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Prepared by: W. H. Power

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GENERAL CHEMISTRY PROGRAM REPORT

M. M. Haring
Laboratory Director

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Classification changed to
by Paul B. Hunt, Jr. 6/23/70
by Albert J. Wenzel, 7/14/70
Reviewed by C. W. Huntington 8/2/79

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GENERAL CHEMISTRY GROUP

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

ABSTRACT

Dialysis Studies of Postum Solutions - S. Barth

No change in the acidity of a pH 6.7 unbuffered solution with a postum content of 2.7×10^{-7} d./min./ml. was observed during a 24-hour period.

Determination of the Standard Potential of Postum by Equilibrium Studies - P. Dismore

The solubility of postum in 1.44 N sulfuric acid at room temperature was found to be 0.004 c./ml.

Concentrations of postum in 1.44 N sulfuric acid solution in contact with the mercury-mercurous sulfate couple for varying periods of time are given. Initial concentrations of 4.19×10^{-6} M are scrubbed to 2.25×10^{-6} M at the end of 70 hours. This partial scrubbing makes the determination of standard potential of postum by this method look promising.

Polarography with the Cathode Controlled Polarograph - M. Ford

Quantitative diffusion currents, decomposition potentials, and half-wave potentials are reported for bismuth in nitric acid solution. Similar quantities are reported for silver nitrate in potassium nitrate solution.

Decomposition Potentials of Postum Solutions - W. Power

An outline of a proposed method for the determination of postum decomposition potentials by the use of the cathode controlled polarograph and an ionization chamber is given.

DETAILED REPORT

DIALYSIS STUDIES OF POSTUM SOLUTIONS - S. Barth

Effect of Activity on pH of Neutral Solutions

Since interest has been shown on the effect of postum on the pH of unbuffered solutions, the experiment previously reported¹ has

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been repeated using refinements to eliminate as far as possible the effect of air and contact with glass on the pH of nearly-neutral solutions. Distilled water was placed in a polystyrene beaker fitted with a rubber stopper through which the glass electrode, calomel electrode, and nitrogen inlet and outlet were inserted. Postum solution was added to the water and the solution back-titrated with base until the desired pH was attained. Nitrogen was passed through the cell for fifteen minutes before taking pH readings in order to free the solution from carbon dioxide. A control sample without activity was checked simultaneously. A research model Beckmann pH meter was used.

REFERENCE

¹Barth, S., General Chemistry Progress Report, MIM-114, May 1-31, 1948.

Table I

EFFECT OF ACTIVITY ON pH OF NEUTRAL UNBUFFERED SOLUTIONS

Postum Concentration - 2.7×10^7 d./min./ml.

<u>Hours</u>	<u>pH of Active Solution</u>	<u>pH of Control Solution</u>
0	6.70	6.62
0.5	6.70	-
1.25	-	6.60
24	6.72	6.60

It is seen that neither the active nor the control solution changed appreciably during the 24-hour period. It is felt that this experiment was run under more carefully controlled conditions than previously reported runs¹, and that drifts of pH formerly observed were caused by carbon dioxide absorption or alkali leaching from the glass rather than from the effect of alpha radiation.

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

Solubility of Postum in 1.44 N Sulfuric Acid

Approximately one curie of postum was purified according to the procedure of Martin.¹ The purified activity was found by calorimetry to

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contain 1.026 c. This quantity was dissolved in 1.05 ml. of concentrated sulfuric acid and diluted to 25 ml. with distilled water. After the dilution, a white precipitate was noticed in the bottom of the flask, so the material was centrifuged for one-half hour. The acid concentration of the supernatant liquid was determined to be 1.44 N microtitration with 1 N sodium hydroxide solution using phenolphthalein as an indicator. The concentration of postum in solution was determined by Method 2.² The average value of six slides was 8.79×10^7 d./min./10 λ or 0.00396 c./ml. or 4.19×10^{-6} M. Thus, 0.099 c. dissolved in 25 ml. of 1.44 N sulfuric acid. The white precipitate was dissolved in nitric acid and was found to contain 0.91 c. Essentially all of the original activity was therefore accounted for. This work indicates that the solubility is less than a tenth of Schulte's³ estimate of less than 0.05 c./ml.

