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PROGRESS REPORT
APPLICATION OF THE POLAROGRAPH TO ANALYSIS
OF TITANIUM-BASE ALLOYS

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SUMMARY

The present report covers the period from December 7, 1952, to February 7, 1953. During this period an extensive study was made of the changes in half-wave potential and in diffusion current of ferric ion with respect to change in the concentration of the potassium fluoride supporting electrolyte and change in pH of the polarographic solution.

SUMMARY OF RESULTS

A. Experimental

Several stock solutions were prepared, each 0.40 mM in ferric ion but varying in potassium fluoride concentration from 1 M to 0.3 M. The pH of each of these solutions was measured and polarograms were taken of each at $25 \pm 0.1^\circ\text{C}$. The pH was then adjusted to values above and below the original values by the addition of small amounts of hydrochloric acid or potassium hydroxide solution, and the polarograms of the resulting solutions were recorded.

B. Interpretation of Data

Analysis of the polarograms obtained yielded the following data:

Potassium Fluoride Molarity	pH	Ferric Ion Species	
		$I_d, \mu\text{amp}$	$E_{1/2}, \text{volts}$
0.3	5.8	1.52	-0.455
0.4	5.8	1.76	-0.467
0.5	5.8	1.47	-0.471
0.6	5.8	1.72	-0.475
0.75	5.8	1.65	-0.481
1.00	5.8	1.55	-0.494
1.00	6.3	0.95	-0.492
0.6	5.4	0.45	-0.478
0.5	6.2	0.11	-0.471
0.5	5.4	0.68	-0.471

From these data, we see that a pH of 5.8 seems to be the optimum pH for the polarographic determination of ferric ion in a fluoride medium. Values of pH on either side of this value show a marked decrease in the diffusion current. This phenomenon could very well explain the discrepancy in the literature as to the $E_{1/2}$ for the ferric-fluoride system. Values of pH very far from 5.8 would completely obliterate the wave, which may explain the fact that West and Dean¹ claimed to have found no reduction wave for ferric ion in fluoride prior to the discharge of sodium ion. Our results are in complete disagreement with those of Stackelburg and Freyhold,² who reported that ferric ion produced a reduction wave with $E_{1/2}$ of -1.36, which remained constant when the concentration of potassium fluoride was increased from 0.04 to 0.8 M. The wave they observed was probably due to hydrogen discharge rather than to ferric ion.

Figure 1 is a graphic representation of the change in $E_{1/2}$ with the concentration of potassium fluoride at pH 5.8. From the graph it can be seen that $E_{1/2}$ varied logarithmically with fluoride concentration. This is in accord with the Nernst expression for the reversible reduction of ferric ion to ferrous ion in the presence of fluoride:

$$E = E_{1/2} + 0.0591 \log (F^-)$$

When the fluoride concentration is 1 M, the E for the system equals $E_{1/2}$, which is the standard electrode potential for the reduction. We have found this value to be -0.494 v.

This logarithmic relationship between fluoride concentration and $E_{1/2}$ indicates that the reduction at the drop interface involves the loss of one fluoride ion from the ferric-fluoride complex.

