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Modeling and Graphic Presentation of Acid–Base Titration Curves. Presentation of an Alternative Method

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Abstract: Titration curves for the acid–base-titration of polyvalent acids and bases and their mixtures can be created in a simple way and presented graphically. The method, an alternative to the existing procedures, shall be presented here for discussion. With the described method it is possible in an easy manner and for didactic purposes to show how the boundary conditions, such as concentrations, pK_a values, K_w values (temperature-dependent), and mixing ratios influence the shape of titration curves.

The method comes from closed mathematical formulas, which can be developed in the form: titration degree, $T = f(\text{pH})$. An increase in the titration volume is, therefore, not considered. It can be neglected in practice by choice of suitable volumes and concentrations. The graphic presentation can be realized with the help of a customary mathematic program, such as MathCAD 7. The titration curves are derived in the familiar form of $\text{pH} = f(T)$. During the derivation of the equations for the titration of polyvalent acids and bases, difficult expressions appear and approximations are suggested with only small deviations from the exact formulas, which nevertheless are both simple and manageable.

The procedure is presented in a series of practical examples where computed and measured titration curves are compared. When using polyvalent acids, such as malonic acid or citric acid, the appropriate activity coefficients have to be considered. If the ionic strength is constant, which can be accomplished by addition of electrolytes like KCl, this is easily accomplished and is demonstrated by examples.

Introduction

Titration curves are always interesting for the practice of analytical chemistry as well as for the education of students. These curves appear in every classical and modern textbook. When utilizing these curves, important information can be gathered, such as the size of the buffer zone and the pK_a value of suitable indicators; therefore, there have been many efforts to simulate titration curves mathematically and to compare the results to experimental outcomes. For some characteristic points, like the initial point, the midpoint, or the equivalence point of acid–base-titrations, the pH can be calculated by simple calculations. Detailed analysis of the modeling and presentation of titration curves has been performed, especially, by de Levie [1–3]. These methods are described in *Principles of Quantitative Analysis* [4] as well as in an article by the same author [5]. Equations are shown for acid–base titrations, complexometric titrations, and redox titrations. Furthermore, for the modeling of titration curves, spreadsheets are applied by Harris [6] and de Levie [7, 8]. For the graphic presentation of titration curves, especially in textbooks, separate equations are used, being only valid before, in, or after the equivalence point, and which have to be combined for the description of the whole curve [9, 10]. Binnewies [11] has shown how using computers can represent titration curves. In his book *pH-Berechnungen* Bliefert [12] has computed acid–base-titration curves on the basis of the function $T = f(H_3O^+)$ with T equal to the degree of titration. In a similar manner Kober presents this material in *pH-Berechnungen mit und ohne Computer*" [13].

In this article an alternative method for modeling and graphic presentation of titration curves is suggested and discussed. It is distinguished by using only one simple mathematic function describing the relation between pH value and titration degree for the complete progression of the titration. The equations contain the physicochemical parameters as concentrations, strength of acids (pK_a values), and the pK_w value.

They also can easily be formulated for the titration of polyvalent acids and bases as well as mixtures. From these equations the titration curves can be generated by computing point by point and forming a chart in the classical manner or, more conveniently, by using a graphical mathematics program, for example, MathCad 7.

As already shown by de Levie [7] and Bliefert [12], titration curves of acid–base-titrations cannot be represented, except in special cases, in mathematically closed form in the manner of $\text{pH} = f(T)$ with T equal to the titration degree ($T = V/V_{\text{ÄP}}$ with V equal to the volume of titrant and $V_{\text{ÄP}}$ equal to the volume of titrant consumed before reaching the equivalence point). We do the same here. On the other hand, it is possible to indicate the inverse function in a closed form. The titration curves, first obtained, are then transformed into the usual form, $\text{pH} = f(T)$, by permuting the x and y axis. This is simple to accomplish using a mathematics program.

Assumptions for Deriving the Equations

The equations are derived completely in the Appendix. Here, only the assumptions and preconditions are presented.

The central factor is the *titration degree*, which is formulated as a quotient of concentrations. For the titration, for example, of a dibasic acid, it is formulated as follows:

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$$T = \frac{c_0(\mathrm{B})}{c_0(\mathrm{H_2A})}$$

$c_0(H_2A)$ is the concentration of the acid to be titrated by the base, B, and $c_0(B)$ is the concentration of the base in the titration volume if there is no reaction between the acid and base. The value of $c_0(B)$ increases linearly during the titration, beginning at zero. As an example, in the titration of HCl, the concentration of HCl equals 0.1 mol L^{-1} and its volume equals 100 mL, the concentration of NaOH equals 1 mol L^{-1}, and the value of T is 0.5 if the consumption of NaOH amounts to 5 ml:

$$T = \frac{c_0(\mathrm{NaOH})}{c_0(\mathrm{HCl})} = \frac{1\frac{\mathrm{mol}}{\mathrm{L}}\frac{0.005\mathrm{L}}{0.1\mathrm{L}}}{0.1\frac{\mathrm{mol}}{\mathrm{L}}} = 0.5$$

During the titration of a dibasic acid, at the first equivalence point, T has the value of 1 and in the second the value of 2. The value of T is always proportional to the volume of titrant and should be perceived as a standardized volume of titrant.

