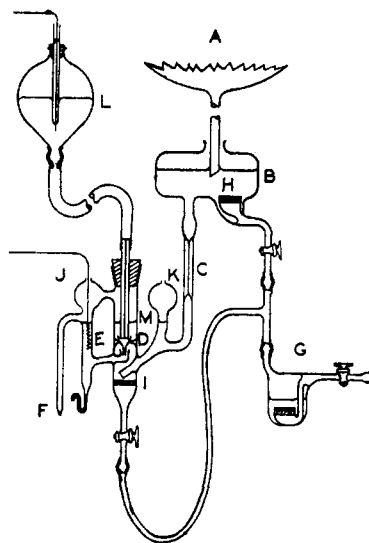


Fig. 2.

Results and Discussions

Variation of Potential with Concentration.

A series of oxygen-nitrogen mixtures of known composition was obtained from General Electric Wire Works, Cleveland, Ohio. The oxygen contents of the samples were 0.200, 0.554 and 1.028%. The mixture with lowest oxygen content was prepared by accurately mixing pure oxygen and nitrogen, while the other mixtures were prepared by mixing and analysis by a combustion method. The oxygen content for each mixture was guaranteed to be accurate to within 0.01 per cent. (absolute).

Air-free nitrogen was prepared by the conventional method of passage over copper turnings heated to 400°. The purity was indicated by the fact that the maximum potential difference developed during the formation of the mercury drops was less than 2 millivolts (corresponding to less than 0.005% of oxygen). The e. m. f. observed with the purified nitrogen against the particular silver-silver chloride electrode in 0.1 *N* KCl was 500 millivolts, as compared with the theoretical value of 558 millivolts calculated from the potential of the electrocapillary maximum (550 millivolts in 0.1 *N* KCl against normal calomel electrode). The disagreement would correspond to 0.1% of oxygen, and a fluctuation of 58 millivolts would then be expected during the drop formation. The discrepancy may be partly attributed to a lack of

equilibrium at the silver-silver chloride electrode, but should be further investigated. For all practical purposes, the value of 500 millivolts can be used as the potential corresponding to the electrocapillary maximum because the error could not exceed 0.005% of oxygen.

The observed ΔE values, using 1 *N* potassium chloride as the electrolyte, are plotted against the oxygen concentration in Fig. 3 (A). The curve is linear for oxygen concentrations from 0 to 0.5% but shows a slight curvature at 1.0%.

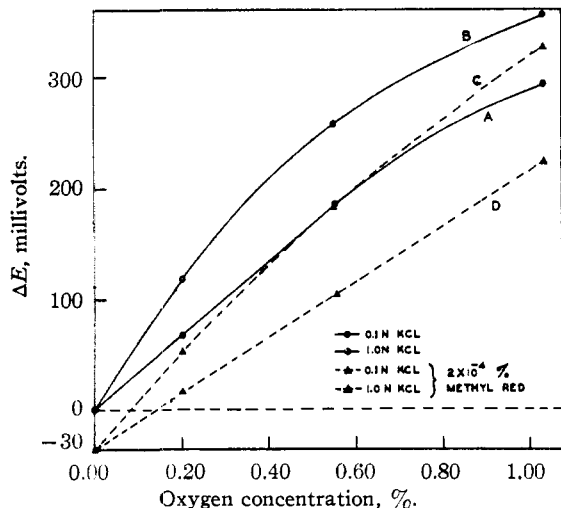


Fig. 3.—Potential shift vs. O_2 concentration.

A similar plot, Fig. 3 (B), with 0.1 *N* potassium chloride as the electrolyte, shows a more pronounced curvature and a greater sensitivity for a given percentage of oxygen. The change in sensitivity can be attributed to the increase in oxygen solubility and to the decrease in capacity of the double layer as the potassium chloride concentration is decreased.

