Redox Buffer Strength

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The Acid–Base Buffer Strength

The buffer value is a quantity related to titrations. The traditional acid–base *titration curve* provides the pH as a function of the volume V_t of titrant added. By exchanging the axes, one obtains the *progress curve*, which plots the volume V_t as a function of the pH. The *buffer value* as defined by van Slyke (*1*) is the derivative of the progress curve when the sample is titrated with infinitely concentrated strong base, which makes the resulting value independent of the concentration of that base. For example, the buffer value for the aqueous solution of weak monoprotic acid of total analytical concentration C_a is given by

$$\beta = C_a \left(\frac{d\phi_{ab}}{d(pH)} \right)_{C_b \to \infty} = C_b \left(\frac{d\left(V_b/V_a \right)}{d(pH)} \right)_{C_b \to \infty} = C_b \left(\frac{d}{d(pH)} \frac{C_a \alpha_{A^-} - \Delta}{C_b + \Delta} \right)_{C_b \to \infty} =$$

$$\left(\frac{d}{d(pH)} \frac{C_a \alpha_{A^-} - \Delta}{1 + \Delta/C_b} \right)_{C_b \to \infty} = \frac{d\left(C_a \alpha_{A^-} - \Delta \right)}{d(pH)} =$$

$$\frac{d\left(\frac{C_a K_a}{\left[H^+\right] + K_a} - \left[H^+\right] + \left[OH^-\right] \right)}{d\left[H^+\right]} \frac{d\left[H^+\right]}{d(pH)} = \tag{1}$$

$$2.3 \left(\frac{C_a \left[H^+\right] K_a}{\left(\left[H^+\right] + K_a \right)^2} + \left[H^+\right] + \left[OH^-\right] \right) = 2.3 \left(C_a \alpha_{HA} \alpha_{A^-} + \left[H^+\right] + \left[OH^-\right] \right)$$

$$\alpha_{A^-} = \frac{[A^-]}{[HA] + [A^-]} = \frac{K_a}{\left[H^+\right] + K_a} \; ; \quad \alpha_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{\left[H^+\right]}{\left[H^+\right] + K_a} \tag{2}$$

where $\phi_{ab} = C_b V_b / C_a V_a$ is the degree of completion of the titration, $\Delta = [H^+] - [OH^-]$, 2.3 is shorthand for $\ln(10)$, and where we have used the expression for the progress of the titration of a weak acid with a strong base (*2, 3*),

$$\frac{V_b}{V_a} = \frac{C_a \alpha_{A^-} - \Delta}{C_b + \Delta} = \frac{\dfrac{C_a K_a}{\left[H^+\right] + K_a} - \left[H^+\right] + \left[OH^-\right]}{C_b + \left[H^+\right] - \left[OH^-\right]} \tag{3}$$

Equation 1 can be simplified somewhat when we define, instead of van Slyke's buffer value (subsequently also called buffer index or buffer capacity), a *buffer strength B* = $\beta/2.3$, thereby eliminating the term $\ln(10) = 2.3$, so that eq 1 becomes

$$B = \frac{\beta}{2.3} = \left[H^+\right] + C_a \alpha_{HA} \alpha_{A^-} + \left[OH^-\right] \tag{4}$$

In a concentrated monoprotic acid or base, the buffer strength therefore equals the concentration of that acid or base, just as the ionic strength of a strong 1,1-electrolyte is equal to the concentration of that electrolyte.

Often, the concentrations of sample and titrant are similar, in which case dilution of the sample by the titrant makes the buffer index or buffer strength deviate considerably from the derivative of the progress curve. We therefore need not worry too much about jettisoning the factor 2.3, which derives from that differentiation. On the other hand, this rather trivial simplification does make it somewhat easier to visualize and manipulate the concept of buffer action, and consistently leads to simpler equations—the reason why we have adopted this streamlined notation in the past (*3, 4*) and will continue to do so here.