In the progression of a titration, electric neutrality must always be maintained. For the titration of a dibasic acid H_2A with a strong base, like NaOH, this condition is formulated as

$$c(\mathrm{H_3O^+}) + c(\mathrm{Na^+}) = c(\mathrm{OH^-}) + c(\mathrm{HA^-}) + 2c(\mathrm{A^{2-}})$$

Furthermore, mass balance must be achieved for the acid H_2A and the products of hydrolysis, which has the following form for a dibasic acid:

$$c_0(\mathrm{H_2A}) = c(\mathrm{H_2A}) + c(\mathrm{HA^-}) + c(\mathrm{A^{2-}})$$

For a dibasic acid, both equations of protolysis have to be considered, which results in the need to apply the equilibrium constant expression to the expression for the acid dissociation constants, that is,

$$\frac{c(\mathrm{H_3O^+}) * c(\mathrm{HA^-})}{C(\mathrm{H_2A})} = K_{\mathrm{a_1}}$$
$$\frac{c(\mathrm{H_3O^+}) c(\mathrm{A^{2-}})}{c(\mathrm{HA^-})} = K_{\mathrm{a_2}}$$

The expression for the selfionization of water will also be used, that is,

$$c(\mathrm{H_3O^+})c(\mathrm{OH^-}) = K_{\mathrm{w}} = 10^{-14}\,\mathrm{mol^2/L^2} \text{ (at 25 °C)}$$

In the derivation, the well-known definitions for the pH and the pK_a values are needed, which are

$$\mathrm{pH} = -\log c(\mathrm{H_3O^+})$$
$$\mathrm{p}K_{a1} = -\log K_{a1}$$
$$\mathrm{p}K_{a2} = -\log K_{a2}$$

During this derivation, the dilution of the analyte by the volume of the titrant will not be taken into account. This is in contrast to the assumptions of de Levie [1] in his derivations. Is this approach legitimate? It is easy to show that a change of the pH value during the course of the titration due to dilution can be represented by the expressions

$$\mathrm{pH_{eff}} = \mathrm{pH_{theor}} + \log\left(1 + \frac{V_\mathrm{T}}{V_\mathrm{P}}\right) \text{ for pH} < 7$$

and

$$\mathrm{pH_{eff}} = \mathrm{pH_{theor}} - \log\left(1 + \frac{V_\mathrm{T}}{V_\mathrm{P}}\right) \text{ for pH} > 7$$

with pH_{eff} equal to the effective pH value (with dilution), pH_{theor} equal to the theoretical pH value (without dilution), V_T equal to the volume of titrant and V_P equal to the volume of analyte.

This means that in the progression of the titration, the pH values are raised in the acid region and decreased in the alkaline region by addition of the titrant. What is the effect of the dilution to the pH values? Assume an analyte volume (at the beginning of titration) of 200 mL and take into account that during the titration, 20 mL of titrant volume is added, then, the additive term at the end of the titration is

$$-\log\left(1 + \frac{20}{200}\right) = -0.04$$

The pH value at the end of the titration is reduced by the dilution by 0.04 pH units. During the titration, in the region where pH is less than 7, the pH value is increased. If the volume of titrant is 5 mL (in the acid region) the amount increases by 0.01 pH units; thus, it is clear that for presenting titration curves for didactic purposes, as well as for analytical reflection, these corrections can be neglected. It is possible to estimate how large the volume of the titrant may be in the presence of a given volume of analyte; the deviation of the pH value by the effect of dilution remains smaller than 0.1 pH units.

$$\log\left(1 + \frac{V_\mathrm{T}}{V_\mathrm{P}}\right) \le 0.1$$

The result is $V_\mathrm{T} \le 0.259 V_\mathrm{P}$. Using a volume of analyte of 100 mL, the total volume of titrant must stay lower than 25 mL.

On the other hand, if pH titrations are used to investigate the pK_a values of acids or pK_b values of bases, the measured pH values must be corrected for dilution due to the higher demand for accuracy. This can be done with the above formulas. For example, if the K_a value is to be detected with an error of less than 5 %, it can be estimated that the pH value in the usable buffer region may not change by more than 0.02 pH units. This corresponds to a quotient of dilution of V_T/V_P equals 0.05. If the analyte volume is 200 mL, the volume of titrant may not be larger than 10 mL. Either the analyte should be further diluted or the measured pH values will have to be corrected with reference to the equations above.

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For usual titrations and didactic relevance, it should be stated that the discrepancy in the pH values by dilution, owing to addition of the titrant, is of no consequence. In particular, the dilution should not be included in the derivation of the equation of for titration curves because much more complicated formulas are obtained without gain in value. From a practical standpoint, it seems warranted to approach the derivations without accounting for the effect of dilution and to correct the results afterwards with the formulas above. One can begin by comparing computed and experimental data with sufficiently small values of V_T/V_P.

The activity coefficients do not have to be considered, but for comparison of measured and computed data with higher claims of accuracy, they must be considered with reference to the respective ionic strengths, which shifts the progression of titration. This can be done by correcting using relevant charts, for example, reference 6. Alternatively, activity coefficients can be calculated by means of the Davies equations, as de Levie has demonstrated in his book *Principles of Quantitative Analysis* [4]. Another method consists of adjusting an almost constant ionic strength during the titration by addition of an inert electrolyte like KCl,where the alteration of the activity coefficient by variation of the ionic strength is negligible, so one can proceed from the assumption of a constant activity coefficient. This strategy is also almost always used in the determination of constants of complex stability on the basis of potentiometric titrations [14].

