[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Potential of the Silver–Silver Ferrocyanide Electrode at 25°

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The electrode potentials[3] of metals in solutions of their ions as well as certain non-metallic electrodes have been investigated. Among the latter may be mentioned the calomel and the silver–silver chloride electrodes, the potentials of which have been determined with a high degree of precision. Electrodes of an organometallic nature, however, have been studied less extensively. In this research we have undertaken to determine the potential of the silver–silver ferrocyanide electrode.

Materials.—Electrolytic silver crystals were used in the preparation of the silver–silver ferrocyanide electrodes.

Potassium ferrocyanide was twice precipitated from a filtered, saturated aqueous solution by the addition of absolute alcohol. The salt, dried spontaneously, was dissolved in oxygen-free water and kept under nitrogen in the dark.

Silver ferrocyanide, prepared immediately before use in the cells, was precipitated in an atmosphere of nitrogen from a diluted portion of the potassium ferrocyanide stock solution with an excess of dilute silver nitrate solution. The precipitate was washed by decantation until no turbidity was detectable upon the addition of sodium chloride solution.

All solutions were prepared on the weight molal basis with conductivity water. All other chemicals used were purified by approved methods.

Measurements were made of the electromotive force of the concentration cells

$$\mathrm{Ag} \mid \mathrm{Ag_4Fe(CN)_6},\ \mathrm{K_4Fe(CN)_6}\ (0.1\ m) \mid (0.05\ m)\mathrm{K_4Fe(CN)_6},\ \mathrm{Ag_4Fe(CN)_6} \mid \mathrm{Ag}$$

$$\mathrm{Ag} \mid \mathrm{Ag_4Fe(CN)_6},\ \mathrm{K_4Fe(CN)_6}\ (0.1\ m) \mid \mathrm{KHg} \mid (0.05\ m)\ \mathrm{K_4Fe(CN)_6},\ \mathrm{Ag_4Fe(CN)_6} \mid \mathrm{Ag}$$

The electrode vessels used in these experiments were of the same type as those described by Harned.[4] The electrodes were prepared by placing dried silver crystals upon a mat of glass wool held by the constriction in the electrode vessel. A silver plated platinum wire electrode was inserted and around this the silver crystals were packed tightly. Air was displaced from the cells with nitrogen. As quickly as possible, silver ferrocyanide mixed with silver crystals was added to the silver crystals surrounding the silver-plated platinum wire and pressed in place. Solutions were forced into the cells under nitrogen pressure.

Half-cells of equal molality, connected by salt bridges, were short circuited to hasten equilibrium between the electrodes. Following this procedure the salt bridges were removed and a modified Lamb and Larson[5] flowing junction device inserted, connecting half-cells of unequal molality. After measurements were made with this set-up the flowing junction apparatus was removed and the amalgam reservoirs put in place. The amalgam reservoirs were washed out by alternately evacuating and filling with nitrogen several times before filling them with potassium amalgam.

The silver–silver ferrocyanide electrodes could be duplicated to 1 mv. Duplicate half-cells were found to differ by ±1.5 mv. Measurements of the cells with ion-transference would remain constant to within 0.5 mv. for a period from two to four hours. As many measurements of the cells without ion-transference as were possible were taken in the time (ten to fifteen min.) necessary for the amalgam reservoirs to empty. The electromotive force measurements of four cells are given in Table I where E and E_t represent the observed potentials of cells without ion-transference and with ion-transference, respectively.

TABLE I

ELECTROMOTIVE FORCES OF SILVER–SILVER FERROCYANIDE CONCENTRATION CELLS AT 25°

E, volt	E_t, volt
0.0208	0.0131
.0221	.0134
.0205	.0137
.0194	.0156
.0207 Av.	.0139 Av.

Measurements of concentration cells afford a method for obtaining the mean transference number of the cation for the molalities used. The average values for E and E_t from Table I were substituted in the formula

$$n_c = E_t/E$$

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[1] Deceased Nov. 14, 1936.

[2] Acknowledgment is made to Dr. W. G. Eversole for valuable suggestions and criticism offered in the preparation of this paper.

[3] "International Critical Tables," 1929, Vol. VI, p. 332.

[4] Harned, THIS JOURNAL, 51, 416 (1929).

[5] Lamb and Larson, *ibid.*, 42, 229 (1920).

where n_c is the mean transference number. The value obtained for n_c is 0.672.

