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GENERAL CHEMISTRY PROGRESS REPORT

Submitted by C.W. Huntington 8/2/79
P.B. David 6/18/70
7/11/70
8/2/79

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M. M. Haring
Laboratory Director

Signature: <i>P.B. David</i>	Date: <i>2/12/80</i>
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GENERAL CHEMISTRY GROUP

S. Barth, M. Ford, P. Dismore, and W. Power

ABSTRACT

Polarography with the Cathode Controlled Polarograph

Decomposition potentials of bismuth solutions of 1.037 and 0.509 grams of the metal per 100 ml. of 1.5 nitric acid were found to be -0.06 and -0.09 volts to N.C.E. These results confirm previous values and indicate that bismuth will not be reduced from production solutions at the potential of the normal calomel electrode.

A summary of research in progress, completed, or anticipated is given.

DETAILED REPORT

Polarography with the Cathode Controlled Polarograph - M. Ford

A request was received¹ to redetermine the reduction potential of bismuth in 1.5 N nitric acid in concentrations comparable to those used in production (0.5 grams of bismuth per 100 ml. of acid).

Reduction potentials were determined by use of the cathode controlled polarograph, using circuit "I" of Plate 31. The 12-point, 150 mv. Speedomax was used for recording the reduction current. Potentials were measured with a 100 mv. electronic voltmeter with 5000 megohms impedance. Reduction potentials were -0.06 volts to the N.C.E. for a bismuth concentration of 1.037 grams per 100 ml. of 1.5 N nitric acid, and -0.09 volts for a bismuth concentration of 0.519 grams per 100 ml. of acid. These values check closely the value of -0.050 to S.C.E. (or -0.084 to N.C.E.) reported by Haring² for bismuth concentrations of 10^{-2} molal (.209 grams per 100 ml.). These results substantiate the conclusion that bismuth solutions of the above concentrations will not be reduced at the potential of the normal calomel electrode.

Tracings of bismuth polarograms are given by Plates P-50 and P-51. Two unexplained anomalies are noticed. (1) It would normally be expected that the diffusion current for a bismuth solution of 1.037 grams per 100 ml. would be twice that for a solution of 0.519 grams per 100 ml. The experimental ratio of 650 to 135 microamperes does not check the expected 2 to 1 ratio. (2) A second inflection

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CATHODE CONTROLLED POLAROGRAM

1.1559 gms. Bi_2O_3 (1.037 gms. Bi)

per 100 ml. 6.5N HNO_3

Circuit "I" Plate 31 0.06 Volts/Min.

150 mv. Speedomax 18"/Hr. $R_2 = 100 \sim$

Platinum Wire Cathode

and Anode

30 min. N_2 Flush

Gears 24-72-48

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CATHODE CONTROLLED POLAROGRAM

0.519 gms. Bi per 100 ml. 1.5 N HNO₃

Circuit "I" Plate 31 0.06 Volts/Min.

150 mv. Speedomax 18"/Hr. R_s = 100-Ω

Platinum Wire Cathode and Anode

30 min. N₂ Flush

Gears 24-72-48

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Plate P-58

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at -0.2 volts (Point "A", Plate P-50) is unexplained. Hydrogen elimination would not be expected until a potential of at least -0.29 was reached.

The bismuth decomposition potential in a concentration of 0.519 grams per 100 ml. of -0.09 volts (Plate P-50) is about the value to be expected from previous work. In this concentration, the second inflection corresponds to the expected hydrogen reduction potential of -0.3 volts to N.C.E.

Two polarograms in 1.5 N nitric acid solutions without bismuth were made in order to locate oxygen and hydrogen waves. Plate P-52 is a polarogram in the acid saturated with oxygen. The oxygen wave starts at 0.25 volts and the hydrogen at the expected value of -0.30 volts. The presence of the oxygen wave at this potential necessitates the removal of oxygen from bismuth solutions before determining the bismuth diffusion current or decomposition potential. Plate P-53 is a polarogram of the acid flushed with nitrogen to remove oxygen. A perfectly flat base line was realized until the hydrogen reduction potential of -0.29 volts was reached.

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1. Staniforth, R., "Production Electrolysis Studies I", Information Report, MM-130, June 16, 1948.
2. Haring, M., "Polarization Studies", Information Report No. 22, January 22, 1945.