The tabulated thermodynamic $\mathrm{p}K_a$ and K_a values are different from the experimental data because the first are based on the ionic strength, $I = 0$. In determining $\mathrm{p}K_a$ values by titration, this must be taken into account. Two examples are used to demonstrate this point, the titrations of malonic acid and citric acid with a very strong base (KOH).

The Equations for the Titration Curves

The derivation of the equations (see Appendix) within the given suppositions and preconditions yields the following expressions:

(a) Titration of a monovalent acid with a very strong monovalent base

$$T = \frac{10^{\mathrm{pH}-\mathrm{p}K_w} - 10^{-\mathrm{pH}}}{c_0(\mathrm{HA})} + \frac{1}{1+10^{\mathrm{p}K_a-\mathrm{pH}}} \tag{1}$$

2. Titration of a monovalent base with a very strong monovalent acid

$$T = \frac{10^{-\mathrm{pH}} - 10^{\mathrm{pH}-\mathrm{p}K_w}}{c_0(\mathrm{B})} + \frac{1}{1+10^{\mathrm{pH}-\mathrm{p}K_a}} \tag{2}$$

3. Titration of a polyvalent acid with a very strong monovalent base:

$$T = \frac{10^{\mathrm{pH}-\mathrm{p}K_w} - 10^{-\mathrm{pH}}}{c_0(\mathrm{H_nA})} + \frac{1}{1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}} + \frac{1}{1+10^{\mathrm{p}K_{a2}-\mathrm{pH}}} + \cdots + \frac{1}{1+10^{\mathrm{p}K_{an}-\mathrm{pH}}} \tag{3}$$

The equations of titration curves of polyvalent acids and bases represent approximations with only very small deviations from the exact expressions. This will be discussed in the Appendix, particularly in the context of deriving the equations.

4. Titration of a polyvalent base with a very strong monovalent acid:

$$T = \frac{10^{-\mathrm{pH}} - 10^{\mathrm{pH}-\mathrm{p}K_w}}{c_0(\mathrm{B})} + \frac{1}{1+10^{\mathrm{pH}-\mathrm{p}K_{a1}}} + \frac{1}{1+10^{\mathrm{pH}-\mathrm{p}K_{a2}}} + \cdots + \frac{1}{1+10^{\mathrm{pH}-\mathrm{p}K_{an}}} \tag{4}$$

$c_0(\mathrm{H}_n\mathrm{A})$ and $c_0(\mathrm{B})$ are the total concentrations of the acids and bases, $\mathrm{p}K_{an}$ are the $\mathrm{pK_a}$ values of the acids during a titration of acids with bases and the $\mathrm{pK_a}$ values of the corresponding acids during a titration of bases with acids, T is the titration degree, and $\mathrm{p}K_w$ is the (temperature-sensitive) negative base-10 logarithm of the numerical value of the ionic product of water.

5. Titration of mixtures of monovalent acids with a very strong monovalent base:

$$T = X_1\frac{10^{\mathrm{pH}-\mathrm{p}K_w} - 10^{-\mathrm{pH}}}{c_0(A_1)} + X_1\left(\frac{1}{1+10^{\mathrm{p}K_{a1}-\mathrm{pH}}}\right)_1 + X_2\frac{10^{\mathrm{pH}-\mathrm{p}K_w} - 10^{-pH}}{c_0(A_2)} + X_2\left(\frac{1}{1+10^{\mathrm{p}K_{a2}-\mathrm{pH}}}\right)_2 + \ldots + X_n * \frac{10^{\mathrm{pH}-\mathrm{p}K_w} - 10^{-\mathrm{pH}}}{c_0(A_n)} + X_n * \left(\frac{1}{1+10^{\mathrm{p}K_{an}-\mathrm{pH}}}\right)_n \tag{5}$$

X_1, X_2, ... X_n are the individual mole ratios of each acid as they apply to: $X_1 + X_2 + \ldots + X_n = 1$.

These equations are analogously constructed for the titration of mixtures of polyvalent acids with very strong bases and for the titration of mixtures of polyvalent bases with very strong acids. The resulting expressions are easily determined by the extension of eq 4.

Visualization of the Titration Curves

For the illustration of titration curves, it is always necessary to enter the chosen $\mathrm{p}K_a$ values and the $\mathrm{p}K_w$ value into the equations and then enter the different pH values. In this manner, for any pH value a corresponding T value is calculated. The data are recorded in a chart and presented graphically, plotting the T values on the x axis and the pH values on the y axis as is usual in analytical chemistry.

By using mathematical programs, such as MathCad 7, this step can be accomplished quite easily. Only the appropriate equation needs entered. The program delivers the corresponding titration curve, which can be configured as desired and printed. In MathCad 7, several curves can be shown simultaneously in one diagram with comparison between curves, where the parameters are changed, impressibly presented. The curves are generated in the usual form as $\mathrm{pH} = f(T)$ by adequately choosing the axis (permuting x and y).

The application of MathCad 7 may be explained by the example of generation of the titration curve of diphosphoric

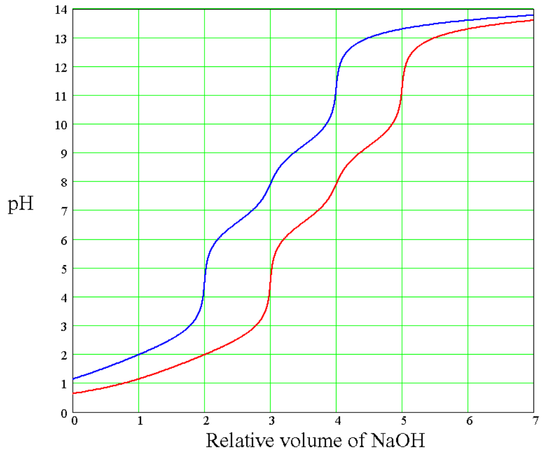

Figure 1. Titration of $H_4P_2O_7$ (blue curve) and $H_4P_2O_7$/HCl mixture (red curve), mole ratio 1:1 with NaOH.