Preparation of Cells for Equilibrium Study

Cells were prepared using redistilled mercury, mercurous sulfate prepared according to the directions of Hulett⁴, and the postum solution. The cells were placed in a thermostat at 25.5°C. and shaken for various periods of time. The cells were then centrifuged for one-half hour, opened and a sample of the liquid taken for counting according to Method 7² and the results multiplied by 1.1 as recommended. The e.m.f. of the cell against a similar mercurous sulfate half-cell was measured. A similar series of cells was made except that commercial mercurous sulfate was used. Results are given in Table II.

Table II

POSTUM-MERCURY, MERCUROUS SULFATE, SULFURIC EQUILIBRIUM

Run	Shaking Time Hours	Average c./min./ml.	Prob. Error of Mean ^a	Molarity	e.m.f. mv.
-	-	4.40×10^9	0.0%	4.19×10^{-6}	-
1	25.5	5.14×10^6	1.0	4.89×10^{-9}	1.2
2	70	2.36×10^6	0.1	2.25×10^{-9}	1.8
3	142	2.12×10^6	1.5	2.02×10^{-9}	2.1
4 ^b	27	2.15×10^6	1.1	2.05×10^{-9}	1.1
5 ^b	143	2.12×10^6	0.8	2.02×10^{-9}	-
6 ^c	66	1.31×10^6	-	1.25×10^{-9}	2.5

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a. Probable error (50 per cent index) calculated from six slides due to slide preparation only.

b. These cells contained commercial mercurous sulfate.

c. This cell was shaken at room temperature (not controlled), the sulfuric acid concentration was 1.50 N, and the sample was tumbled on a different tumbler.

The data are not yet complete enough to draw any definite conclusions. However, it is interesting to speculate on the results. The first three runs indicate that cells using mercurous sulfate prepared according to the method of Hulett are approaching equilibrium, although this state has not been reached at the end of six days. The concentrations of runs 4 and 5 lead one to believe that equilibrium has been reached. These cells used commercial mercurous sulfate and thus commercial mercurous sulfate may be better than that prepared electrolytically. It is interesting to note that runs 3 and 5 have the same concentration. This may mean that equilibrium has been reached. Run 6, however, indicates that something is wrong. Although there were slight differences in the way this cell was handled, it is not thought that these would make such a great difference in the concentration. There are two other ways to explain this cell. It may be that the equilibrium concentration is lower than that indicated in the first five runs or it may be that the cells are greatly affected by some unknown cause. In order to answer the questions raised in the paragraph further work is necessary.

Additional cells will be constructed and tumbled for longer time intervals to determine when equilibrium is reached. A series of samples using commercial mercurous sulfate will be prepared. In order to check reproducibility, another series of cells using purified mercurous sulfate will be prepared. A fourth series of samples will be prepared starting with a lower initial concentration of postum. The equilibrium concentration of postum should be independent of the starting concentration. However, the rate of attaining equilibrium should be a function of the initial concentration and thus kinetic data can be obtained.

REFERENCES

1. Martin, A., Gamma Scale Progress Report, June 1-30, 1948, p-4.
2. Dismore, P., General Chemistry Progress Report, May 1-31, 1948, p. 5-6.
3. Schulte, J., Final Report No. 14, p. 53.
4. Hulett, Phys. Rev., 32, 257 (1911).

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POLAROGRAPHY WITH THE CATHODE CONTROLLED POLAROGRAPH - M. FordBismuth Solutions

Decomposition potentials and diffusion currents of solutions of bismuth in nitric acid solution were determined with the stationary platinum electrode and cathode controller as previously described. Diffusion currents, decomposition potentials, and half-wave potentials are listed in Table III.

