WHEN ACID-BASE TITRATIONS ARE CARRIED OUT IN UNUSUAL CONDITIONS

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ABSTRACT. Uncommon aspects in acid-base titrations are presented, which occur in titrations between both mono- and/or poly-functional acid and bases but are rarely introduced in ordinary analytical chemistry courses.

1. Introduction

The sound knowledge of the acid-base behaviors is very important in chemistry, for most chemical reactions can be interpreted in terms of acid-base interactions [1, 2]. In analytical chemistry the fundamentals are elucidated by traditional elementary cases when the titration curves are introduced in volumetric analysis [3–5].

The functional relationship between pH change and the added volume of titrant is connected with the mutual acid-base affinity, expressed by the dissociation constants of the reacting acid and base and the self-dissociation constant of the solvent medium (in aqueous solution for the reaction $HA + BOH \rightleftharpoons A^- + B^+ + H_2O$; $K = K_a \cdot K_b / K_w$), together with the dilution factor as determined by the $C_{titrant}/C_{titrand}$ (titrand: hereafter analyte) ratio. Because the titration curves are specific bi-dimensional parametric functions of multi-variable relationships [6–10], singularly they show only marginal aspects of the general problem and it can be appropriate to deepen the topic with more articulate though less common examples.

The pursuit and presentation of particular unusual cases is surely a very useful but time consuming laboratory task and it can be preferable to use numeric-graphic simulations based on the mass balance equations and the principle of electroneutrality of the solutions [6, 8, 10]. The second approach has been followed during many years of academic lectures in analytical chemistry by one of the authors. The titration curves have been experienced by computer simulation by using an original routine written by one of the authors. The routine is available from the authors free of charge on request. Many other simulators can be downloaded from the web or easily found in literature [8] or obtained from the various Chemical Societies in the world.
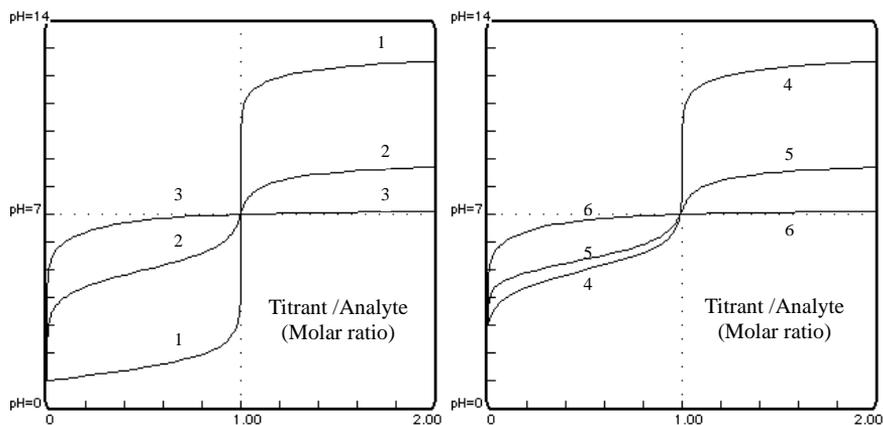
Figure 1. Titration curves of strong or weak acid HA with strong base BOH as dependent on the concentration of the titrant. Curves 1, 2, 3: strong acid $0.1M$ titrated with strong base $10^{-1}M$, $10^{-5}M$ and $10^{-7}M$ respectively; curves 4, 5, 6: weak acid HA ($K_a = 10^{-5}$) titrated with strong base $10^{-1}M$, $10^{-5}M$ and $10^{-7}M$ respectively.

At the beginning the unusual cases were faced as a mere curiosity, but the detailed analysis of the various examples revealed itself to be highly formative in advanced curricula when the canonical behaviors have been already deeply understood and adequately assimilated. In the following some meaningful examples are reported without pretension to exhaust the arguments with the present considerations.

2. Unusual examples

2.1. Generality. In the titrations, the change of the dependent variables (pH, absorbance, conductivity, etc.) arises from two different but simultaneous causes: (i) the chemical reaction between analyte and titrant and (ii) the dilution of the analyte solution. The relative contribution of the two mechanisms on the overall change of the dependent variable is related to the ratio between the titrant and the analyte molar concentration ($C_{titrant}/C_{analyte}$). In ordinary cases, for practical aims, $C_{titrant} > C_{analyte}$ is frequently used. On such conditions the concentration of the titrated analyte mainly occurs for chemical reaction and the titration curve shows the usual canonical shape. On the contrary when the titrant solution is more dilute than the analyte one $C_{titrant} > C_{tanalyte}$ - the case is impractical for laboratory experiences - the dilution of the analyte solution on adding the titrant becomes the most important factor as more dilute titrant solutions are used.