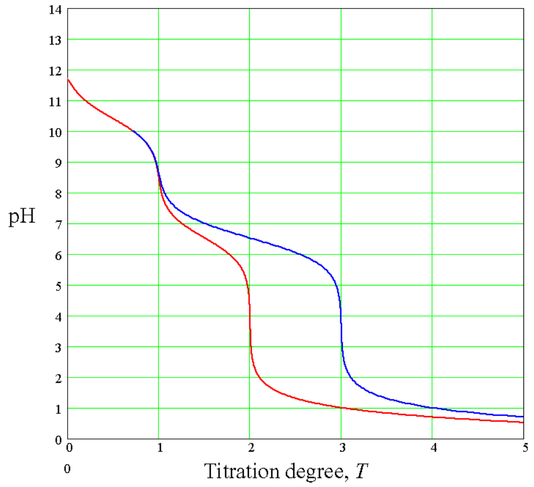

Figure 2. The titration of carbonate (red line) and hydrogen carbonate in a 1:1 mole ratio (blue line) with HCl

acid by titration with a very strong base. The equation for the titration is constructed form eq 3, the pK_a values from the literature [6] (0.8, 2.2, 6.7, and 9.4) are inserted, as well as the chosen total concentration of the acid (in the following example $c_0 = 0.2$ mol L^{-1}, $f(x)$ is T, and x is the pH. Graphics mode is chosen (draw an xy diagram), the range is entered, the step width for the calculation is inserted (here 0.01), and the notation for the axis is selected (x for the ordinate and y for the abscissa). The complete titration curve appears in the classic manner, which can be configured and enlarged according to choice (Figure 1). Labeling of the axes and text as desired can be inserted into the diagram. Grids for the coordinates can also be added as desired. In the same diagram more curves might be drawn by choosing new variables, such as y and $g(y)$ in addition to x and $g(x)$. For instance, in Figure 1 the following two functions were plotted versus pH:

$$f(x)=\frac{10^{x-14}-10^{-x}}{0.2}+1+\frac{1}{1+10^{1.52-x}}+\frac{1}{1+10^{2.36-x}}$$
$$+\frac{1}{1+10^{6.6-x}}+\frac{1}{1+10^{9.25-x}}$$

$$g(x)=\frac{10^{y-14}-10^{-y}}{0.2}+1+\frac{1}{1+10^{1.52-y}}+\frac{1}{1+10^{2.36-y}}$$
$$+\frac{1}{1+10^{6.6-y}}+\frac{1}{1+10^{9.25-y}}$$

An example of the titration of a binary mixture of acids, hydrochloric acid and diphosphoric acid in a 1:1 mole ratio, is shown in Figure 1 (red curve). In contrast to the titration of pure diphosphoric acid, no additive jump occurs. The reason for this is that $H_4P_2O_7$ is in the first ionization step with a pK_a that shows it to be a relatively strong acid.

A mixture of two acids can be analyzed quantitatively by recording the complete titration curve. For $H_4P_2O_7$, the steps at pH = 4 and pH =11 can be used. These can be visualized with suitable indicators. On the other hand, the step at pH = 8 is less pronounced and, therefore, less suitable for a titration with color indicators. With the titrant volumes for the first and last obvious pH changes represented by V_1 and V_2, the concentration of diphosphoric acid can be calculated as 0.5 ($V_2 - V_1$). For the concurrent determination of HCl, the expression $V_1 - (V_2 - V_1) = 2V_1 - V_2$ is applied. Observations are performed simply by using the respective titration curves. They are helpful to demonstrate titration procedures.

An example of the titration of bases with strong acids, the titration of carbonate (as a bivalent base) with HCl, is shown in Figure 2. The concentration of carbonate was chosen to be 0.2 mol L^{-1}. The pK_a values that should be inserted into eq 4 are those of the corresponding acids: HCO_3^- with pK_{a1} of 10.4 and H_2CO_3 ($CO_2 + H_2O$) with pK_{a2} of 6.52. The two equivalence points at $T = 1$ and $T = 2$ with pH values at 8.3 and 4.2 can be identified. The titration curve for the titration of a mixture of carbonate and hydrogen carbonate in a mole ratio of 1:1 is also shown in Figure 2 (blue line).

Influence of the Activity Coefficients on the Shape of the Titration Curve

For an exact comparison between experimental and calculated titration curves, especially with the titration of polyvalent acids, the actual activity coefficients have to be considered. The following example shows the titration of malonic acid with a strong base (KOH).

Test conditions: batch reactor, continuous titration at 1 mL min^{-1} with a plunger pump and reading the pH with a glass electrode. The pH-electrode was calibrated with standard buffer solutions.

c_0 (malonic acid) = 2.5×10^{-2} mol L^{-1}, volume = 200 mL.

Addition of KCl; ionic strength, $I = 0.1$ M.

c(KOH) = 1 mol L^{-1}.

Temperature of 20 °C.