Equation 4 shows that a concentrated strong acid or a concentrated strong base is a powerful pH buffer. However, the buffer action of concentrated strong acids or bases is restricted to extreme pH values; buffer mixtures made from a weak acid and its conjugated base must be used at more moderate pH values. In the latter case one can often neglect the terms $[H^+]$ and $[OH^-]$ in eq 4, in which case it simplifies to

$$B \approx C_a \alpha_{HA} \alpha_{A^-} = C_a \alpha_{HA}(1 - \alpha_{HA}) = C_a (1 - \alpha_{A^-}) \alpha_{A^-} \tag{5}$$

which shows that the buffer strength has a maximum value of $C_a/4$ at pH = pK_a, where the two alphas each have the value $\frac{1}{2}$.

In the above relations, C_a is the *total* analytical concentration of the acid, so that we can rewrite eq 5 as

$$B \approx C_a \alpha_{HA} \alpha_{A^-} = C_a \alpha_{HA} \times C_a \alpha_{A^-}/C_a = [HA][A^-]/([HA]+[A^-]) \tag{6}$$

or

$$\frac{1}{B} \approx \frac{1}{[HA]} + \frac{1}{[A^-]} \tag{7}$$

which becomes the Henderson approximation (*5*) when one associates [HA] with the concentration of the acidic form of the buffer used to make a buffer mixture, and [A$^-$] with the corresponding concentration of its basic form.

The Analogy between Acid–Base and Redox Behavior

We can write the mass action law of Guldberg and Waage (*6–8*) for the monoprotic acid–base equilibrium $A^- + H^+ \rightleftharpoons HA$ in logarithmic form as

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$$pH = pK_a + \log \frac{[A^-]}{[HA]} \qquad (8)$$

which can be compared with the Nernst equation (*9, 10*) for the monoelectronic equilibrium $O + e^- \rightleftharpoons R$

$$fE = fE^o_{OR} + \log \frac{[O]}{[R]}; \qquad f = \frac{F}{RT \log (10)} \qquad (9)$$

or

$$ph = pk + \log \frac{[O]}{[R]}; \qquad h = 10^{-fE}; \qquad k = 10^{-fE^o_{OR}} \qquad (10)$$

where F is the Faraday, R the gas constant, T the absolute temperature, E the potential, and E^o_{OR} its standard value.

The Redox Buffer Strength for a Redox Couple Involving a Single One-Electron Step

Exploiting the above formal analogy between eqs 10 and 8, we have shown that redox titrations can be described by a formalism quite analogous to that of acid–base titrations (*3, 4, 11*). For example, for the titration of Fe^{2+} with Ce^{4+} we have

$$\frac{V_t}{V_s} = \frac{C_s \alpha_{Fe^{3+}}}{C_t \alpha_{Ce^{3+}}} \qquad (11)$$

where the subscripts s and t denote the sample and titrant, respectively, and the α's represent the concentration fractions of the species identified by the subscripts; that is,

$$\alpha_{Fe^{3+}} = \frac{\left[Fe^{3+}\right]}{\left[Fe^{3+}\right] + \left[Fe^{2+}\right]} = \frac{k_s}{h + k_s} \qquad (12)$$

$$h = 10^{-E/0.059}; \quad k_s = 10^{-E^o_{Fe32}/0.059}$$

$$\alpha_{Ce^{3+}} = \frac{\left[Ce^{3+}\right]}{\left[Ce^{4+}\right] + \left[Ce^{3+}\right]} = \frac{h}{h + k_t} \qquad (13)$$

$$h = 10^{-E/0.059}; \quad k_t = 10^{-E^o_{Ce43}/0.059}$$

while 0.059 is the numerical value of $1/f = [RT \ln(10)]/F$ at room temperature, in volts.

Upon comparing eqs 3 and 11, we notice two main differences. Most importantly, the expression for the progress of a redox titration does not contain terms for the redox properties of the solvent equivalent to the terms in Δ in eq 3, because oxidation and reduction of the solvent are seldom thermodynamically reversible (i.e., equilibrium) processes. Moreover, such solvent redox reactions only affect the behavior at potentials beyond those typically encountered in redox titrations, and the corresponding terms are therefore left out altogether.

The second difference is really the consequence of the first. Absent comparison with the solvent, the concept of a strong or weak redox agent does not exist, and eq 8 is therefore formally analogous to that for the titration of a weak acid with a weak base. Because we are interested here in the redox buffer strength, a quantity that is defined so as to be independent of the nature

of the reagent used, this second difference need not concern us.

