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MONSANTO CHEMICAL COMPANY - UNIT III

DAYTON, OHIO

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GENERAL CHEMISTRY PROGRESS REPORT

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GENERAL CHEMISTRY GROUP

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

ABSTRACT

Diffusion Studies - S. Barth

Acidities of unbuffered active solutions with initials pH's of 4 and 6 were followed over periods of 7 and 44 hours. Little change was noticed in the case of the pH 4 solution, while a drift toward the basic region was observed with the pH 6 solution.

Measurement of Standard Potential of Postum - P. Dismore

Nine techniques were tried for counting sulfuric acid solutions of postum. The most satisfactory method used consisted of displacement plating of postum on silver foil followed by washing the non-volatile electrolyte from the surface. Results were consistently about 10 per cent low for counts of approximately 4000 c./min./10 lambda but were satisfactory for concentrations in the range of 10^7 d./min./10 lambda.

Polarography with the Cathode Controller - M. Ford

The use of the electronic cathode controller as a refinement for polarography with microplatinum electrodes is discussed.

Determination of Decomposition Potential by Ionization Chamber Technique - W. Power

Apparatus has been constructed for following the reduction of postum by an ionization current inflection.

DETAILED REPORT

Diffusion Studies - S. Barth

The stability of unbuffered active solutions toward change of pH has been questioned in connection with diffusion studies in unbuffered media. To obtain evidence in this connection, the acidities of unbuffered inactive solutions with pH's of 4 and 6 were followed with a Beckman glass electrode meter over periods of 7 and 44 hours. Solutions were contained in open beakers.

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Table I

THE ACIDITY OF UNBUFFERED NITRIC ACID SOLUTIONS INITIAL pH 6.5

Hours	Control Solution (No Activity)
0	6.32
1	6.38
3	6.45
19	7.01
20	7.08
25	7.09
43	6.98
44	7.00
Initial pH 4.1	
0	4.38
4	4.45
6	4.49
7	4.47

Apparently, unbuffered solutions of the pH used have a tendency to drift in pH. This drift seems to be in the direction of increasing pH.

Future Plans

Additional work on the behavior of unbuffered solutions in glass is necessary to determine whether the effect apparently detected is real.

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MEASUREMENT OF STANDARD POTENTIAL OF POSTUM - P. Dismore

The determination of the standard potential of postum in sulfuric acid solution by equilibrium methods requires a method of accurately counting activity in that electrolyte. The use of non-volatile solvents as sulfuric acid present a slide preparation problem more difficult than the usual method of evaporating volatile solvents on glass surfaces. Nine techniques were tried, all consisting of displacement deposition of postum onto silver or copper foil followed by washing the non-volatile electrolyte from the disk. A known active solution was prepared by dissolving 0.9633 c., determined by calorimetry, in 1 ml. of concentrated nitric acid and diluting with distilled water to 10 ml. One hundred lambda of this solution was diluted to 10 ml. with 1.5 N sulfuric acid to make solution "A". 0.005" silver foils, one inch in diameter, were etched with 8 N nitric acid until the silver had a crystalline appearance, washed with distilled water and dried. Methods of preparing the counting samples are listed below.

Method 1 - Ten lambda of solution "A" was pipetted onto a silver disk and allowed to stand over water for one hour. The disk was then rinsed with a stream of distilled water, dried, and counted. Six slides gave an average count of 1.86 x 10^7 d./min./10 lambda which was 2.6 per cent below the calculated value.

Method 2 - Another set of six slides was made as described in Method 1 except that the pipette was rinsed with 1 N hydrochloric acid. These slides had an average count 1.7 per cent below the calculated value. From these results, it is concluded that slides in the Logac range can be prepared satisfactorily by plating onto silver

Method 3 - Solution "A" was diluted so that a ten lambda sample would contain about 4000 c./min./10 lambda. This was known as solution "B" Five slides were prepared from this solution by placing ten lambda on the silver foil, placing the foil over water for one hour, rinsing, drying, and counting. The average of these slides was 10 per cent below the calculated value.

Method 4 - A ten lambda rinse of 1 N hydrochloric acid was added to the slides as prepared in Method 3. The average count of these slides was 8 per cent below the calculated value.

Method 5 - Slides were prepared as in Method 4 but allowed to stand over water for two hours instead of one hour. The results were 10 per cent low.

