# SOME COMPARISONS OF FORMAL AND MOLAL OXIDATION POTENTIALS*

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**Introduction.**—Molal oxidation potentials are idealized reaction constants. Molal potentials may be evaluated by the use of three independent experimental procedures. The electrochemical method is most direct and results in the use of the least complicated experimental procedure. A second method involves the determination of reaction equilibrium constants. The third procedure is based upon the calculation of potentials using heat of reaction data. Molal potentials determined as a result of all three procedures should give identical results.

Formal oxidation potentials are practical rather than idealized constants. Formal potentials rarely conform in magnitude to molal potentials. The differences between conditions under which molal potentials and formal potentials are determined involve conformity to and deviation from the requirements classed as "standard state." Molal potentials require hydrogen ion concentrations to be calculated to include activity relationships; formal potentials ignore such corrections. Molal potentials include hydrolysis effects, formal potentials do not. Formal solutions from other circumstances do not conform strictly to the prerequisites of conditions of "standard state." The chief discrepancy probably consists in the formation of complex ions the dissociation constant of which is unknown.

It is the purpose of the present discussion to point out some of the wide discrepancies which result from the assumption that reaction constants for oxidation-reduction reactions can be even approximated from the use of molal potential values. The distinction between molal and formal oxidation potential data has been discussed with this point in view by Swift.[1]

"These molal potentials are often of little practical value, and may be misleading, when one attempts to predict from the behavior of oxidizing and reducing agents in the relatively concentrated salt and acid solutions encountered in analytical chemistry . . . These formal potentials could be calculated from the molal potentials (or the reverse) if there were available adequate data for the hydrolysis constants, for the dissociation constants of any complex ions which may be formed, and, finally, for the activity coefficient of the reactants in these relatively concentrated solutions. Since such data are usually inadequate, it is advantageous to have the experimentally measured formal potentials." The situation as it exists was one which may have prompted a Dutch chemist's warning that, 'theory guides, experiment decides.'"
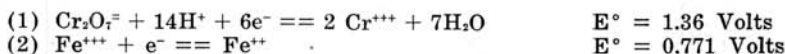
**Section of reactants.**—Many oxidizing agents and reducing agents could be selected to illustrate the point of distinction between molal and formal potentials. Two commonly employed reagents will be selected for illustration; namely, ferrous and dichromate ions.

**Experimental apparatus.**—A potentiometric titration assembly of the usual type consisting of a working cell (2 dry cells), a decade resistance box, a student potentiometer and tapping key, a moderately sensitive galvanometer and a standard Weston cell. The electrode pair used was a platinum wire and a saturated calomel half cell. By the use of a double throw switch the calibration of the galvanometer circuit can be made with reference to the standard Weston cell or the potential of the unknown reaction cell can be measured. The titration apparatus was provided with a mechanical stirrer and calibrated buret. Samples for determination were transferred to the reaction cell by the use of standard pipets. The accuracy claimed for the potentials determined is such that the value is approximate in the third place of decimals.

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**Descriptive procedure.**—A description in detail will be given of a familiar reaction: $Cr_2O_7^= + 6Fe^{++} + 14H^+ \rightarrow 2Cr^{+++} + 6Fe^{+++} + 7H_2O$. The half cell reactions[1] involved are as follows:[*]

(1) $Cr_2O_7^= + 14H^+ + 6e^- == 2\ Cr^{+++} + 7H_2O$ $\qquad$ E° = 1.36 Volts
(2) $Fe^{+++} + e^- == Fe^{++}$ $\qquad$ E° = 0.771 Volts

**Reactants.**—$FeCl_3 \cdot 6H_2O$ (app. 0.2 mol.) dissolved in 162.2 ml. of reagent hydrochloric acid (sp. gr. 1.19) and diluted to 2000 ml. making a solution 0.1 formal in ferric ion and formal in hydrochloric acid.

An approximately 0.01666 formal solution of $K_2Cr_2O_7$ in formal hydrochloric acid (0.1 N $Cr_2O_7^=$ in F HCl).

Formal hydrochloric acid for dilution purposes made by dilution of 81.1 ml. of reagent hydrochloric acid (sp. gr. 1.19) to 1000 ml.