Electromotive force measurements were made also of cells of the type

$$Ag \mid Ag_4Fe(CN)_6, K_4Fe(CN)_6(m/_4) \mid (m)KCl, Hg_2Cl_2 \mid Hg$$

The electromotive force values obtained are the mean values of two to seven cells in which each half-cell contained two to five electrodes. The individual electrodes of the calomel half-cells came to equilibrium quickly and were constant to within ±0.03 mv. The individual electrodes of the ferrocyanide half-cells reached equilibrium in from six to forty-eight hours and differed by about 0.5 mv. The duplicate half-cells differed by about ±3 mv. in 0.0125 *m* and by ±0.3 mv. in 0.05 *m* solutions.

Liquid junction potentials were calculated by means of the Lewis and Sargent[6] formula

$$E_L = 0.05915 \log \lambda_1/\lambda_2$$

where λ_1 and λ_2 are the equivalent conductances of ferrocyanide and chloride solutions[7] in which the potassium ion molalities are equal. In the range of the concentrations used the liquid junction potential adds to the true potential of the cell; therefore, its value must be subtracted from the observed potential of a cell in order that the single electrode potential may be obtained. The experimental data are compiled in Table II.

TABLE II

ELECTROMOTIVE FORCES OF CALOMEL–FERROCYANIDE CELLS AT 25°

m, $K_4Fe(CN)_6$	0.05	0.025	0.0125
m, KCl	.2	.1	.05
$E_{\text{obsd.}}$, v.	.1096	.1210	.1310
E_L, v.	.0083	.0069	.0053
E_{298}, v.	.1013	.1141	.1257

To obtain the potentials of the ferrocyanide electrodes in the various solutions, the values of E_{298} are subtracted from the potentials of the corresponding calomel electrodes. The values for the latter were calculated using $E^0_{298} = 0.2676$ v. for the electrode $Hg,Hg_2Cl_2,Cl^-(a = 1)$. These were checked using Harned's[4] mean activity coefficients for the respective molalities of potassium chloride solutions. Table III contains the data covering the foregoing.

The single electrode potential of the 0.1 *m* electrode can be evaluated from the data for the cells with ion-transference and the potential for the electrode in which the potassium ferrocyanide molality is 0.05. Following a reasoning similar to that of MacInnes,[8] the relation

$$E_L = E_t(1 - 1/5n_c)$$

is obtained where E_L, E_t, and n_c have their usual significance. The value calculated for E_L, using 0.672 as the cation transference number, is 0.0098 v. and is subtracted from the observed potential of the cell. The cell potential corrected for liquid junction then is 0.0041 v. The potential, E_{298}, for the 0.1 *m* electrode is 0.2126 v.

TABLE III

POTENTIALS OF THE CALOMEL AND SILVER FERROCYANIDE ELECTRODES AT 25°

m, KCl	E_{298} calomel	E_{298} calomel Harned's $\gamma\pm$	m, $K_4Fe(CN)_6$	E_{298} Ag, $Ag_4Fe(CN)_6$
0.2	0.3180	0.3177	0.05	0.2167
.1	.3337	.3337	.025	.2196
.05	.3498	.3498	.0125	.2241

In order to evaluate E^0_{298} for the silver–silver ferrocyanide electrode, a method similar to that employed by Lewis and Randall[9] was used. The potential, E^0, is given by the equation:

$$E = E^0 - 0.01479 \log a_{Fe(CN)_6^{----}} \tag{1}$$

Subtracting 0.01479 log $m_{Fe(CN)_6^{----}}$ from both sides of (1) and rearranging, the relation

$$0.01479 \log (a/m)_{Fe(CN)_6^{----}} = E^0 - (E + 0.01479 \log m_{Fe(CN)_6^{----}}) \tag{2}$$

is obtained. At infinite dilution $\log (a/m)_{Fe(CN)_6^{----}}$ is equal to zero and therefore $E^0_{298} = E + 0.01479 \log m_{Fe(CN)_6^{----}}$. If the right member, $E^{0\prime}$, is plotted against any function of $m_{Fe(CN)_6^{----}}$ the intercept $m = 0$ is equal to E^0_{298}.

Plotting the $E^{0\prime}$ values against the square root of the molality groups the points so that a straight line more nearly fits the data. Using the method of averages,[10] the equation

$$E^{0\prime} = 0.1943 + 0.012597\sqrt{m} \tag{3}$$

is obtained for the straight line. The constant, 0.1943 v., is the value for the standard electrode potential of the silver–silver ferrocyanide electrode at 25°.

By substituting for $E^{0\prime}$ its value in (3), the relation

$$E = 0.1943 + 0.012597\sqrt{m} - 0.01479 \log m_{Fe(CN)_6^{----}} \tag{4}$$

is obtained. Using this equation, single electrode potentials were calculated for several molalities of

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[6] Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909).

