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## A Summary of Oxidation-Reduction Potentials

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Double layers, complex-ions, hydrolysis, etc., find ready explanation by the theory.

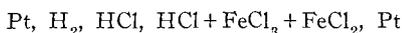
STATE UNIVERSITY OF IOWA,  
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## A SUMMARY OF OXIDATION-REDUCTION POTENTIALS

- A. FERRIC-FERROUS ELECTRODE.
- B. MERCURIC-MERCUROUS ELECTRODE.
- C. MANGANESE DIOXIDE ELECTRODES.

STEPHEN POPOFF, A. H. KUNZ, J. A. RIDDICK, and W. W.  
 BECKER

a. The Standard Oxidation-reduction Potential of the Ferric-ferrous electrode was determined from electromotive force measurements of the cell:

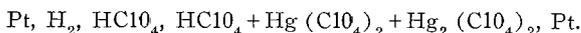


The concentration of the hydrochloric acid was kept the same in both half cells in each series but the concentration of the ferric and ferrous salts was varied keeping the ratio equal to one. The acid concentration in the series consisted of 0.05, 0.1, 0.2, 0.5 and 1 molal hydrochloric. From inspection of the equation

$$E = E_0 - 0.05915 \log \frac{C_{\text{Fe}'''} }{C_{\text{Fe}''}} - 0.05915 \log \frac{\gamma_{\text{Fe}'''} }{\gamma_{\text{Fe}''}} \pm E_1$$

it can be seen that the terms to the right of  $E_0$  must be made equal to zero in order that  $E$  may equal  $E_0$ . By suitable mathematical, experimental, and graphical treatments, the foregoing were reduced to zero, and thus two of the former difficulties in interpreting oxidation-reduction potentials were eliminated. These difficulties are the uncertainty in regard to liquid junction potentials and activity of one ion in the presence of other ions.<sup>1</sup>

2. Electromotive force measurements of the cell



were made. The mode of attack was similar to that in a.

c. Attempts to measure the potentials of the permanganate ion hydrogen ion manganese dioxide electrode and that of the manganese dioxide, hydrogen ion, manganous ion electrode failed be-

<sup>1</sup> Popoff and Kunz, J. Am. Chem. Soc. 51, 382 (1929).

cause of secondary reactions at the electrode and because of the irreversibility of these electrodes. Directions are given for the preparation and analysis of pure manganese dioxide.

In a, b, and c a number of analytical methods are given, some of which are new and others improve the precision of existing analytical methods.

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### THE INFLUENCE OF $p_H$ VALUES ON THE OXIDATION OF FERROUS SULPHATE

JACOB CORNOG and ALBERT HERSHBERGER

Weighed quantities of ferrous sulfate were dissolved in buffered solutions after which the resulting buffered solutions of ferrous sulfate were aerated for three hours. The quantity of iron remaining unoxidized after three hours aeration was, in each case determined, by titrating the aerated solution with potassium permanganate solution. The degree of oxidation was found to vary both with the initial concentration of ferrous sulfate and with the  $p_H$  value of the solution. These data are shown in the following table.

(1) pH OF SOLUTION	(2) % OXIDATION 0.1 M $FeSO_4$	(3) % OXIDATION 0.1 M $FeSO_4$	(4) % OXIDATION .001 M $FeSO_4$
1	0.00	0.00	0.00
2	0.00	0.00	0.00
3	0.00	0.00	0.00
4	4.28	0.00	0.00
5	44.25	25.91	2.20
6	54.85	82.19	71.64
7	76.73	93.62	94.29
10	57.64	92.94	96.03

These data indicate that under the experimental conditions used

(1) That little or no iron is oxidized in solution having a  $p_H$  value less than 5.

(2) That in solutions buffered to a  $p_H = 5$  the degree of oxidation increases with increasing iron concentration, but in solutions buffered to a  $p_H = 10$  the degree of oxidation decreases with increasing iron concentration.

*B. The Influence of the Length of Time of Aeration on the Degree of Oxidation of A 0.01 M Ferrous Sulfate Solution Buffered to  $p_H = 5$ .*

In the experiments here recorded different portions of the same