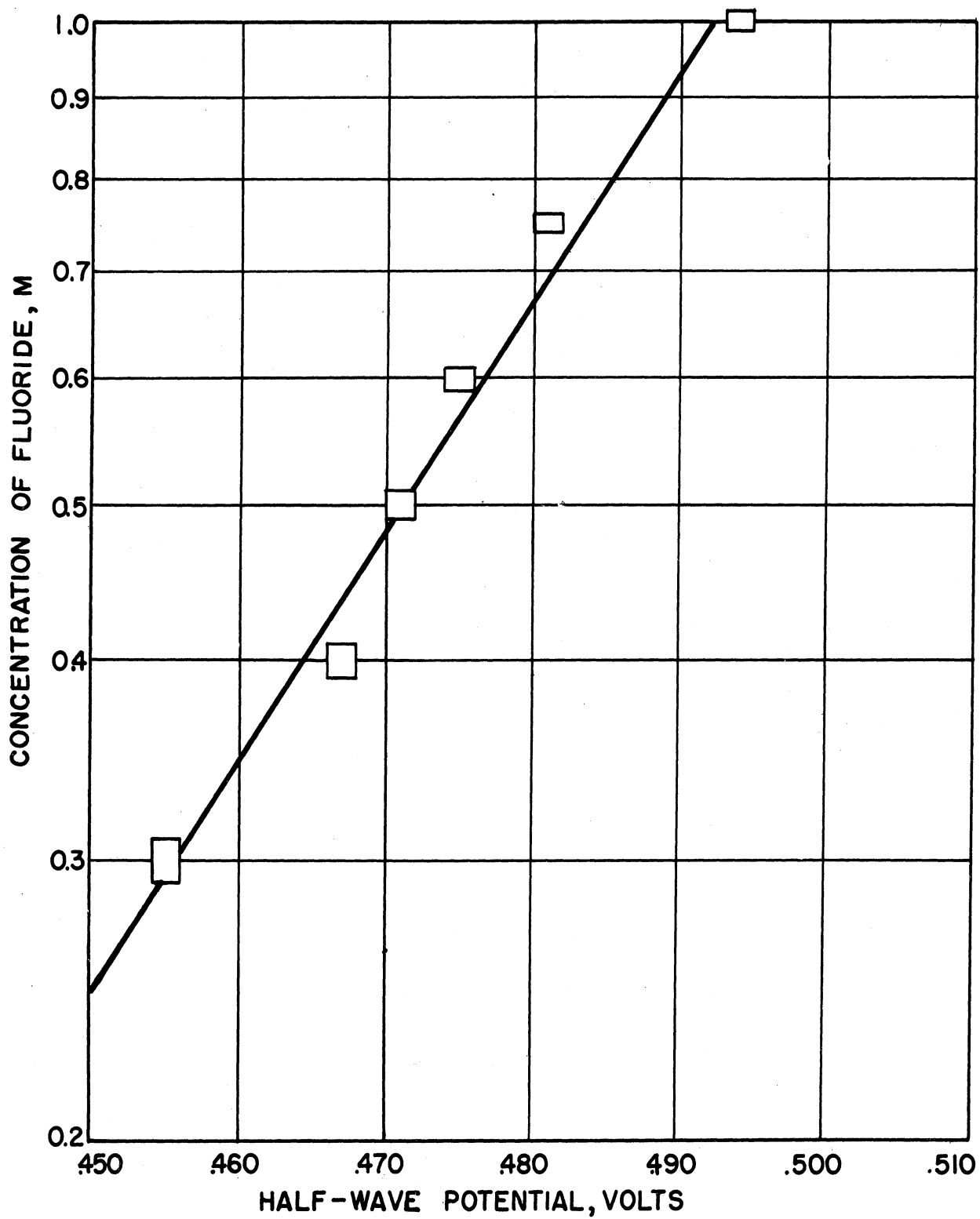
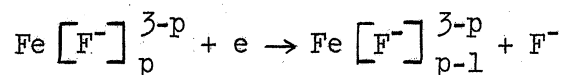


FIG. I. VARIATION OF HALF-WAVE POTENTIAL OF FERRIC ION WITH FLUORIDE CONCENTRATION



We propose the above expression to represent the electrode reaction.

The use of the Ilkovic equation enables us to calculate the diffusion coefficient for the ferric-fluoride complex. For an aqueous medium at 25°C which is 1.0 M in potassium fluoride, we found that $D = 5.81 \times 10^{-5} \text{ cm}^2 - \text{sec}^{-1}$.

FUTURE WORK

Next the chromic system will be investigated in fluoride at pH 5.8. It is desirable to obtain suitable polarographic waves for iron and chromium from the same solution at the same pH. It is, however, possible that the chromium wave may be best defined at a different pH, in which case it will be necessary to adjust the pH of the solution between polarograms for iron and chromium.

BIBLIOGRAPHY

1. West, P. W., and Dean, J. F., Ind. Eng. Chem., Anal. Ed., 17, 686 (1945).
2. Von Stackelberg, M., and Von Freyhold, H., Z. Electrochem., 46, 120 (1940).

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