[7] "International Critical Tables," 1929, Vol. VI, pp. 234 and 253.

[8] MacInnes, THIS JOURNAL, **37**, 2301 (1915).

[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., 330 West 42d St., New York, N. Y., 1923, p. 334.

[10] Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., New York, N. Y., 1928, p. [illegible].

potassium ferrocyanide. From the calculated electrode potentials the activities of the ferrocyanide ion were computed using equation (1). The activity coefficients of the ferrocyanide ion for the several molalities were determined by dividing the activities by the corresponding molalities.

In addition the activities of the silver ion can be calculated from the relation

$$E_{298} = 0.7978 + 0.05915 \log a_{Ag^+}$$

where 0.7978 v. is the standard electrode potential for the silver electrode.[3] The activities of the ferrocyanide and silver ions being known, the activity product constant for silver ferrocyanide

$$K_a = (a_{Ag^+})^4 \times (a_{Fe(CN)_6^{----}})$$

can be evaluated. In Table IV calculations are brought together under headings which are self-explanatory.

If s is the molal solubility of silver ferrocyanide, $4s$ and s are the molal solubilities of the silver and ferrocyanide ions, respectively. Taking the solubilities equal to the activities, the equation

$$(4s)^4 \times s = 256s^5 = 1.546 \times 10^{-41}$$

is obtained. Solving for s, the value 2.27×10^{-9}, the molal solubility of silver ferrocyanide in water, is obtained.

TABLE IV

m	$a_{Fe(CN)_6^{--}} \times 10^2$	$\gamma^{-}_{Fe(CN)_6^{--}}$	$a_{Ag+} \times 10^{10}$	$K_a \times 10^{41}$
0.01	0.8143	0.81	2.089	1.552
.02	1.518	.76	1.786	1.546
.04	2.742	.69	1.542	1.549
.06	3.686	.61	1.429	1.537
.08	4.585	.57	1.355	1.546
.10	5.357	.54	1.303	1.546
				1.546 Av.

Summary

From a series of measurements at 25°, the potential of the electrode $Ag, Ag_4Fe(CN)_6, Fe(CN)_6^{----}$ ($a = 1$) is found to be 0.1943 v.

The activity product constant and the molal solubility in water of silver ferrocyanide, 1.546×10^{-41} and 2.27×10^{-9}, respectively, have been calculated.

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The Interaction of Ozone and Hydrogen Peroxide in Aqueous Solution

BY WILLIAM C. BRAY

In 1917 Rothmund and Burgstaller[1] concluded that hydrogen peroxide at low concentration is an efficient catalyst for the decomposition of ozone

$$2O_3 = 3O_2 \qquad (1)$$

and that

$$H_2O_2 + O_3 = H_2O + 2O_2 \qquad (2)$$

is the net reaction when the peroxide is present in large excess. The latter result is well supported by their four quantitative experiments[1] (p. 297), and by the work of others. Proof of the catalytic action of hydrogen peroxide depends on the results of their three rate experiments in the presence of dilute sulfuric acid; they determined the concentrations of both ozone and peroxide, and calculated the ratios of decomposed ozone to decomposed peroxide. These ratios decreased rapidly during each experiment. In spite of evident inaccuracies in the experimental data, it will be shown in this paper that the results are in fair agreement with the relation

$$\frac{v_1 + v_2}{v_2} = \frac{-d(O_3)/dt}{-d(H_2O_2)/dt} = 1 + 5.2\,\frac{(O_3)}{(H_2O_2)} \qquad (3)$$

where v_1 and v_2 are the rates of reactions (1) and (2), respectively. The two rates and the two corresponding concentrations are the values at a given instant during an experiment. At high and low values of the concentration ratio, the limiting stoichiometric results are reactions (1) and (2), respectively. It is evident, therefore, that ozone at low concentration is not a catalyst for the decomposition of hydrogen peroxide in dilute acid solution.

Weiss[2] recently has plotted the Rothmund and Burgstaller ratios of the "mean consumption values," $\Delta O_3/\Delta H_2O_2$, against the ratios of the "corresponding mean values of the concentrations." Equation (3) was not revealed by this non-differential method; but the results did indicate that relative rates and relative concentrations might be related, and led me to estimate actual instead of average rates.

Table I contains the results of calculations made with the assistance of Mr. E. L. Derr. In expt. I $-d(H_2O_2)/dt$ could not be determined

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(1) Rothmund and Burgstaller, *Monatsh.*, **38**, 295–303 (1917).

(2) Joseph Weiss, *Trans. Faraday Soc.*, **31**, 668–681 (1935).