Table III

POLAROGRAMS OF BISMUTH SOLUTIONS IN 1.5 N HNO₃ WITH PLATINUM ELECTRODE

Concentration of Bismuth		Decomposition Potential vs. N.C.E. Volts	Half-Wave Potential vs. N.C.E. Volts	Diffusion Current Microamps	Ratio Conc.	Diff. Curr.
gm. Bi ₂ O ₃ Per Liter	Molar					
11.148	0.048	-0.06	-0.065	640	2.00	2.14
5.574	0.024	-0.06	-0.065	300	2.00	2.18
2.787	0.012	-0.08	-0.09	138		

Reasonable values for diffusion current ratios give weight to the selection of the current inflections as being due to bismuth reduction (rather than due to the reduction of possible impurities). The observed values of diffusion current ratios of greater than the theoretical value of 2-1 may be explained by the fact that the cathode area is increasing more rapidly in the case of the more concentrated solutions.

Improved technique used when making the above runs including shutting off the stirring motor when measuring diffusion currents, has eliminated the diffusion current ratio anomaly mentioned in the last report.

Polarograms of Silver with the Cathode Controlled Polarograph

In order to demonstrate the application of the cathode controller for polarography with inert electrodes, a series of polarograms was prepared of silver nitrate in 0.1 N potassium nitrate solution. Typical polarograms are shown by Plate P-56. Due to the fact that base lines and plateaus were not parallel, a record was made with the potassium nitrate base solution and this superimposed on those made with silver nitrate added. Diffusion currents were measured at three potentials in order to ascertain the best potential for quantitative measurements.

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POLAROGRAPHIC DETERMINATION OF SILVER

Gears 96-60-24
R-25000
150 mv Speedomax
Electrode 2
Constant temperature 25°C
N₂ swept
Hook-Up I Plate 31

CURRENT
3X10⁻⁶ amps

$E_{1/2} = .247$

$E_d = .272$
 $E_d = .254$

0.00010 N AgNO₃

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The same platinum cathode, 4 mm. of No. 24 wire, was used for all determinations. The cell was thermostated at 25°C. During the run, all motors were turned off so as not to shake the cell. Solutions were swept with nitrogen for 30 minutes before running to free them from oxygen.

To determine the reproducibility of the polarograms, ten runs were made at each silver concentration.

Table IV

POLAROGRAMS OF SILVER NITRATE IN 0.1 N KNO₃

Concentration of Silver Nitrate, Molar
Diffusion Current, Microamperes
(Average of Ten Runs)

	0.0005	0.00025
at .10 volt	2.04 ± .096* (4.7%)	.96 ± .018* (1.9%)
at .15 volt	1.95 ± .066 (3.4%)	.93 ± .018 (1.9%)
at .20 volt	1.92 ± .060 (3.1%)	.89 ± .012 (1.3%)

Diffusion Current Ratio

at .10 volt	2.12	
at .15 volt	2.10	
at .20 volt	2.16	
Decomposition Potential	0.272 ± .008	.254 ± .004
Half-Wave Potential	0.265 ± .002	.247 ± .006

* Probable error, 50 per cent index.²

Polarograms for the lower concentration were much more regular and the plateaus flatter than for the 0.0005 M solution. Polarograms for the stronger solution showed undesirable maxima which made quantitative measurements difficult. These maxima were not present for the lower concentration, so it is hoped that precision will be better and the diffusion current ratios closer to theoretical values as the concentration of silver ion is decreased.

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The consistency with which diffusion currents can be reproduced is gratifying, since the usual precision of polarograms run with stationary electrodes is in the order of five per cent. The theoretical 18 millivolt shift toward more negative potentials of the decomposition potential was realized. The half-wave potentials were not independent of concentration, however, as is true for reversible waves run with the dropping mercury electrode.

REFERENCES

1. Ford, M., Fundamental Research Progress Report, June 1-15, 1947.
2. Staniforth, R. A., Seminar of December 9, 1946, p. 10-11.
3. Ford, M., General Chemistry Progress Report, MM-133, June 1-30, 1948.