If activity coefficients are not taken into account, calculation of the titration curve using the default concentration by inputting the pK_a values from the literature [6] at 20 °C (2.847 and 5.696) yields the blue curve in Figure 3. If the activity coefficients are taken into account, the red curve in Figure 3 is obtained.

For calculation of the activity coefficients, the equation of Davies was used, a method described in detail by de Levie in *Principles of Quantitative Chemical Analysis* [4]. The

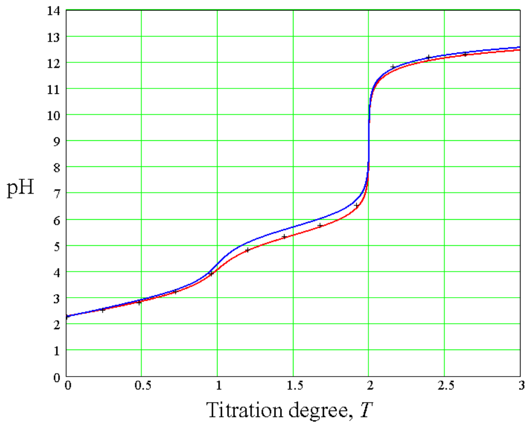

Figure 3. Titration of malonic acid with KOH: (a) without consideration of activity coefficients (blue curve), (b) with consideration of activity coefficients (red curve), and (c) experimental data (crosses).

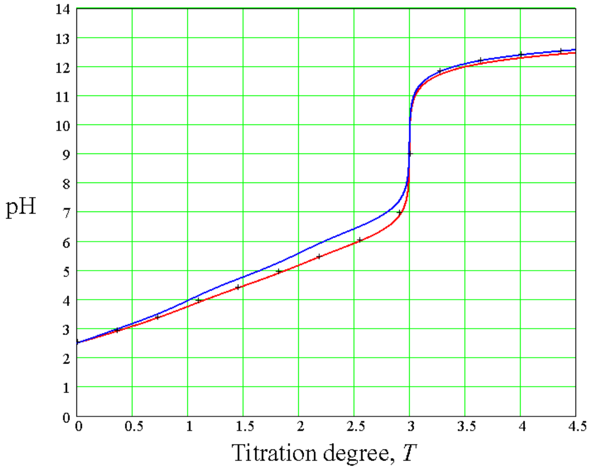

Figure 4. Titration of citric acid with KOH: (a) without consideration of activity coefficients (blue curve), (b) with consideration of activity coefficients (red curve), and (c) experimental data (crosses).

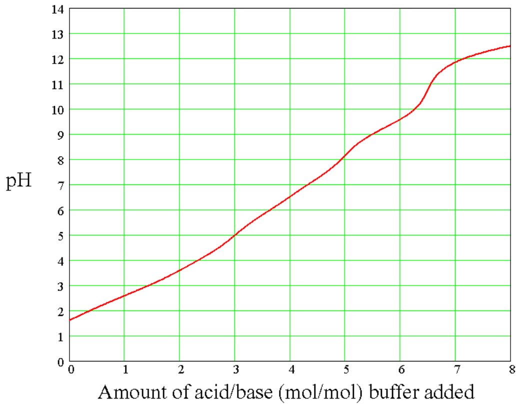

Figure 5. Titration of the universal buffer of Theorell and Steinhagen [15] (mixture of citric acid, phosphoric acid, and boric acid) with NaOH/HCl.

technique is explained briefly. At first, the activity coefficient f is calculated from the ionic strength:

$$f = 10^{-0.5\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right)}$$

For a maintained ionic strength with $c(\mathrm{KCl}) = 0.1$ mol L^{-1}, an activity coefficient of 0.785 is obtained. The exact pK_a values are computed according to de Levie [4] from the thermodynamic data at 20 °C to be 2.64 and 5.28.

$$\mathrm{p}K_{a1} = \mathrm{p}K_{a1}^{(\mathrm{th})} + 2\log f = 2.64$$

$$\mathrm{p}K_{a2} = \mathrm{p}K_{a2}^{(\mathrm{th})} + 4\log f = 5.28$$

The p$K_a^{(\mathrm{th})}$-values are the thermodynamic data based on an ionic strength of $I = 0$. For the calculation of the red curve in Figure 3, the influence of the activity coefficients to the pH values as well as the pK_w value were considered [4].

In the same manner, the titration curve of citric acid titrated with KOH was calculated and compared with experimental data (Figure 4).

Test-conditions: batch reactor, c_0(citric acid) = 1.672 × 10^{-2} mol L^{-1}, volume = 200 mL. Addition of KCl; ionic strength, I = 0.1 M.

c(KOH) = 1 mol/L.

Temperature of 20 °C.

It is very instructive to recognize that in case of the titration of citric acid the difference between the curves with and without considering the activity coefficients is much greater than with malonic acid, because the activity coefficients differ significantly from 1 at the higher ionic strength.

Investigation of the Buffer Region of Complicated Buffer Systems

In the same manner as in the previous examples, titration curves and, especially, the buffer regions of mixtures of different acids with distinct pK_a values can be calculated. For accurate results in the presence of polyvalent ions, the activity coefficients have to be considered, thus, the corresponding pK_a values, the pK_w value, and the pH values have to be converted as in the examples of malonic acid and citric acid. It is therefore advisable to use a constant ionic strength as a basis.

The titration of an acid mixture (without consideration of the activity coefficients) of citric acid, phosphoric acid, and boric acid with NaOH is used as an example. This mixture is known as the universal buffer of Theorell and Steinhagen [15]. It shall be studied in the pH region between pH = 2 and pH = 12. There is a large buffer region between pH 2 and 12 with a lower buffer capacity (bigger slope) in the refion at about pH = 11 (Figure 5).