A 25.00 ml. portion of the ferric chloride solution after passing through a Walden silver reductor was transferred to a 400 ml. beaker and diluted to 250 ml. by addition of formal hydrochloric acid. This solution was then titrated using the 0.1 N $K_2Cr_2O_7$ solution and the resulting potentials were plotted (fig. 1 and table 1).

TABLE 1.—THE POTENTIOMETRIC TITRATION OF FERROUS IONS BY DICHROMATE IONS IN FORMAL HYDROCHLORIC ACID SOLUTION

| $Cr_2O_7^=$ ml. | E.M.F.[a] Volts | $Cr_2O_7^=$ ml. | E.M.F. Volts | $Cr_2O_7^=$ | E.M.F. Volts |
|---|---|---|---|---|---|
| 0.00 | 0.5380 | 16.00 | 0.6981 | 25.85 | 0.8661 |
| 0.50 | 0.5907 | 18.00 | 0.7073 | 25.90 | 1.0064 |
| 1.00 | 0.6083 | 20.00 | 0.7181 | 26.00 | 1.0250 |
| 2.00 | 0.6255 | 22.00 | 0.7306 | 26.10 | 1.0403 |
| 5.00 | 0.6510 | 23.00 | 0.7386 | 26.30 | 1.0491 |
| 10.00 | 0.6748 | 24.00 | 0.7510 | 27.00 | 1.0586 |
| 12.00 | 0.6838 | 25.00 | 0.7713 | 30.00 | 1.0700 |
| 12.50 | 0.6858 | 25.50 | 0.7908 | 40.00 | 1.0778 |
| 13.00 | 0.6876 | 25.60 | 0.8008 | 50.00 | 1.0843 |
| 14.00 | 0.6906 | 25.70 | 0.8213 | 51.80 | 1.0925 |

[a]E.M.F. values are corrected to refer to hydrogen electrode as standard.

From the results of Table 1 the formal half cell reactions involved are the following:

(1) $Cr_2O_7^= + 14H^+ + 6e^- == 2Cr^{+++} + 7H_2O$ $\qquad$ E°′ = 1.09 Volts
(2) $Fe^{+++} + e^- == Fe^{++}$ $\qquad$ E°′ = 0.69 Volts
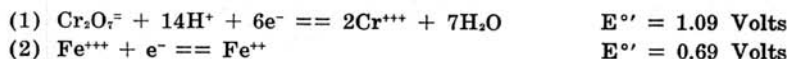
The formal potential for reaction (1) is seen to be at variance with the molal potential to the extent of 20 per cent and for reaction (2) over 10 per cent. It is of interest to calculate the most important reaction constants for the reaction between ferrous and dichromate ions based upon molal potential data as compared to formal potentials. The constants calculated and the general formulation for each constant is as follows:

$$E_e \begin{pmatrix} \text{equiv.} \\ \text{point} \\ \text{potential} \end{pmatrix} = \frac{bE°_1 + aE°_2}{a + b}$$

$$-\log K_{(equil.)} = \frac{(E°_1 - E°_2)n}{.059}$$

$$[Red_2] / [Ox_2] = {}^{a+b}\sqrt{\left(\frac{a'b}{ab'}\right)^a K}$$

Then

| | Molal | Formal |
|---|---|---|
| $E_e$ | 1.276 Volts | 1.033 Volts |
| K. equil. | $1.26 \times 10^{-60}$ | $1.66 \times 10^{-41}$ |
| $[Red_2] / [Ox_2]$ | $3.06 \times 10^{-9}$ | $1.65 \times 10^{-6}$ |

TABLE 2.—THE FORMAL POTENTIALS OF THE FERRIC-FERROUS AND DICHROMIC-CHROMIC SYSTEMS IN SULFURIC ACID AND HYDROCHLORIC ACID OF VARIOUS CONCENTRATIONS

| Acid Used | $Cr_2O_7^= + 14H^+ + 6e^- == 2Cr^{+++} + 7H_2O$ E°′ Values in Volts E° | | $Fe^{+++} + e^- == Fe^{++}$ E°′ Values in Volts E° | |
|---|---|---|---|---|
| 1 F HCl | 1.09(3) | 1.36 | 0.68(8) | 0.771 |
| 2 F HCl | 1.10(7) | | 0.67(7) | |
| 3 F HCl | 1.19(0) | | 0.67(1) | |
| 4 F HCl | 1.15(0) | | 0.65(8) | |
| 2 F $H_2SO_4$ | 1.10(9) | | 0.68(8) | |
| 4 F $H_2SO_4$ | 1.14(7) | | 0.68(7) | |
| 6 F $H_2SO_4$ | 1.30(0) | | 0.68(1) | |
| 8 F $H_2SO_4$ | 1.34(6) | | 0.65(8) | |