A strict proportionality between $(E - E_{\max.})$ and concentration could not be expected to hold for an $(E - E_{\max.})$ value greater than about 300 millivolts since the diffusion current of oxygen is not reached until a potential of about minus 200 millivolts (with reference to silver-silver chloride). Other factors which could affect the linear relationship are a lack of constancy of the capacity of the double layer at varying potentials, especially in dilute salt solutions, and a maximum on the oxygen-reduction curve induced by effects of electrical stirring.⁷ Such a maximum can be suppressed by the addition of capillary-active substances, which compress the electrical double layer at the mercury-solution interface, and therefore would also increase the capacity of the double layer. Thus, the sensitivity would be decreased by the addition of maximum suppressing agents.

These effects were studied by the addition of

(7) J. Rasch, *Collection Czechoslovak Chem. Commun.*, **1**, 560 (1929); E. Varasove, *ibid.*, **2**, 8 (1930); B. Rayman, *ibid.*, **3**, 314 (1931); E. Hamamoto, *ibid.*, **5**, 427 (1933).

$2 \times 10^{-4}\%$ of methyl red as a maximum suppressor. The range of linearity was increased and the sensitivity was decreased both in 0.1 *N* and 1 *N* potassium chloride, as is shown in Fig. 3 (C and D, respectively). Methyl red undergoes reduction at the dropping mercury electrode at a potential slightly more positive than the electrocapillary maximum. Therefore, the curves can be extrapolated to a false oxygen content at zero potential, because methyl red behaves like oxygen in producing a cathodic current.

Further work is in progress to find a suitable non-reducible oxygen suppressor for practical analytical work.

The data represented in Fig. 3 were obtained at a drop time of approximately 3.7 seconds, except for curve C which was obtained at 2.8 seconds per drop.

Variations of Potential with Flow Rate of Mercury.—According to equation (7), the observed potential difference should be independent of the rate of flow of mercury through the capillary. This would indicate that the experimental readings would be independent of the capillary characteristics, and dependent only on the drop time. Experimental verification of this lack of dependency would be of considerable practical importance for routine analytical purposes.

In Fig. 4, the observed potential values at two known oxygen concentrations are plotted against the rate of flow of mercury for several capillaries chosen to cover a wide range of values of "*m*." The measurements were made at a constant drop rate to eliminate this variable. It is evident from the curve that the observed potential is for all practical purposes independent of "*m*" over a two-fold change in the flow rate. The slight variation is probably due to a deviation from the Ilkovic equation because of the large drops associated with large "*m*" values.

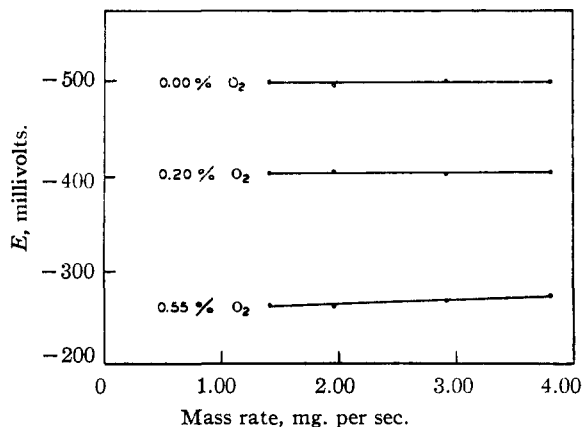


Fig. 4.—Effect of mass rate on observed potential: electrolyte, 0.1 *N* KCl; drop time, 4.0 sec.

Variation of Potential with Drop Time.—Since the instantaneous potential of the dropping

mercury electrode should vary linearly with the square root of time (equation 8) and is independent of " m ," the maximum e. m. f. for a constant oxygen concentration should give a straight line when plotted against the square root of drop time, either for various capillaries or for a given capillary operated at various heights of a mercury column.