With the aid of titration curves, the buffer mixtures for definite pH regions can be selected.

Appendix

The Derivation of the Titration Equations

We want to find the function $T = f(\mathrm{pH})$ for the titration of two basic acids with very strong bases (as a typical example). The derivation corresponds to that presented by Bliefert in *pH-Wert-Berechnungen* [7].

We look at a dibasic acid, H_2A, protolyzing water in two steps:

$$H_2A + H_2O \rightarrow H_3O^+ + HA^-$$

$$HA^- + H_2O \rightarrow H_3O^+ + A^{2-}$$

By adding a strong base B with the titrant the following reaction occurs:

$$B + H_3O^+ \rightarrow BH^+ + H_2O$$

The titration degree T will now be defined as the quotient

$$T = \frac{c_0(\mathrm{B})}{c_0(\mathrm{H_2A})}$$

A very strong base, like NaOH, will be completely ionized, so the following applies

$$c(\mathrm{NaOH}) = c(\mathrm{Na^+})$$

The following ions are present during the titration: H_3O^+, OH^-, HA^-, A^{2-}, and Na^+. The concentrations of each ion have to obey several restrictions, first, the principle of electroneutrality:

$$c(\mathrm{H_3O^+}) + c(\mathrm{Na^+}) = c(\mathrm{OH^-}) + c(\mathrm{HA^-}) + 2c(\mathrm{A^{2-}}) \qquad \text{(A1)}$$

Therefore, the definition of T,

$$T = \frac{c_0(\mathrm{Na^+})}{c_0(\mathrm{H_2A})} = \frac{c(\mathrm{OH^-}) - c(\mathrm{H_3O^+}) + c(\mathrm{HA^-}) + 2c(\mathrm{A^{2-}})}{c_0(\mathrm{H_2A})} \qquad \text{(A2)}$$

becomes

$$T = \frac{c(\mathrm{OH^-}) - c(\mathrm{H_3O^+})}{c_0(\mathrm{H_2A})} + \frac{c(\mathrm{HA^-}) + 2c(\mathrm{A^{2-}})}{c_0(\mathrm{H_2A})} \qquad \text{(A3)}$$

Furthermore, mass balance must be satisfied.

$$c_0(\mathrm{H_2A}) = c(\mathrm{H_2A}) + c(\mathrm{HA^-}) + c(\mathrm{A^{2-}}) \qquad \text{(A4)}$$

Equation A3 changes to

$$T = \frac{c(\mathrm{OH^-}) - c(\mathrm{H_3O^+})}{c_0(\mathrm{H_2A})} + \frac{c(\mathrm{HA^-}) + 2c(\mathrm{A^{2-}})}{c(\mathrm{H_2A}) + c(\mathrm{HA^-}) + c(\mathrm{A^{2-}})} \qquad \text{(A5)}$$

or

$$T = \frac{c(\mathrm{OH^-}) - c(\mathrm{H_3O^+})}{c_0(\mathrm{H_2A})} + \frac{\dfrac{c(\mathrm{HA^-})}{c(\mathrm{A^{2-}})} + 2}{\dfrac{c(\mathrm{H_2A})}{c(\mathrm{A^{2-}})} + \dfrac{c(\mathrm{HA^-})}{c(\mathrm{A^{2-}})} + 1} \qquad \text{(A6)}$$

Finally the principle of mass action has to be valid for the two expressions for the constants K_{a1} and K_{a2}

$$\frac{c(\mathrm{H_3O^+})c(\mathrm{HA^-})}{C(\mathrm{H_2A})} = K_{a1} \qquad \text{(A7)}$$

$$\frac{c(\mathrm{H_3O^+})c(\mathrm{A^{2-}})}{c(\mathrm{HA^-})} = K_{a2} \qquad \text{(A8)}$$

Equations A7 and A8 in the following forms:

$$\frac{c(\mathrm{HA^-})}{c(\mathrm{A^{2-}})} = \frac{c(\mathrm{H_3O^+})}{K_{a2}}$$

$$\frac{c(\mathrm{H_2A})}{c(\mathrm{A^{2-}})} = \frac{c^2(\mathrm{H_3O^+})}{K_{a1} * K_{a2}}$$

can now be substituted into eq A6 to obtain

$$T = \frac{c(\mathrm{OH^-}) - c(\mathrm{H_3O^+})}{c_0(\mathrm{H_2A})} + \frac{\dfrac{c(\mathrm{H_3O^+})}{K_{a2}} + 2}{\dfrac{c^2(\mathrm{H_3O^+})}{K_{a1}K_{a2}} + \dfrac{c(\mathrm{H_3O^+})}{K_{a2}} + 1} \qquad \text{(A9)}$$

Using the well-known definitions:

$$\mathrm{pH} = -\log c(\mathrm{H_3O^+})$$

$$\mathrm{p}K_{a1} = -\log \mathrm{K}_{a1}$$

$$\mathrm{p}K_{a2} = -\log K_{a2}$$

and the ionic product of water

$$c(\mathrm{H_3O^+}) \times c(\mathrm{OH^-}) = K_w = 10^{-14} \text{ (at 20 °C)}$$

we find

$$T = \frac{10^{\mathrm{pH}-p\mathrm{K}_w} - 10^{-\mathrm{pH}}}{c_0(\mathrm{H_2A})} + \frac{10^{\mathrm{p}K_{a2}-\mathrm{pH}} + 2}{10^{\mathrm{p}K_{a1}+\mathrm{p}K_{a2}-2\mathrm{pH}} + 10^{\mathrm{p}K_{a2}-\mathrm{pH}} + 1} \qquad \text{(A10)}$$