**Formal potentials of the ferric-ferrous and dichromic-chromate systems at various concentrations.**—The determination of the ferric-ferrous formal potentials at 2, 3, and 4 formal strength of hydrochloric acid were similarly determined (as described in Table 1 and shown graphically in Figure 1). The same procedure

[*]The molal potentials (E°) are taken from Latimer "Oxidation Potentials," Prentise-Hall, 1938. Formal potentials will be indicated by the symbol E°′.
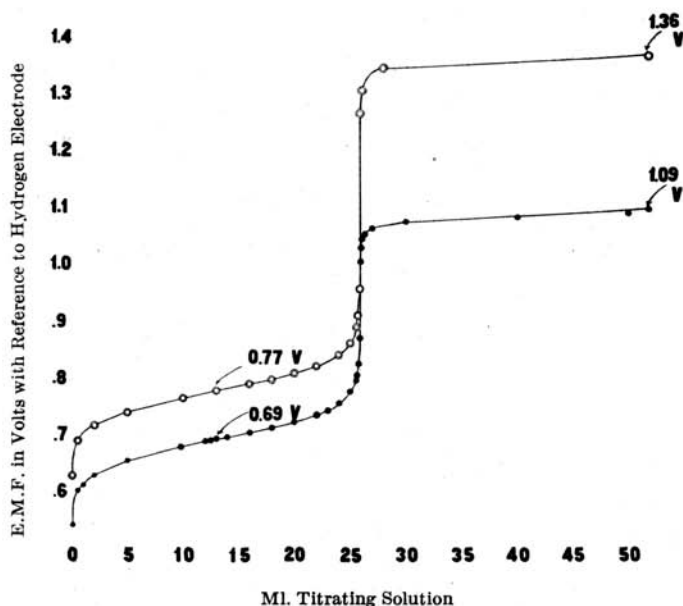
**Fig. 1.**—The titration of FeCl$_2$ in 1 FHCl solution bv Cr$_2$O$_7$ = in 1F HCl.   (25.00 ml 0.1 N Fe$^{++}$ by 0.1 N Cr$_2$O$_7^-$)



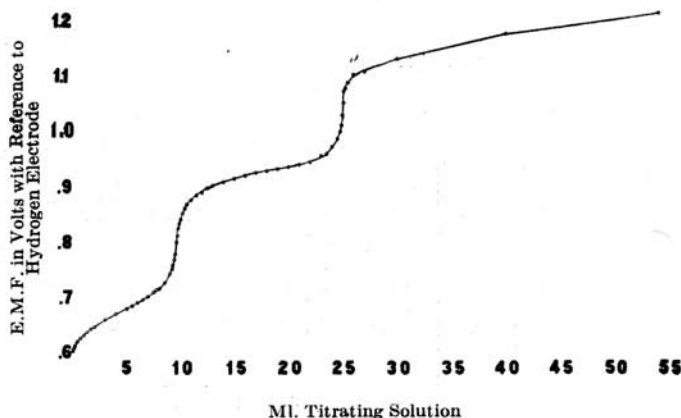**Fig. 2.**—The titration of 10.0 ml of Fe$^{++}$ solution plus 15.0 ml of ferrous methyl orthophenanthroline using Cr$_2$O$_7^-$. Solutions approximately 0.1 N and 4 F H$_2$SO$_4$ used throughout.  Fe$^{+++}$ + e$^-$ = Fe$^{++}$ potential 0.68 volts, methyl ferrin + e$^-$ = methyl ferroin 9.06 volts.

gave also the formal potentials for the dichromic-chromic system at the same concentration of acid. In all cases the potentiometric titrational curves were just as smooth and precise and the formal potential values determined could be evaluated with an equal degree of precision. Duplicate titrational curves were obtainable at will and the formal potentials thus determined agreed to within ± 0.01 volt. The same type experiments were carried out with the same systems in sulfuric acid solution except that the ferrous sulfate solutions in the various formal strengths of sulfuric were prepared from ferrous sulfate hexahydrate

and therefore required no reduction before titration. The results appear in Table 2.

