

The General Equation for the Equivalence Point Potential in Oxidation-Reduction Titrations

A survey of thirty-four quantitative analysis textbooks, both at the elementary and advanced levels, revealed that no general equation for the equivalence point potential in oxidation-reduction titrations has been described. In four of these texts the calculation was completely ignored. In another thirteen an equation for the equivalence point potential was not given but the potential was calculated for a simple titration, commonly for the ferrous-ceric system. In twelve books, $a\text{Red}_1 + b\text{Ox}_2 = a\text{Ox}_1 + b\text{Red}_2$ was given as the general titration reaction, and the equation

$$E_{\text{eq. p.}} = (bE_1^\circ + aE_2^\circ)/(a + b) \quad (1)$$

given as the general equation for the equivalence point potential. In several of these the explicit statement was made that equation (1) is a *completely* general expression. On the other hand, Pierce, Haenisch, and Sawyer¹ recognize that equation (1) may be used only when the reactants are substances for which the numbers of moles are the same for the oxidized and reduced forms. Blaedel and Meloche² also realize this fact, and derive the expression for the equivalence point potential in the titration of iron(II) sulfate by potassium dichromate which shows that the potential is a function of the concentration of the reactants. Michaelis³ also mentions titration curves in which the equivalence point potential is dependent upon the initial concentration of the substance to be titrated. In the standard reference of potentiometry, Kolthoff and Furman,⁴ a more general reaction is mentioned in connection with equilibrium concentrations, but in the chapter on oxidation-reduction titrations only equation (1) is given. Lingane⁵ treats a much more complicated system, the titration of iodide ion with ceric ion, in which he takes into account the iodine-triiodide equilibrium and the solubility of iodine in aqueous solutions. However, he does not give an equation for the general case.

Described below is the derivation of a general equation for the equivalence point potential which is valid for all oxidation-reduction titrations in which no additional equilibria are extant. The significance of this

equation is not primarily its pragmatic aspect, but rather its indication that the equivalence point potential is in general a function of the concentration of the reactants and not a simple weighted average of the standard (or formal) potentials, as is usually assumed.

Derivation

Consider the titration of a reductant Red_2 by an oxidant Ox_1 , assuming first that no additional species (e.g., hydrogen ion) are involved in either half-reaction. The potential throughout the titration is governed by the half-reactions of species (1) and (2):



The titration reaction is



The potential during the titration is governed by the Nernst expression:

$$E_1 = E_1^\circ - \frac{RT}{xF} \ln \frac{[\text{Red}_1]^b}{[\text{Ox}_1]^a} \quad (5)$$

$$E_2 = E_2^\circ - \frac{RT}{yF} \ln \frac{[\text{Red}_2]^d}{[\text{Ox}_2]^c} \quad (6)$$

where brackets denote activities (or concentrations if E° is the formal potential).

At equilibrium, $E_1 = E_2$, and the familiar expression:

$$\ln \frac{[\text{Red}_1]^b [\text{Ox}_2]^{xc}}{[\text{Ox}_1]^a [\text{Red}_2]^d} = \ln K = \frac{xyF}{RT} (E_1^\circ - E_2^\circ) \quad (7)$$

is obtained.

At the equivalence point (stoichiometric point):

$$xc [\text{Red}_1]_{\text{eq. p.}} = yb [\text{Ox}_2]_{\text{eq. p.}} \quad (8)$$

and,

$$ya [\text{Red}_2]_{\text{eq. p.}} = xd [\text{Ox}_1]_{\text{eq. p.}} \quad (9)$$

Applying (8) and (9) to (5) and (6):

$$E_{\text{eq. p.}} = E_1^\circ - \frac{RT}{xF} \ln \frac{(yb/xc)^b [\text{Ox}_2]_{\text{eq. p.}}^b}{(ya/xd)^a [\text{Red}_2]_{\text{eq. p.}}^a} \quad (10)$$

and,

$$E_{\text{eq. p.}} = E_2^\circ - \frac{RT}{yF} \ln \frac{[\text{Red}_2]_{\text{eq. p.}}^d}{[\text{Ox}_2]_{\text{eq. p.}}^c} \quad (11)$$

Finally, multiplying (10) by x and (11) by y and adding, with simplification:

$$E_{\text{eq. p.}} = \frac{x E_1^\circ + y E_2^\circ}{(x + y)} - \frac{RT}{(x + y)F} \ln \frac{(yb/xc)^b [\text{Ox}_2]_{\text{eq. p.}}^{b-c}}{(ya/xd)^a [\text{Red}_2]_{\text{eq. p.}}^{a-d}} \quad (12)$$

A more convenient and useful formula is obtained

¹ PIERCE, W. CONWAY, HAENISCH, EDWARD L., AND SAWYER, DONALD T., "Quantitative Analysis," 4th ed., John Wiley & Sons, Inc., New York, 1958, p. 424.