By analogy with eq 4 we now define the redox buffer strength of a mixture of Fe^{3+} and Fe^{2+} as

$$B = \frac{C_t}{2.3} \left(\frac{d\left(V_t/V_s \right)}{d\left(fE \right)} \right)_{C_t \to \infty} = C\alpha_{Fe^{2+}}\alpha_{Fe^{3+}} = \frac{Chk}{\left(h + k \right)^2} \qquad (14)$$

$$k = 10^{-fE^o_{Fe32}}$$

where we have deleted the now superfluous subscript s (for sample) on C and k. Figure 1 illustrates the relation between the progress curve of a redox titration and the redox buffer strength.

Since $C = [Fe^{3+}] + [Fe^{2+}]$ we can rewrite eq 14 as

$$\frac{1}{B} = \frac{1}{\left[Fe^{3+}\right]} + \frac{1}{\left[Fe^{2+}\right]} \qquad (15)$$

The Redox Buffer Strength for a Redox Couple Involving Several One-Electron Steps

As our example we will here consider a solution of vanadium, which (depending on the potential) can contain the following species: V^{2+}, V^{3+}, VO^{2+}, and VO_2^+. We now have three standard redox potentials, E^o_{54} for the VO_2^+/VO^{2+} couple, E^o_{43} for the VO^{2+}/V^{3+} couple, and E^o_{32} for the V^{3+}/V^{2+} couple. Moreover, the VO_2^+/VO^{2+} and VO^{2+}/V^{3+} couples involve terms dependent on the concentration of hydrogen ions, which are conveniently incorporated into the formalism by using conditional redox potentials E^* instead,

$$E^*_{V54} = E^o_{V54} - 2 \times 0.059 \, pH; \quad E^*_{V43} = E^o_{V43} - 2 \times 0.059 \, pH \qquad (16)$$

Now consider the progress of the titration of VSO_4 with $KMnO_4$. The corresponding progress curve is
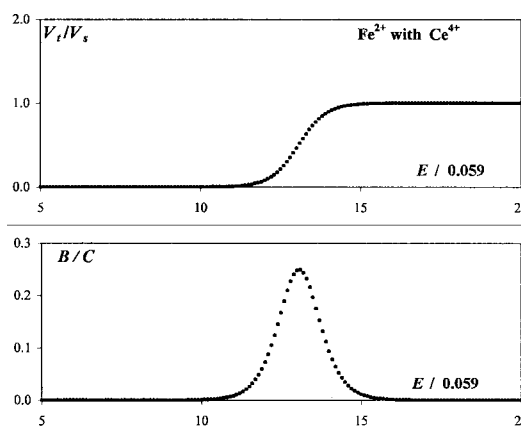

Figure 1. The first half of the progress curve for the titration of Fe^{2+} with Ce^{4+} and the corresponding ratio B/C of the redox buffer strength B and the total analytical concentration C of the Fe^{3+}/Fe^{2+} couple, both plotted as a function of the dimensionless potential $E/0.059$, the room-temperature value of fE. The curve for B/C is identical to 2.3 times the derivative of the progress curve, that is, $(^1/_{2.3}) \, d(V_t/V_s)/d(fE)$.

$$\frac{V_t}{V_s} = \frac{C_s\left(\alpha_{V^{3+}} + 2\alpha_{VO^{2+}} + 3\alpha_{VO_2^+}\right)}{C_t\alpha_{Mn^{2+}}} \qquad (17)$$

from which we abstract the redox buffer strength as

$$B = \frac{C_t}{2.3}\left(\frac{d\left(V_t/V_s\right)}{d\left(fE\right)}\right)_{C_t\to\infty} = \qquad (18)$$

$$C_s(\alpha_{V^{3+}}\alpha_{V^{2+}} + \alpha_{VO^{2+}}\alpha_{V^{3+}} + \alpha_{VO_2^+}\alpha_{VO^{2+}}$$
$$+ 4\alpha_{VO^{2+}}\alpha_{V^{2+}} + 4\alpha_{VO_2^+}\alpha_{V^{3+}} + 9\alpha_{VO_2^+}\alpha_{V^{2+}}) =$$
$$\frac{C_s(h^5 k_1 + h^3 k_1^2 k_2 + hk_1^2 k_2^2 k_3 + 4h^4 k_1 k_2 + 4h^2 k_1^2 k_2 k_3 + 9h^3 k_1 k_2 k_3)}{(h^3 + h^2 k_1 + hk_1 k_2 + k_1 k_2 k_3)^2}$$