**Choice of oxidation-reduction indicators for use in the determination of iron by dichromate.**—The oxidation-reduction indicator selected for the titration of iron by dichromate has generally been diphenylamine or diphenylamine sulfonic acid. These indicators are of quite low values in potentials which bring about their color change. (0.76 volts and 0.84 volts respectively). For this reason phosphoric acid is always added to lower the oxidation potential of the ferric-ferrous system below the value ordinarily attained in either sulfuric or hydrochloric acid solutions. The use of these indicators is obviously not fully satisfactory. It would be reasoned that because of the presence of the green chromic ion in these titrations, a more vividly colored and more reversible indicator of the ortho-phenanthroline type would be used.

The fact that ferroin indicator is not employed in the determination of iron by dichromate is rather unexplained on the basis of the molal oxidation potential values given for the half cell reaction of the $Cr_2O_7^= \rightarrow 2Cr^{+++}$ (1.36 volts) and the ferriin-ferroin system (1.14 volts). The difference between the molal and formal potentials given in Table 2 indicates the failure of conditions to be suitable except in 6 to 8 formal sulfuric acid solution and unsatisfactory conditions at any strength of hydrochloric acid.

**Influence of acid concentration on the oxidation potential of indicators of the phenanthroline series.**—The indicator ferroin (1-10-orthophenanthroline ferrous sulfate) and substituted phenanthroline indicators such as 5-methyl-1-10-orthophenanthroline ferrous sulfate (methyl ferroin) are subject to very material changes in oxidation potential with changes in hydrogen ion concentration in solutions in which they are employed. These values have been determined in previous work (a report of which is now in press) and are reprinted as given in Table 3.

From the data in Table 3 it is observed that just as with the oxidation of iron by dichromate, wide changes in oxidation potential occur in the indicator system. This requires that both the variations should be taken into consideration when

TABLE 3.—THE FORMAL OXIDATION POTENTIALS OF FERROIN AND METHYL FERROIN INDICATORS

| Reactions: Ferriin $+ e^- \rightarrow$ Ferroin | $E^\circ = 1.16$ Volts |
| Methyl Ferriin $+ e^- \rightarrow$ Methyl Ferroin | $E^\circ = 1.10$ Volts |

| Acid Conc. | Ferriin   Ferroin $E^{\circ\prime}$ in Volts | Methyl Ferriin-Ferroin $E^{\circ\prime}$ in Volts |
|---|---|---|
| 1 Formal | 1.06 | 1.02 |
| 2 Formal | 1.03 | 1.00 |
| 3 Formal | 1.00 | 0.96 |
| 4 Formal | 0.96 | 0.93 |
| 6 Formal | 0.89 | 0.86 |
| 8 Formal | 0.76 | 0.70 |

reaction conditions are to be selected. With this point in view the methyl ferroin indicator would be selected for dichromate titrations of iron because its oxidation potential is lower than that of ferroin. If would be predicted that satisfactory conditions prevail at 4 formal strength of sulfuric acid. A test case potentiometric titration of a mixture of ferrous and methyl ferroin ferrous ions in 4 formal sulfuric acid was titrated using the dichromate ion in 4 formal sulfuric acid solution as oxidant. The values obtained are shown graphically in figure 2. It will be observed that a satisfactory differential titrational procedure results. The use of 2 formal sulfuric acid results in a differential titration the second stage of which reaction is not satisfactory and does not give a vertical break in potential but rather a gradual one. The use of 6 formal sulfuric acid results in a very satisfactory oxidation of the indicator but a somewhat gradual break in potential for the oxidation of the ferrous ion. At 8 formal sulfuric acid concentration there is no sign of a differential oxidation of ferrous and methyl ferroin ferrous ions.

**Conclusions.**—Formal versus molal oxidation potentials differ over such a wide range under normal variations in titrational environments that special cognizance of this situation is of prime importance. The cases cited in this discussion are typical, not isolated examples. The system of recording formal potentials and molal potentials in the same table of reaction constants as instigated by Swift (loc. cit.) should be extended and emphasis should be placed on the use of these formal potentials in preference to molal potentials as a guide to predicting suitable reaction conditions.