Future Plans

Research studies being conducted or anticipated by the General Chemistry Group are listed below. Detailed discussions are either given in this report or will follow in future reports as indicated.

<u>Subject</u>	<u>Chemist</u>	<u>Status</u>
Determination of the Standard Potential of Postum by Equilibrium Studies	P. Dismore	A-F
Dialysis Studies of Postum Solutions	S. Barth	A-F
Polarography with the Cathode Controlled Polarograph	M. Ford	A-F

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CATHODE CONTROLLED POLAROGRAM

1.5 N HNO_3 10 min O_2 Flush
Circuit "I" Plate 31 0.03 Volts/min.
150 mv Speedomax 18 in/hr. $R_2 = 1000 \sim$
Platinum Wire Anode and Cathode
Gears 24-60-96

Current
7.5 μa

Cathode Potential vs. N.C.E.

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Plate P-52

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CATHODE CONTROLLED POLAROGRAPH

1.5 N HNO₃ 30 min. N₂ Flush
 Circuit I: Plate 3V 0.03 Volts/min.
 150 mv. Speedomax 18 in/hr. R₂ = 1000 ~
 Platinum Wire Anode and Cathode
 Gears 24-60-96

Cathode Potential Vs. N.C.E.

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Plate R53

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<u>Subject</u>	<u>Chemist</u>	<u>Status</u>
Decomposition Potentials of Postum Solutions	W. Power	A-G
Transference Studies	S. Barth	B-G
Zinc Analysis in Postum Solutions	M. Ford	E-G
Study of Postum Solutions by Use of Alpha Autoradiographs	W. Power	C-G
Study of Stability of Chemical Substances in Presence of Alpha Radiation	P. Dismore	C-G
Preparation of Organic Compounds of Postum	P. Dismore	C-G
Phase Study of Postum with Other Metals		D-G

- A - Research in Progress.
- B - Research Completed.
- C - Anticipated Research.
- D - Proposed Research for this or Other Groups.
- E - Research Dropped.
- F - Plans Outlined in this Report.
- G - Write-up to Follow.

DETERMINATION OF THE STANDARD POTENTIAL OF POSTUM FROM EQUILIBRIUM STUDIES -
P. Dismore

I. Statement of Problem

This research has for its purpose the determination of the standard potential of postum by the application of equilibrium studies.

This method has been suggested by Dr. John H. Payne, Jr., who has used the equilibrium technique to study hydrochloric acid systems.

II. Reason for Interest in the Problem

A precise determination of the standard potential of postum would be of considerable interest, both practically and academically.

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From a practical standpoint, the reversible voltage in a given electrolyte could be calculated from the standard potential if suitable activity coefficients and knowledge of the complexity of the postum ion in a given solvent were known. This reversible potential should correlate with the most positive plating potential that could be expected for postum deposition. Also, if the standard potential were known, e.m.f. data could be used to determine the complexity of postum ions in solution.

The standard potential allows one to calculate free energy and equilibrium data by the use of the expression:

$$-nFE^{\circ} = \Delta F^{\circ} = -RT \ln K$$

If the temperature coefficient of an electrolytic cell is known, it is possible to calculate the heat of reaction:

$$\Delta H = nF \left(T \frac{\partial E}{\partial T} - E \right)$$

Equilibrium data may be used to assign a value to the oxidation state of postum in solution. For instance, if two couples of potential difference, ΔE , in the same solvent medium are allowed to scrub postum, the oxidation state, n , may be calculated by the expression

$$\Delta E = \frac{-0.059}{n} \log \frac{a_1}{a_2}$$

where a_1 and a_2 are the postum activities in the two scrubbed solutions.

III. Present State of Knowledge of the Problem

Kasarnovsky¹⁵, by extrapolation of the standard potentials of Group VI elements, calculated the value for the postum couple, $Q = Q^{++} + 2e$. $E^{\circ} =$ approximately -1.0.