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Method 6 - Ten lambda of solution "B" and an equal quantity of 1 N hydrochloric acid were allowed to stand on silver for eighteen hours. The average count was 2.5 per cent higher than the calculated value, but there was too great a spread among the individual counts for this to have significance.

Method 7 - In most of the cases where hydrochloric acid was present, a darkening of the slide due to silver oxide formation was observed. (See English translation of Gmelin, p. 118). Gmelin states that this oxide is not formed in the presence of a reducing agent as hydrazine. To test this, slides were made by placing ten lambda of solution "B" on the foil and adding ten lambda of a 1 per cent solution of hydrazine sulfate in 1 N hydrochloric acid. After standing for one hour, the slides were rinsed, dried and counted. These slides also had a deposit of silver oxide. Two sets of slides were made in this manner, one set counting 10 per cent low and the other 8.6 per cent low.

Method 8 - If the sulfuric acid is neutralized with ammonium hydroxide and the neutral solution allowed to stand one hour before rinsing, drying, and counting, the results are again 9 per cent low.

Method 9 - An attempt was made to deposit the activity on copper. Copper discs were etched with dilute nitric acid, washed and dried. Ten lambda samples were placed on the slides and allowed to stand over water for one hour before rinsing, drying, and counting. In this case the results were 15 per cent low.

No technique has been found to date which will give accurate counting results of postum dissolved in 1.5 N sulfuric acid in concentration ranges of 4000 c./min./10 lambda, although consistently low results have been obtained. Due to the logarithmic form of the Nernst equation, a fairly large error in measuring the concentration of postum makes only a small error in the standard potential calculation. Thus, if the valence change is four and if there is a five per cent error in the concentration determination, the error in the potential is

$$\frac{0.05915}{4} \log 1.05 = 0.0003 \text{ volts.}$$

Thus, it is thought that it will be satisfactory to deposit the activity on silver and multiply the measured value by 1.1 to obtain the true counts in the region of 4000 c./min./10 lambda.

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Future Plans

It is planned to proceed with equilibrium studies between mercury and postum in sulfuric acid solution, using the silver displacement technique for determination of concentration.

POLAROGRAPHY WITH THE CATHODE CONTROLLER - M. Ford

The conventional dropping mercury electrode limits the range of polarographic analysis to those ions which reduce at a potential more negative than the reducible potential of mercury. This is due to the fact that the oxidation current of mercury itself would overwhelm any minute reduction current occurring at potentials more positive than that of mercury. Also, the concentration of the reducible ion would be constantly diminished by the mercury anode.

Platinum electrodes, although not as satisfactory as dropping mercury electrodes in more negative potential regions can be used in the more positive range. For a variety of reasons, the platinum electrodes are not as stable as the dropping mercury electrodes, and the problem of electrode potential control without a stable anode is more difficult. The accuracy of polarography with platinum electrodes is, accordingly, about ± 5 per cent in the best cases; whereas, an accuracy of ± 0.5 per cent is possible when using dropping mercury electrodes.

In order to facilitate the control of platinum electrode potential, the Electronics Section has proposed to adapt the standard electronic plating control unit. If the bias between the grid of one 6J7 tube and ground is uniformly varied instead of being held constant as in the usual application of the plating control, the cathode potential will also be varied in a similar uniform manner. Cell current can then be continuously recorded, (refer to Progress Report dated June 15, 1947). Such uniform control of the microplatinum cathode potential may improve the accuracy of polarograms obtained with the solid electrode.

Future Plans

It is proposed to demonstrate the use of the potential controller for polarographic work by analyzing for silver ion in potassium nitrate supporting electrolyte. The use of the platinum electrode in conjunction with the usual polarographic arrangement for such silver analysis has been reported by Laithenen and Kolthoff,

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(J. Phys. Chem. 45, (1941)). This technique will be duplicated and then run with the addition of the cathode controller to the circuit. If successful, the analysis for other ions reducible at potentials positive to mercury will be attempted.

DETERMINATION OF DECOMPOSITION POTENTIAL BY IONIZATION CHAMBER TECHNIQUE - W. Power

Apparatus has been constructed for following the reduction of postum by an inflection in the ionization current as the potential of the alpha transparent cathode is made increasingly negative. This inflection should be associated with postum reduction only. The usual electrolysis currents in active solutions may be due to reductions of solvent decomposition products such as hydrogen peroxide or oxygen rather than reduction of the postum itself. A detailed description of the method will be given in the next report.

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