which is quite analogous to the corresponding expression for, say, orthophosphoric acid, H_3PO_4, when we delete the terms $[H^+]$ and $[OH^-]$ and substitute in the second portion of eq 18 the α subscripts H_3PO_4 for V^{2+}, $H_2PO_4^-$ for V^{3+}, HPO_4^{2-} for VO^{2+}, and PO_4^{3-} for VO_2^+, and, in the bottom line of that equation, $[H^+]$ for h, and K_{ai} for k_i. When the various conditional potentials are sufficiently far apart, the terms with coefficients 4 and 9 are negligible, and eq 18 reduces to

$$B \approx C\left(\alpha_{V^{3+}}\alpha_{V^{2+}} + \alpha_{VO^{2+}}\alpha_{V^{3+}} + \alpha_{VO_2^+}\alpha_{VO^{2+}}\right) =$$

$$\frac{C\left(h^5 k_1 + h^3 k_1^2 k_2 + hk_1^2 k_2^2 k_3\right)}{\left(h^3 + h^2 k_1 + hk_1 k_2 + k_1 k_2 k_3\right)^2} \approx$$

$$C\left(\frac{hk_1}{\left(h + k_1\right)^2} + \frac{hk_2}{\left(h + k_2\right)^2} + \frac{hk_3}{\left(h + k_3\right)^2}\right) = \qquad (19)$$

$$\frac{1}{\dfrac{1}{[V^{3+}]} + \dfrac{1}{[V^{2+}]}} + \frac{1}{\dfrac{1}{[VO^{2+}]} + \dfrac{1}{[V^{3+}]}} + \frac{1}{\dfrac{1}{[VO_2^+]} + \dfrac{1}{[VO^{2+}]}}$$

just as it would in the case of orthophosphoric acid. In this case the three redox buffer regions are completely *uncoupled*, so that each can be considered in isolation as that of a mono-electronic redox system, with a maximum redox buffer strength of $C_s/4$ at the corresponding value of E° or E^*, and a buffer strength given by the approximation $1/B \approx 1/[O] + 1/[R]$. Figure 2 illustrates the progress curve for the titration of VSO_4 with $KMnO_4$ and the corresponding redox buffer strength, both as a function of the dimensionless potential $fE \approx E/0.059$ at room temperature.

The Redox Buffer Strength for a Redox Couple Involved in a Multielectron Step

When the standard or conditional potentials occur in reversed order, we obtain what appear to be multielectron steps, as in the 3-electron reduction of MnO_4^- to MnO_2 in neutral and basic medium, or its 5-electron reduction to Mn^{2+} in acid solution. (The acid–base equivalent would have the pK_a's in reversed order, an uncommon situation.) In this case, the appropriate approximation is to neglect all terms except the one with the highest coefficient. For the MnO_4^-/MnO_2 couple this leads to

$$B \approx 9C\alpha_{MnO_4^-}\alpha_{MnO_2} = \frac{9Ch^3 k^3}{\left(h^3 + k^3\right)^2}$$
$$k = 10^{-fE^*_{Mn74}}; \quad E^*_{Mn74} = E^\circ_{Mn74} - \frac{4pH}{3f} \qquad (20)$$