Paneth and Hevesy¹ and Haissinsky^{2,3,24} have studied the potentials for the cathodic reduction of postum to the metal. From their work, the standard potential lies in the range:

$$Q = Q^{++} + 2e \quad E^{\circ} = -0.65 \text{ to } -0.85$$

Haissinsky and Guillot¹³ state that in the presence of chemical reducing agents postum exhibits the oxidation number of three, and:

$$Q = Q^{+++} + 3e \quad E^{\circ} = -0.53$$

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A later value of Haissinsky⁴, assuming an oxidation state of four in nitric acid solution, is:

$$Q = Q^{++++} + 4e \quad E^{\circ} = -0.77$$

These values were obtained by first determining the decomposition potentials of the metal from extremely dilute solutions, of the magnitude of 10^{-8} to 10^{-9} N, and calculating the standard potential at unit activity by use of the Nernst equation. The applicability of the Nernst equation for these very dilute solutions has been questioned.^{5,6,12} Haissinsky^{2,7,11} however, claims that the equation is valid. He states that the element exhibits oxidation states of two and four depending upon whether the acid medium is reducing or oxidizing.^{7,8,9} The presence of reducing agents (hydrazine, hydroylamine, oxalic acid, or hydrogen peroxide) is claimed to greatly decrease the decomposition potential. This was interpreted as the deposition of postum from a valence state lower than four. In addition to the consideration of cathode decomposition potentials, anode deposition is also discussed.^{2,4,6,8,10}

Haissinsky^{10,12,13} claims that the deposition potential is influenced by the acidity of the solvent, by the nature of the cathode material, and by the presence of salts in the electrolyte.

Standard potentials can be calculated from the decomposition potential data of Haring¹⁶. The following values were calculated, using 0.245 for the potential of the saturated calomel electrode, an oxidation state of two and an activity coefficient of 0.75 for postum ion in 1.5 N nitric acid.

<u>Concentration of</u> <u>Postum, Mols/Liter</u>	<u>Calculated E°</u> <u>(Average of 8 Values)</u>
4×10^{-4}	-0.678
4×10^{-5}	-0.679

Attempts to determine the electrode potential of postum directly have not been successful.¹⁷ It has been found that solvent decomposition products govern the solution potential of a postum solution rather than the postum-postum ion couple.

IV. Proposed Method

A. Methods Available for the Determination of the Standard Potential of a Couple

1. Direct measurement of the reversible potential over an

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appropriate concentration range and the use of extrapolation methods recommended by Lewis and Randall¹⁸ is used when possible. This method has been found to be unfeasible for postum due to solvent decomposition from alpha bombardment.

2. Potential values from thermal data¹⁹ are not applicable for postum, since the measurement of heat of reaction and specific heat of the minute quantities of materials which are heat sources by virtue of their radioactivity is not possible.

3. Decomposition potentials have been used to obtain the existing data on the solution potential of postum. Several questionable points arise when considering this method, however. Recognition of the decomposition potential by the initiation of a reduction current at the cathode is open to the criticism that cathode reduction may be due to solvent decomposition products such as oxygen, ozone, hydrogen peroxide, or chlorine and not to postum reduction itself. If the initial process of the decomposition potential determination is the deposition of postum, the method may be applicable, but if reduction of other materials precedes that of postum, the inflections are misleading.

Irreversible methods in general must be treated with caution for the determination of equilibrium conditions. Reduction potentials are frequently more negative than the reversible potentials, depending upon overvoltage characteristics of the cathode material.

4. The determination of potential values from equilibrium constants is a general method which is thought to be applicable for establishing the standard potential of postum. If a suitable couple M/M^{++} can be found which will partially reduce postum in a given solvent;

where M and M^{+} are the reduced and oxidized form of the controlling couple and n is the valence of Q , the equilibrium constant can be calculated.

The equilibrium constant, K , is related to the standard potential, E° , by the expressions:

$$K = \frac{a_Q a_{n+}^n}{a_n a_{Q^{n+}}}$$

$$-nFE^{\circ} = \Delta F^{\circ} = -RT \ln K$$

B. Possible Systems for Equilibrium Study

Choice of a suitable solvent for postum requires consideration of several points:

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1. As far as is known, postum is soluble only in strong acids or bases.

2. To minimize hydrolysis, strong acids should be selected. To avoid complication in the oxidation-reduction system of the equilibrium study, oxidizing acids should be avoided.

To facilitate interpretation of results, acids known to strongly complex with postum should be avoided. Also, equilibrium in hydrochloric acid solution is being studied by the Production Research Group. Sulfuric acid, perchloric acid, and potassium hydroxide are the most promising solvents.