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Table A1. $\mathrm{p}K_\mathrm{a}$ Values of Some Polyvalent Acids

Acid	$\mathrm{p}K_{\mathrm{a}2}-\mathrm{p}K_{\mathrm{a}1}$	$\mathrm{p}K_{\mathrm{a}3}-\mathrm{p}K_{\mathrm{a}2}$	$\mathrm{p}K_{\mathrm{a}4}-\mathrm{p}K_{\mathrm{a}3}$
Oxalic acid	3.03		
Succinic acid	1.29		
Tartaric acid	1.33		
Phthalic acid	2.46		
Citric acid	1.63	1.64	
Diphosphoric acid	1.4	4.5	2.7

For the titration of tribasic acids with very strong bases, we obtain analogously,

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_\mathrm{w}}-10^{-\mathrm{pH}}}{c_0(\mathrm{H_3A})}+\frac{10^{\mathrm{p}K_{\mathrm{a}2}+\mathrm{p}K_{\mathrm{a}_3}-2\mathrm{p}H}+210^{\mathrm{p}K_{\mathrm{a}_3}-\mathrm{pH}}+3}{10^{\mathrm{p}K_{\mathrm{a}_1}+\mathrm{p}K_{\mathrm{a}2}+\mathrm{p}K_{\mathrm{a}3}-3\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}2}+\mathrm{p}K_{\mathrm{a}3}-2\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}3}-\mathrm{pH}}+1} \tag{A11}$$

For the titration of quadribasic acids, for example, EDTA or $\mathrm{H_4P_2O_7}$, we obtain eq A12:

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_\mathrm{w}}-10^{-\mathrm{pH}}}{c_0(\mathrm{H_3A})}+\frac{10^{\mathrm{pK}_{\mathrm{a}2}+\mathrm{p}K_{\mathrm{a}_3}+\mathrm{p}K_{\mathrm{a}4}-3\mathrm{pH}}+210^{\mathrm{p}K_{\mathrm{a}3}+\mathrm{p}K_{\mathrm{a}4}-2\mathrm{pH}}+310^{\mathrm{p}K_{\mathrm{a}4}-\mathrm{pH}}+4}{10^{\mathrm{p}K_{\mathrm{a}_1}+\mathrm{p}K_{\mathrm{a}2}+\mathrm{p}K_{\mathrm{a}3}+\mathrm{p}K_{\mathrm{a}4}-4\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}2}+\mathrm{p}K_{\mathrm{a}3}+\mathrm{p}K_{\mathrm{a}4}-3\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}3}+\mathrm{p}K_{\mathrm{a}4}-2\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}4}-\mathrm{pH}}+1} \tag{A12}$$

The equation expands for acids with an increasing number of protons, being separable into an easily understand scheme. The corresponding expressions for the titration of polyvalent acids can be obtained without a new derivation.

For the titration of monobasic acids we obtain in an analogous way the expression

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_\mathrm{w}}-10^{-\mathrm{pH}}}{c_0(\mathrm{HA})}+\frac{1}{1+10^{p\mathrm{K}_a-\mathrm{pH}}} \tag{A13}$$

which can be approximated for very strong acids, for example, HCl ($\mathrm{p}K_\mathrm{a} < 0$) for the usual pH region with

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_\mathrm{w}}-10^{-\mathrm{pH}}}{c_0(\mathrm{HA})}+1 \tag{A14}$$

The equations above can also be used to calculate T for the titration of polyvalent bases with acids. Only the signs of the first summation and of the exponentials in the second summation need changed. The $\mathrm{p}K_\mathrm{a}$ values are assigned to the corresponding acids.

Equations A11 and A12 show that for polyvalent acids the complexity of the equations of titration curves of higher valence increases quickly. The same is true for the titration curves of polyvalent bases.

It is now possible to deduce a good approximation, which is sufficient for all practical cases of titration of polyvalent acids and bases. In eq A10, it is possible to replace the expression

$$10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{pH}}$$

in the numerator as well as in the denominator by the approximate expression

$$\left(10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{p}K_{\mathrm{a}_1}}+1\right)10^{\mathrm{p}K_{\mathrm{a}_1}-\mathrm{pH}} \text{ if } \left(10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{p}K_{\mathrm{a}_1}}\right) >> 1$$

that is, that the difference in the $\mathrm{p}K_\mathrm{a}$ values is greater than ca. 1. This is usually the case for polyvalent acids. Some examples are listed in Table 1A.