In Figure 5, ΔE is plotted as a function of $t^{1/2}$ for a single capillary ($m = 2.27$ milligrams per second; $t = 3.52$ seconds at 55 centimeters of mercury pressure) operated at various heights of a mercury column. The three standard oxygen mixtures were studied in 0.1 N potassium chloride in the presence and absence of methyl red. In the absence of methyl red, a distinct curvature was noted at short drop times, under which conditions the oxygen maximum is known to be most pronounced.⁸ In the presence of methyl red, a linear relationship was observed over a range of drop time from 2 to 6 seconds, except in cases where the e. m. f. exceeded 300 millivolts, above which the true diffusion current of oxygen is not reached and linearity would no longer be expected.

In practice, it is recommended that a drop time of 3 to 5 seconds be used.

Application to Gases.—The new method should be applicable to a wide variety of gases, such as nitrogen, hydrogen or hydrocarbon gas mixtures, since such gases are in general inert at the dropping mercury electrode at the range of potentials involved. The only serious interferences which can be foreseen would be caused by strong oxidizing agents, such as halogen vapors which are readily reducible at the dropping electrode, and by materials which anodically depolarize the dropping electrode by the formation of insoluble mercury salts or stable mercury complexes. Examples of the latter class of interfering materials are hydrogen sulfide and hydrocyanic acid.

Substances that are readily adsorbed on the mercury surface would be expected to change the sensitivity of the method. For example, naphthalene and mercaptan vapors would be expected to show such adsorption effects. It would seem likely that the addition of maximum suppressing agents which themselves are strongly adsorbed would minimize the interference of adsorbable impurities in the sample. Capillary-active ions such as iodide would shift the electro-capillary maximum in addition to changing the capacity of the double layer.

Application to Water or Aqueous Solutions.—In principle, the method could be applied in the absence of oxygen to the determination of traces of strong oxidizing agents in aqueous solutions.

(8) J. Heyrovsky, "A Polarographic Study of the Electrokinetic Phenomena of Adsorption, Electroreduction and Overpotential displayed at the Dropping Mercury Cathode," *Actualities Scientifiques et Industrielles*, No. 90, Paris, 1934.

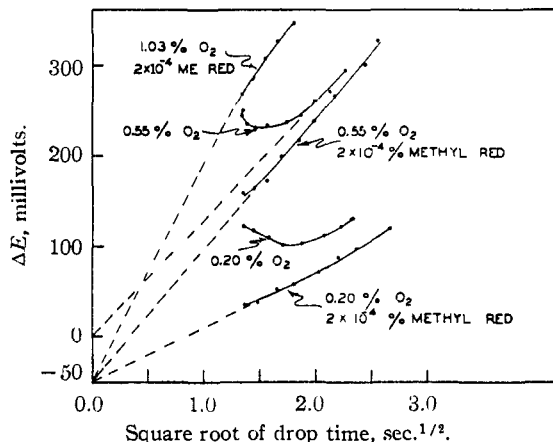


Fig. 5.

In addition to the interferences mentioned for gaseous substances, interference would be caused by many strong oxidizing agents in solution in water. Examples are ferric iron, permanganate and mercurous or mercuric salts, all of which are reducible at potentials more positive than the electrocapillary maximum and which would show the same effect as oxygen.

The change in the capacity of the double layer with changing electrolyte concentration and by adsorbable materials such as soaps or proteins would be a more serious problem in the analysis of solutions, especially in the case of essentially electrolyte-free water.

Conclusions

1. A simple, rapid and sensitive potentiometric method for the determination of traces of oxygen in gases or in solution, based upon measurement of the null potential of a dropping mercury electrode, has been developed.
2. The maximum potential difference developed during the growth of the mercury drops varied linearly with oxygen concentration over a potential range of zero to 300 millivolts, in the presence of maximum-suppressing agents. The potential varied as the square root of the drop time and was independent of the rate of flow of mercury through the capillary at a constant drop time.
3. Using 0.1 N potassium chloride, with a trace of methyl red as a maximum suppressor, the method was sensitive to 0.01 per cent. of oxygen in a gas; linear relationship was attained over the range of zero to 1 per cent. of oxygen.
4. The sensitivity of the method varied with changes in the capacity of the electrical double layer at the mercury solution interface caused by changes in electrolyte concentration or by traces of capillary-active materials.

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