$$\frac{9}{B} \approx \frac{1}{[MnO_4^-]} + \frac{1}{[MnO_2]} \qquad (21)$$

and for the MnO_4^-/Mn^{2+} couple to

$$B \approx 25C\alpha_{MnO_4^-}\alpha_{Mn^{2+}} = \frac{25Ch^5 k^5}{\left(h^5 + k^5\right)^2}$$
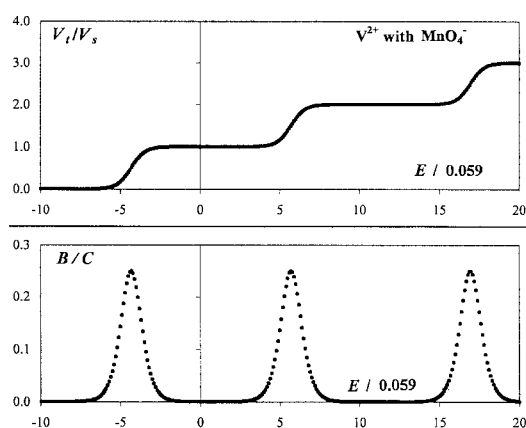$$k = 10^{-fE^*_{Mn72}}; \quad E^*_{Mn72} = E^\circ_{Mn72} - \frac{8pH}{5f} \qquad (22)$$

Figure 2. The initial part of the progress curve for the titration of V^{2+} with MnO_4^-, and the corresponding ratio B/C of the redox buffer strength B and the total analytical concentration C, at pH = 0, of the three vanadium redox couples, V^{3+}/V^{2+}, VO^{2+}/V^{3+}, and VO_2^+/VO^{2+}. Both graphs use as their abscissa the dimensionless potential $E/0.059$, the room-temperature value of fE. The curve for B/C is identical to $(1/2.3)$ times the derivative of the progress curve, that is, $(1/2.3)\, d(V_t/V_s)/d(fE)$.

$$\frac{25}{B} \approx \frac{1}{\left[MnO_4^-\right]} + \frac{1}{\left[Mn^{2+}\right]} \qquad (23)$$

where the coefficients 9 in eqs 20 and 21, and 25 in eqs 22 and 23, represent the much stiffer control of the redox potential by such multielectron systems, the coefficient being the square of the number of electrons transferred: 3 in $MnO_4^- + 4H^+ + \textbf{\textit{3}}e^- \rightleftharpoons MnO_2 + 2H_2O$; 5 in $MnO_4^- + 8H^+ + \textbf{\textit{5}}e^- \rightleftharpoons Mn^{2+} + 4H_2O$. Figure 3 illustrates the buffer strength in latter case.

Discussion

The above calculations presume equilibrium behavior of the redox couple, a condition not always encountered in practice. When slow redox kinetics are involved rather than redox equilibrium, the corresponding buffering action may be slow. Depending on the time scale of the experiment, the redox buffer strength may then be less than that computed here.

The concept of a redox buffer strength is certainly not new. Clark (*12*) used the term *poising action* to describe the stabilizing effect of the presence of a redox couple on the potential of the solution, and Nightingale (*13*) attempted to give a mathematical description for what he called the *redox poising capacity index*. He started from the redox titration curve, but unfortunately included the titrant, thereby hopelessly complicating the definition as well as the mathematics.

The availability of a simple, general mathematical relation for the progress curve of a redox titration (*2, 3, 11*) now makes it possible to provide a rational framework and explicit expressions for the quantitative description of such redox buffer action.

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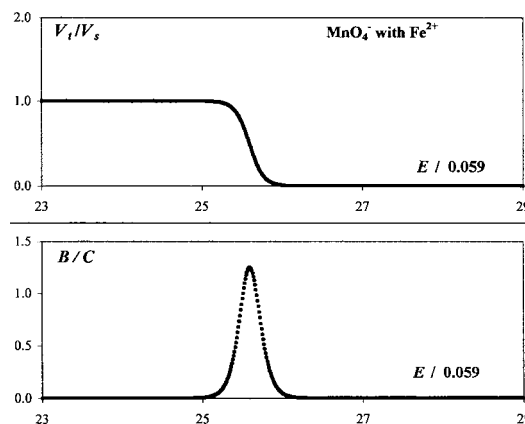13. Nightingale, E. R. Jr. *Anal. Chem.* **1958**, *30*, 267.

Figure 3. The initial part of the progress curve for the titration of MnO_4^- with Fe^{2+}, and the corresponding ratio B/C of the redox buffer strength B and the total analytical concentration C, of the MnO_4^-/Mn^{2+} couple, at pH = 0, both plotted as a function of the dimensionless potential $E/0.059$, the room-temperature value of fE. The curve for B/C is identical to $-(1/2.3)$ times the derivative of the progress curve, that is, $-(1/2.3)\, d(V_t/V_s)/d(fE)$.