The approximate equation for dibasic acids is

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_w}-10^{-\mathrm{pH}}}{c_0(\mathrm{H_2A})}+\frac{10^{\mathrm{p}K_{a1}-\mathrm{pH}}*(10^{\mathrm{p}K_{\mathrm{a}2}-\mathrm{p}K_{\mathrm{a}1}}+1)+2}{10^{\mathrm{p}K_{\mathrm{a}1}+\mathrm{p}K_{\mathrm{a}2}-2\mathrm{pH}}+10^{p\mathrm{K}_{a2}-\mathrm{pH}}(10^{\mathrm{p}K_{\mathrm{a}2}-\mathrm{p}K_{\mathrm{a}1}}+1)+1} \tag{A15}$$

or

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_w}-10^{-\mathrm{pH}}}{c_0(\mathrm{H_2A})}+\frac{10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{p}K_{\mathrm{a}1}}10^{\mathrm{p}K_{\mathrm{a}1}-\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}1}-\mathrm{pH}}+2}{10^{\mathrm{p}K_{\mathrm{a}_1}+\mathrm{p}K_{\mathrm{a}2}-2\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}2}-\mathrm{p}K_{\mathrm{a}1}}10^{\mathrm{p}K_{\mathrm{a}_1}-\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}1}-\mathrm{pH}}+1} \tag{A16}$$

$10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{p}K_{\mathrm{a}_1}}\times10^{\mathrm{p}K_{\mathrm{a}_1}-\mathrm{pH}}$ is identical to $10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{pH}}$, therefore:

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_\mathrm{w}}-10^{-\mathrm{pH}}}{c_0(\mathrm{H_2A})}+\frac{10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}1}-\mathrm{pH}}+2}{10^{\mathrm{p}K_{\mathrm{a}_1}+\mathrm{p}K_{\mathrm{a}2}-2\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}2}-\mathrm{pH}}+10^{\mathrm{p}K_{\mathrm{a}1}-\mathrm{pH}}+1} \tag{A17}$$

Equation 17 can be written as

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_w}-10^{-\mathrm{pH}}}{c_0(\mathrm{H_2A})}+\frac{1}{1+10^{\mathrm{p}K_{\mathrm{a}_1}-pH}}+\frac{1}{1+10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{pH}}} \tag{A18}$$

The titration curve of a tribasic acid can be described analogously by

$$T=\frac{10^{\mathrm{pH}-\mathrm{p}K_\mathrm{w}}-10^{-\mathrm{pH}}}{c_0(\mathrm{H_3A})}+\frac{1}{1+10^{\mathrm{p}K_{\mathrm{a}_1}-\mathrm{pH}}}+\frac{1}{1+10^{\mathrm{p}K_{\mathrm{a}_2}-\mathrm{pH}}}+\frac{1}{1+10^{\mathrm{p}K_{\mathrm{a}_3}-\mathrm{pH}}} \tag{A19}$$

For the titration of an *n*-basic acid with a very strong base we analogously use eq A20,

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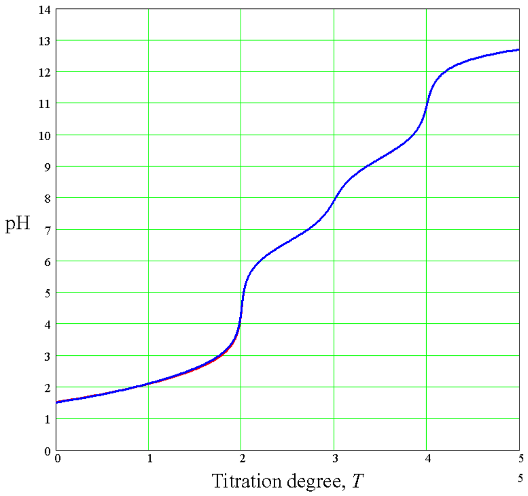

Figure A1. Titration of diphosphoric acid with NaOH without the consideration of activity coefficients: (a) calculated using the exact equation A12 (red line), (b) calculated using the approximate eq A20 (blue line).

$$T = \frac{10^{\mathrm{pH}-\mathrm{p}K_\mathrm{w}} - 10^{-\mathrm{pH}}}{c_0(\mathrm{H}_n\mathrm{A})} + \frac{1}{1+10^{\mathrm{p}K_{\mathrm{a}1}-pH}} + \frac{1}{1+10^{\mathrm{p}K_{\mathrm{a}2}-\mathrm{pH}}} + \cdots + \frac{1}{1+10^{\mathrm{p}K_{\mathrm{a}n}-\mathrm{pH}}} \qquad \text{(A20)}$$

and for the titration of polyvalent bases with very strong acids, we change the signs of the exponentials in eq A20 to obtain

$$T = \frac{10^{-\mathrm{pH}} - 10^{\mathrm{pH}-\mathrm{p}K_\mathrm{w}}}{c_0(\mathrm{B})} + \frac{1}{1+10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a}1}}} + \frac{1}{1+10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a}2}}} + \ldots + \frac{1}{1+10^{\mathrm{pH}-\mathrm{p}K_{\mathrm{a}n}}} \qquad \text{(A21)}$$

Equation A20 is very accurate when used in place of the exact equation, eq A12. This is demonstrated in Figure A1, the titration curve of diphosphoric acid, where the blue curve is generated from eq A20 and the red curve from eq A12. Equations A8 through A12 are clearly simpler and clearer than the exact equations, eqs A8–A12, and they can be easily entered into computer spreadsheets. The proof, that the approximate equations are valid for nearly all practical analytical cases is given here. We believe that the presented method is especially simple and elegant. The procedure can be used by every student in the basic analytical chemistry course.

The question of whether or not titration curves are important in industrial analytical chemistry depends on the particular area of operation. For development of analytical methods for titration of polyvalent acids or bases and mixtures with strong acids or bases, the knowledge of the appropriate titration curves is essential. The questions of which pH step is most suitable for titration and which indicator is applicable can only be answered if the titration curve is known.

Generally it can be shown by calculating the pK_a values for polyvalent acids that the approximate formulas [18–21] produce curves very close to the exact curves as seen in Figure A1.

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