DECOMPOSITION POTENTIALS OF POSTUM SOLUTIONS - W. Power

Future Plans

I. Statement of Problem

This problem is concerned with an experimental determination of the potential at which postum is electrodeposited on an electrode from a variety of solvents. The deposit may be either at the cathode or anode.

II. Reason for Interest in the Problem

Determination of the decomposition potential of postum is of considerable interest from a production standpoint and also for studying the ion nature of postum in various solvents.

In order to effectively separate postum from more active elements by electroplating, it is necessary to have basic information regarding potentials at which postum and the impurities are cathodically reduced. Other interests in decomposition potentials include a determination of the oxidation state of postum in different solvents, and the possible preparation of compounds by either anodic oxidation or cathodic reduction. The cathodic decomposition potentials are expected to be slightly more negative than the reversible potential, and may be used to approximate standard and potential values for the elements and ions being studied.

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III. Present State of Knowledge of Problem

The general problem of determining the reversible potential of postum in aqueous solutions was discussed previously.¹¹ Conventional techniques for determining decomposition potentials or reversible potentials are not applicable for postum due to solvent decomposition caused by alpha activity. In order to distinguish between the reduction of postum and solvent decomposition products, measurement of postum deposition by alpha counting has been used.^{2,3,4,5,6,7,8,9} The method of Hevesy and Paneth² of removing the cathode for alpha counting after deposition is open to the criticism that stripping of the postum deposit is very rapid when the current is released from the cathode. Joliot³ improved the technique by using an alpha-transparent membrane and counting the cathode in position during the plating process. This technique has many advantages over the intermittent method and is the one that will be adapted for future studies by this group.

IV. Method

The problem of controlling cathode potentials in the absence of a stable anode has been discussed.¹¹ The standard plating control unit of the Electronics Section has been adapted for controlling cathode potential. An ionization chamber has been constructed to measure alpha flux outside of an alpha-transparent cathode, and an amplifier and recorder used for continuously recording the ionization current. This ionization is characteristic of only radioactive materials concentrated at the electrode and will not respond to other reduction currents as would the conventional cathode of a polarograph.

A sketch of the cell which has been constructed for decomposition potential study is given by Figure A, Plate P-54. The most critical material is the platinum or gold foil, thin enough to permit the passage of alpha particles but free from pin holes. Platinum foil with a weight of 5 mg./sq. cm. has been successfully used for this purpose. Since the foil was not free from pin holes, a thin coating of platers' stop-off paint was applied to the side which faces the ionization chamber to prevent leakage of active solution to that side of the foil. Two alpha-transparent rubber hydrochloric films were inserted between the foil and the chamber to prevent leakage of active solution into the chamber if a defect should develop in the foil. Electrical contact with the thin foil was made through a 0.010" platinum washer. The ionization chamber tube was made by sawing off the end of a male 18/9 ball and socket joint and grinding the end flat with emery on glass. The active solution compartment was similarly constructed from a male 18/7 ball and socket joint. The cell assembly was fastened together by a ball and socket clamp. The ionization chamber tube was fitted in a hole in the side of a cold box so that the active solution was contained in the box, and electrical equipment and

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Fig. A

CELL FOR MEASUREMENT OF
DECOMPOSITION POTENTIAL

Fig. B.

CALOMEL ELECTRODE

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Plate P-54

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personnel were protected from activity. Figures A and B, Plate P-55 show hook-ups used for controlling the cathode potential of the alpha-transparent foil and for measuring and recording the ionization current produced by deposition of postum on the foil.

PERSONNEL REQUIREMENTS

If this study proves to be fruitful, it will probably be expedient to request the services of an additional man in the group to carry on the work.

VI. Requirements for Additional Equipment and Building Space

At present this work is being done by the writer in very cramped quarters. Another person is conducting "cold" experiments in the same tiny room. It is necessary that additional space be assigned if this work is to be carried on.

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Fig. A

CATHODE CONTROLLED CIRCUIT - J
WITH IONIZATION GAUGE

Fig. B

CATHODE CONTROLLED CIRCUIT - K
WITH IONIZATION GAUGE

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Plate P-55