The choice of an oxidation-reduction couple with which to establish equilibrium is governed by the following considerations:

1. The potential of the couple must be close to that of the postum system. Too great a differential will result in either complete reduction of postum ion or no reduction instead of the desired partial reduction.

2. The electrode system should have stability. This equilibrium method depends upon the potential of the system being fixed by the control couple which is present in much greater quantities than the traces of postum. The impossibility of analysis of minute changes in the control couple requires that its potential and concentration remain fixed, and only the postum concentration need be determined after equilibrium has been attained.

3. In order to assure constancy of potential and to minimize the effect of concentration changes due to the effect of alpha activity on the solvent, it is desirable to use a couple existing in two solid forms, the oxidized form being a slightly soluble salt of the solvent. Such a system would have considerable capacity to oxidation or reduction without changing potential. Couples which may meet the above requirements are listed below.³

<u>Acid Systems for Q/Qⁿ⁺</u>	<u>E°</u>
$\text{SO}_4^{--} + 2 \text{Hg} = \text{Hg}_2 \text{SO}_4$	-.6151
$2\text{H}_2\text{O} + \text{Te} = \text{TeO}_2 (\text{s}) + 4\text{H}^+$	-.529
$\text{SO}_4^{--} + 2 \text{Ag} = \text{Ag}_2 \text{SO}_4$	-.653
$\text{Se} + 3\text{H}_2\text{O} = \text{H}_2\text{SeO}_3 + 4\text{H}^+$	-.740

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Acid Systems for Q^{n+}/QO_2 E° Basic Systems for Q/Q^{n+} Basic Systems for Q^{n+}/QO_3^{m-}

* Does not have solid forms.

The most promising couple is believed to be the mercury-mercurous sulfate system in sulfuric acid. The equilibrium between this couple and postum is:

$$K = \frac{1}{a_{SO_4^{--}} a_{Q^{n+}}} \quad \text{where}$$

$$a_{Q^{n+}} = C_{Q^{n+}} r_{\pm}$$

$r_{\pm}$ = activity coefficient of sulfuric acid.

$$E^\circ = - \frac{RT}{nF} \ln K.$$

Since E° for the mercury couple is known, the standard potential for postum may be calculated by difference if a value for the valence, n , can be assigned. This method is applicable for the determination of valence, since only the correct value will lead to a calculation of the

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same standard potential of postum, regardless of acid concentration. Also, if two couples with slightly varying potentials can be found which will partially reduce postum in the same solvent, the valence of postum can be calculated directly:

$$E_1 = E^\circ - \frac{.059}{n} \log a_1 Q^{n+}$$

$$E_2 = E^\circ - \frac{.059}{n} \log a_2 Q^{n+}$$

$$n = \frac{.059}{E_1 - E_2} \log \frac{a_2 Q^{n+}}{a_1 Q^{n+}}$$

C. Experimental Procedure

Before starting work with activity in sulfuric acid solution, it will be necessary to investigate the practicability of using that medium. Two points of concern are: (1) Is sulfuric acid a suitable solvent?, and (2) Can satisfactory analyses of activity in sulfuric acid solutions be made?

Wehrmann²⁰ states that postum solubility in 1.0 to 1.5 N sulfuric acid is less than 0.05 c./ml. He also states that a pink precipitate forms in dilute sulfuric acid solutions of postum.

Alpha analysis of sulfuric acid is complicated by its non-volatility. Spontaneous deposition on silver, copper, nickel, or stainless steel may be necessary to allow the removal of the non-volatile sulfuric acid by washing. Spontaneous deposition may be accompanied by an undesirable salt formation due to the action of the acid on the metal surface. A counting technique has been developed by displacing the postum on silver discs from 1.5 N sulfuric acid.²² Accurate counts were obtained in the range of 10^7 d./min./10 lambda, and counts which were consistently ten per cent low were obtained in the range of 4000 d./min./10 lambda.

Fortunately, due to the logarithmic form of the Nernst equation, and error of twenty per cent in alpha analysis would result in an error of only two millivolts in the standard potential if the postum concentration is in the neighborhood of 10^{-8} m.

The mercury-mercurous sulfate couple will be prepared according to the directions of Harned and Hamer²¹. The container used for tumbling will be a drawn-out standard centrifuge tube in which the system can be sealed.

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The potentials of the mercury half cells will be checked by preparing the cell:

and comparing the e.m.f. with the values of Harned and Hamer²¹.