² BLAEDEL, W. J., AND MELOCHE, V. W., "Elementary Quantitative Analysis: Theory and Practice," Row, Peterson & Company, Evanston, Illinois, 1957, pp. 716f.

³ MICHAELIS, L., "Physical Methods of Organic Chemistry," 2nd ed., Vol. I, Part II, Interscience Publishers, Inc., New York, 1949, p. 1775.

⁴ KOLTHOFF, I. M., AND FURMAN, N. HOWELL, "Potentiometric Titrations," John Wiley & Sons, Inc., New York, 1926, pp. 57f, pp. 106f.

⁵ LINGANE, J. J., "Electroanalytical Chemistry," 2nd ed., Interscience Publishers, Inc., New York, 1958, pp. 141-147.

in terms of only a single reactant at its initial concentration. By solving (8) and (9) for $[\text{Red}_1]_{\text{eq. p.}}$ and $[\text{Ox}_1]_{\text{eq. p.}}$ and applying to the equilibrium expression for the reaction (7), one obtains:

$$K = \frac{(yb/xc)^{yb} [\text{Ox}_2]_{\text{eq. p.}}^{b+c}}{(ya/xd)^{ya} [\text{Red}_2]_{\text{eq. p.}}^{a+d}} \quad (13)$$

Solving this expression for $[\text{Red}_2]_{\text{eq. p.}}$,

$$[\text{Red}_2]_{\text{eq. p.}} = \left| \frac{(yb/xc)^{yb} [\text{Ox}_2]_{\text{eq. p.}}^{(yb+c)/(ya+xd)} l^{1/(ya+xd)}}{(ya/xd)^{ya} K} \right| \quad (14)$$

and introducing into equation (12) yields, after some simplification:

$$E_{\text{eq. p.}} = \frac{x E_1^\circ + y E_2^\circ}{(x+y)} - \frac{RT}{(ya+xd)F} \ln \left[\frac{(yb/xc)^{db}}{(ya/xd)^{da}} K^{(a-d)/(x+y)} [\text{Ox}]_{\text{eq. p.}}^{db-ca} \right] \quad (15)$$

If the initial concentration of $[\text{Red}_2]$ is C_i , then at the equivalence point (assuming K is quite large, as is usually the case in titrations):

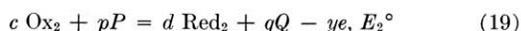
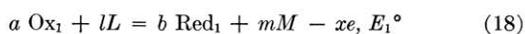
$$[\text{Ox}_2]_{\text{eq. p.}} = (c/d) C_i \frac{V}{V+v} \quad (16)$$

where V is the initial volume and v is the volume of titrant added.

Introducing (16) into (15) and simplifying one obtains:

$$E_{\text{eq. p.}} = \frac{x E_1^\circ + y E_2^\circ}{x+y} - \frac{RT}{(xd+ya)F} \frac{(a-d)}{(x+y)} \ln K - \frac{(db-ca)RT}{(xd+ya)F} \ln C_i \frac{V}{V+v} - \frac{RT}{(xd+ya)F} \ln (y/xd)^{(b-a)d} \times (b^b/a^a)^d (cd)^{ca} \quad (17)$$

For titrations where additional species are involved in either or both half-reactions:



where L , M , P , and Q are substances involved in the half-reactions which are neither oxidized nor reduced (e.g., hydrogen ion, water, etc.), the derivation is quite similar. The general equation in this case is:

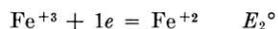
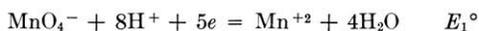
$$E_{\text{eq. p.}} = \frac{x E_1^\circ + y E_2^\circ}{x+y} - \frac{RT}{(xd+ya)F} \frac{(a-d)}{(x+y)} \ln K - \frac{(db-ca)RT}{(xd+ya)F} \ln C_i \frac{V}{V+v} - \frac{RT}{(xd+ya)F} \ln (y/xd)^{(b-a)d} \times (b^b/a^a)^d (cd)^{ca} - \frac{RT}{(x+y)F} \ln \frac{[M]_{\text{eq. p.}} [Q]_{\text{eq. p.}}}{[L]_{\text{eq. p.}}^l [P]_{\text{eq. p.}}^p} \quad (20)$$

where $[M]_{\text{eq. p.}}$ represents the activity or concentration of M at the equivalence point, etc.

Applications

Case I: $a = b = c = d = 1$

This represents the usual titration (e.g., MnO_4^- versus Fe^{+2}).



$$l = 8, x = 5, y = 1, m = p = q = 0$$

$$E_{\text{eq. p.}} = \frac{5E_1^\circ + E_2^\circ}{6} + \frac{RT}{6F} \ln [\text{H}^+]_{\text{eq. p.}}$$

and the equivalence point potential is a simple combination of the E° 's and $p\text{H}$.

Case II: $a = c = d = 1 \neq b$

Titration involving one half-reaction in which the number of moles of oxidized and reduced forms of the reactants are not equal, such as Fe^{+2} versus $\text{Cr}_2\text{O}_7^{2-}$:



$$a = 1, b = 2, c = 1, d = 1, l = 14, x = 6, y = 1, m = p = q = 0$$

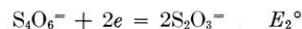
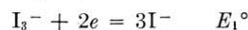
Here the equivalence point potential is:

$$E_{\text{eq. p.}} = \frac{6E_1^\circ + E_2^\circ}{7} + \frac{RT}{7F} \ln [\text{H}^+]^{14} - \frac{RT}{7F} \ln 2^{2/3} - \frac{RT}{7F} \ln C_i \frac{V}{V+v}$$

where C_i is the initial concentration of iron(II). In this case only the $\ln K$ term disappears.

Case III: $a = c = 1 \neq b \neq d$

Titration involving two half-reactions in which the number of moles of oxidized and reduced forms of the reactants are not equal, such as $\text{S}_2\text{O}_3^{2-}$ versus I_3^- :



For the titration reaction, in the form of equation (4):



$x = y = 2, b = 3, d = 2, l = m = p = q = 0$, then

$$E_{\text{eq. p.}} = \frac{E_1^\circ + E_2^\circ}{2} + \frac{RT}{24F} \ln K - \frac{RT}{2F} \ln 4.50 - \frac{5RT}{6F} \ln C_i \frac{V}{V+v}$$

where C_i is the initial concentration of $\text{S}_2\text{O}_3^{2-}$ and assuming that the iodine is almost completely in the I_3^- form and is present in such small concentration that the iodine remains soluble. Expressing K in terms of the E° 's [equation (7)] and at a temperature of 25°C ,

$$E_{\text{eq. p.}} = \frac{E_1^\circ + E_2^\circ}{2} + \frac{E_1^\circ - E_2^\circ}{6} - 0.019 - 0.05 \log C_i \frac{V}{V+v}$$

Since $E_1^\circ = 0.536$ v versus normal hydrogen electrode and $E_2^\circ = 0.08$ v versus N. H. E.,⁶ the equivalence point potential is about 180 mv more positive (assuming 0.01 M initial thiosulfate concentration and negligible volume change, e.g., titration with 0.1 M I_3^-) than the potential calculated from the weighted average of the E° 's for alone. More important, the equivalence point potential changes 50 mv for every tenfold change in C_i .

Conclusion

The treatment given above will hold for all oxidation-reduction titrations in which no additional equilibria are extant. It is seen that the calculated equivalence

⁶ LATIMER, WENDELL M., "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

point potential will involve concentration terms for many common titrations (e.g., I_3^- , Br_2 , $\text{Cr}_2\text{O}_7^{2-}$, $\text{C}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_3^{2-}$, H_2O_2). Although in many cases these corrections are small, and are of little consequence ex-

perimentally (because end-point potentials are usually determined empirically), they are significant from a theoretical point of view and may be important in scaling macro-titrations to micro levels.