Although quantities of each phase present should not be critical, it is probably advisable to measure each ingredient in order to make possible an activity balance if this is believed advisable, or to duplicate times required for reactions with postum to reach equilibrium.

Suggested quantities:

Mercury	6 gm.
Mercurous Sulfate	3 gm.
Sulfuric Acid Solution	1 1/2 ml.

Suggested acid concentrations are 2, 1, 0.5, 0.2 and 0.1 m.

Postum micro foils will be purified by revolatilization, sublimed into a suitable closed tube, calorimetered, and broken under 2 m. sulfuric acid solution. A stock solution of about 0.05 c./ml. will be prepared and a sufficient amount pipetted into the drawn-out centrifuge tube to make a concentration of approximately 10^9 d./min./1.5 ml. The tube will be flushed with nitrogen, sealed, and tumbled at constant temperature (15°C., 25°C., 35°C., and 45°C.) until equilibrium has been attained. This may take several days or weeks. At the end of the tumbling period, the tube will be centrifuged, opened, the potential checked against a known mercury-mercurous sulfate cell, and a sample decanted for a second centrifuging. Counting slides will be prepared as indicated above.

D. Calculations

For values of sulfuric acid concentration for which equilibrium conditions are obtained, the potential of the following cell will be determined:

The potential of the mercury electrode can be referred to the standard hydrogen electrode by subtracting from E_1 the correction between the standard hydrogen and hydrogen in sulfuric acid.

$$E_2 = E_1 - \frac{RT}{nF} \ln a_{\text{H}^+}^2.$$

These values of E_2 are then plotted as a function of acid concentration. The intercept at $m = 0$ is the standard potential of postum.

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In case the concentration range over which equilibrium conditions exist is limited, it may be necessary to calculate the standard potential for a single equilibrium determination. In this case, a value must be assigned to the activity coefficient of postum. This value will be the mean activity coefficient of sulfuric acid.

V. Personnel Requirements

It is estimated that twelve man-months will be required to complete this problem. Dr. Paden Dismore is now working on this equilibrium study.

VI. Requirements for Special Apparatus

A constant temperature tumbler is required for this work. The machine has been designed and is awaiting construction.

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DIALYSIS STUDIES OF POSTUM SOLUTIONS - S. Barth

I. Statement of Problem

This problem is not a new one but is being reopened to augment the previous work of Fainberg¹.

The object of this study is to determine the soluble or colloidal nature of postum in various solvents.

II. Reason for Interest in the Problem

Little is known concerning the nature of postum in solution or in contact with various solvents. It is of considerable interest both from the standpoint of improving the recovery process and studying chemical properties of postum to learn as much as possible about the solution behavior of the material. When working on the biological aspects of postum, it is desirable to know if a given combination of

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postum in a liquid medium exists as a solution or colloid, since mechanisms of absorption and elimination might be different for the two forms.

III. Present State of Knowledge of the Problem

Fainberg¹ studied the dialysis characteristics of postum in acid, neutral, and basic solutions. He has reported that solutions are formed in the acid and basic media but that postum in neutral or only slightly acid or basic solution exists as a colloid. He reports a peculiar increase in dializable material in neutral buffer solutions as compared to slightly dializable regions in weak acids or bases.

IV. Proposed Method

Questionable points after reviewing the previous work are:

1. Does the presence of buffering agents affect postum solubility in neutral regions, or is the solubility peak, previously reported¹, a function of hydrogen ion concentration alone? Dialysis studies in neutral unbuffered solutions will therefore be made.
2. Does the pH of the unbuffered solvent change upon the introduction of activity? This question has been raised both in connection with this work and by biology workers who use unbuffered saline solutions as a postum solvent for injection into animals. A literature review and experiments to clarify this question are in order.
3. What interpretation can be given to diffusion studies? It is not entirely adequate to say that materials diffusing through a membrane are "soluble" and that materials left behind are in suspension or colloidal form. It would be more satisfactory to be able to assign definite particle sizes to material which is not dializable and to test the technique with materials of known particle size. A literature review is required.
4. Are solution concentrations being affected by any process other than diffusion? It may be possible that adsorption of activity by glass or by the collodion membrane itself is causing concentration changes which should not be assigned to solution diffusion. Conducting activity balances of material introduced into a diffusion system and the activity present in various parts after the experiment should clarify this point.

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5. Is the fifteen minute diffusion time recommended by Fainberg adequately long to permit precise results? Since after fifteen minutes diffusion time, the per cent of diffused material is rising rapidly, it is thought that longer periods to permit a closer approach to equilibrium conditions would be advisable. If longer diffusion times were used, such variable factors as solvent type, postum concentration, temperature, degree of agitation, variable membrane thickness and pore size would affect the per cent diffused less. It is planned to control temperature to eliminate this variable.

6. Do all concentrations of postum diffuse at the same rate? Fainberg uses the same proportionality constant for all concentrations, but S. Barth has indications that this assumption may not be true.

It may be advisable to augment dialysis technique with the alpha autoradiograph method of Boyd² in which "star bursts" on a photographic plate indicate the presence of aggregates.

V. Personnel Requirements

S. Barth is now working on this problem. It is estimated that twelve man-months will be required to complete the work.

VI. Requirements for Additional Equipment and Building Space

In order to prepare radioautographs, it is necessary to have a darkroom. Preliminary experiments, at least, can be performed if one of the darkrooms at Unit III can be borrowed. Also, a research microscope and camera attachment for examining alpha tracks, and darkroom developing photographic equipment would be required.

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POLAROGRAPHY WITH THE CATHODE CONTROLLER - M. Ford

I. Statement of Problem

The object of this research is to develop a method of polarography with inert electrodes whereby the potential of the cathode may be gradually and uniformly varied and the reduction current continuously recorded as a function of the cathode potential.

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II. Reason for Interest in the Problem

When studying the reduction potentials and diffusion currents of ions reducible at potentials more positive than mercury, it is necessary to use inert electrodes. (Refer to General Chemistry Progress Report, May 1-31, 1948). When using the conventional polarographic system, continuous control of the cathode potential is not possible. To illustrate this point, a polarogram of 0.001 M silver nitrate in 0.1 N KNO_3 was run with the Fisher "Electropode" and the results plotted on Plate P-54. The applied potential between platinum electrodes was increased at the rate of 0.1 volt every two minutes. Cathode potentials against the saturated calomel electrode were measured with a potentiometer through an L & N Thermionic Amplifier. Readings of potential and current were taken every two minutes $\pm$ ten seconds. Both anode and cathode potentials are plotted against time on Plate P-55. It is noticed that during the first twenty minutes, the cathode potential is not affected by application of increasing voltage between the electrodes, the inert anode being the only electrode to change its potential. It is not until the anode starts to gas oxygen (at point A) that it attains a reasonably constant potential and the cathode potential forced to more negative potentials. By using the standard plating control unit developed by the Electronics Section, it is thought that the cathode potential may be more uniformly varied, the reduction current continuously recorded by a Speedomax recorder, and the precision of polarography with inert electrodes increased. Such an improvement would be of general interest to those conducting polarographic work with inert electrodes.

Another interest in this technique is the application of essentially the same apparatus for determining the decomposition potential of postum. Here again, mercury electrodes cannot be used, and a platinum or gold anode is not stable. Ionization current due to postum deposition on an alpha-transparent platinum cathode will be continuously recorded on a Speedomax in this case instead of the reduction current.

III. Present State of Knowledge of Problem

No system for continuous electronic control of cathode potential has been reported in the literature. (1) Stationary electronic cathode control has been devised for electrochemical analysis, but this method has not been used for polarography.

IV. Proposed Method

The cathode controlled polarograph is described in General Chemistry Progress Reports for June 1-15, June 15-31, and July 1-15, 1947. It is proposed to extend its application to non-radioactive

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Plate P-54

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ions reducible at potentials more positive than mercury such as silver, ferric, or chromate ions, or organic materials such as quinone, nitrobenzene, or nitrophenol, or such elements as iodine or bromine. Also, oxidation potentials might be studied with controlled anode potential.

V. Personnel Requirements

It is estimated that the problem can be completed in six man-months. M. Ford has started work on the study.

VI. Requirements for Special Apparatus

The Electronics Section has constructed the cathode potential control unit and an electronic voltmeter. A motor-driven voltage divider with a smooth, continuous action and variable speed reducing gears is required.

REFERENCE

1. Diehl, H., "Electrochemical Analysis with Graded Cathode Control", G. Fredrick Smith Chemical Co., 1948.

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