On limit conditions when $C_{titrant}/C_{analyte}$ ratio tends to 0, all the titration curves collapse on a single curve coincident with the dilution of the titrated solution and the identifier elements of the equivalent point disappear also for titrations of strong acid with strong base which at the equivalent point in ordinary conditions show very sharp pH changes (Fig. 1).
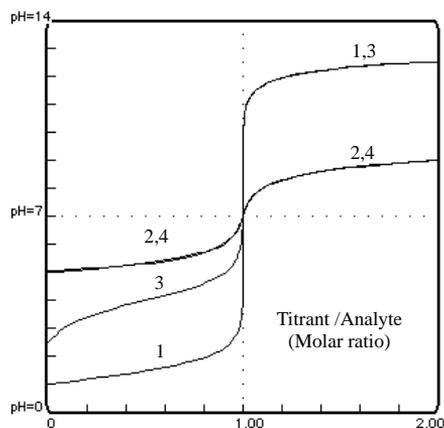
Figure 2. Titration curves of strong or weak acid HA with strong base BOH respectively. Curves 1, 2: strong acid $10^{-1}M$ or $10^{-5}M$ respectively titrated with strong base $10^{-1}M$. Curves 3, 4: weak acid ($K_a = 10^{-4}$) $10^{-1}M$ or $10^{-5}M$ respectively titrated with strong base $10^{-1}M$. Strong and weak acids show different behaviors only in concentrated solutions (curves 1,3). In diluted solutions strong and weak acids show identical behaviors.

2.2. Titrations of mono-functional acids with strong bases. The behavior of weak acids titrated with strong bases differs from the behavior of strong acids titrated with strong bases only in concentrated solution. When the initial sample concentration of the weak acid yields $pH \geq -0.5 \cdot log(K_a + (K_a^2 + 4 \cdot K_w)^{1/2})$ ($\alpha = [A^-]/C_a \geq 0.5$), the titration curves of weak acids tend to coincide with the titration curves of strong acids with the same initial concentration (e.g.: $C_a = 10^{-5}M$, $K_a = 10^{-5}$ titrated with strong base compared with the titration of strong acid $C_a = 10^{-5}M$ titrated with strong base, Fig. 2) and for highly dilute solutions and/or extremely weak acids, when the initial pH of the analyte solution tends to $pK_w/2$, the titration curves tend to coincide with (and at least to be approximated by) the dilution curves of the titrant base. In laboratory this is clearly evident by comparing the titrations of solutions of acetic acid (universally intended weak – partially dissociated – acid) $C_a \geq 10^{-5}M$ with the titrations of solutions of strong acid with equal molar concentrations, both titrated with the same strong base solutions. Therefore strong and weak acid (bases) have finite range of experimental conditions (concentration ranges) within which they are indistinguishable for their analytical behavior and their classification as strong or weak electrolytes is strictly connected with the experimental condition range (the concentration range) ordinarily used for investigating the analytical properties.

In different words weak acids/bases (as CH_3COOH, H_3PO_4, ...) are totally dissociated (hence strong) in dilute solutions and strong acids/bases are partially dissociated (hence weak) in concentrated solutions.

2.3. Titrations of poly-functional acids with mono- or poly-functional bases. Poly-functional acids (bases) in practice are mainly titrated with mono-functional titrants but

seldom with poly-functional titrants. In selected cases, titrations between poly-functional electrolytes show subtle behaviors.

The titrations of poly-functional acids with mono- or poly-functional bases are contained between the titration of extremely weak and analytically unreactive acids with strong base at one side and the titration of strong acids with very weak and analytically unreactive base on the opposite side. Both sets of titration curves evidence no equivalence point because the *pH* change comes from the dilution of the titrated solution. In intermediate, cases of titrations of poly-functional acids with mono- or poly-functional bases are very numerous for the great multiplicity of functionality and strength of both the reactants and analytes. Some of them, such as the titrations of H_2SO_4 with $Ca(OH)_2$ or $Ba(OH)_2$ in concentrated solutions, are canonical titrations.

In the following, a few cases of bi-functional acids titrated with mono- or bi-functional bases are analysed.

The acid functions of bi-functional acids react simultaneously or separately with mono-functional bases not only depending on the K_{a1}/K_{a2} ratio, but also on the actual K_{a1} and K_{a2} values. According to the dissociation constants K_{a1} and K_{a2} of the acid together with the dissociation constant K_b of the base, the titration curve of bi-functional acids H_2A with mono-functional $B(OH)$ solution will show:

(1) no equivalence point (e.g.: $C_{H_2A} = 10^{-1} M$, $K_{a1} = 1$, $K_{a2} = 10^{-4}$, $C_{B(OH)} = 10^{-1} M$, $K_b = 10^{-12}$), no analytically valid reaction, (see Fig. 3, curve 1);

(2) one equivalence point (e.g.: $C_{H_2A} = 10^{-1} M$, $K_{a1} = 10^{-2}$, $K_{a2} = 10^{-5}$, $C_{B(OH)} = 10^{-1} M$, $K_b = 10^{-5}$, or $C_{H_2A} = 10^{-1} M$, $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-5}$, $C_{B(OH)} = 10^{-1} M$, $K_b = 10^{-5}$, see Fig. 3, curves 2 and 3), occurring reaction: $H_2A + 2B(OH) \rightleftharpoons A^{2-} + 2B^+ + 2H_2O$; the two acid functions of H_2A are indistinguishable because they react simultaneously;

(3) two separate equivalence points (e.g.: $C_{H_2A} = 1 M$, $K_{a1} = 10^{-2}$, $K_{a2} = 10^{-5}$, $C_{B(OH)} = 1 M$, $K_b = 10^{-5}$; occurring reactions: $H_2A + B(OH) \rightleftharpoons HA^- + B^+ + H_2O$ followed by $HA^- + B(OH) \rightleftharpoons A^{2-} + B^+ + H_2O$).

The titrations of bi-functional acids with bi-functional bases can show one, two or three equivalence points (Fig. 3). One equivalence point occur:

(1) on the titration of strong acid with strong base (e.g.: H_2SO_4 titrated with $Ca(OH)_2$; occurring reaction: $H_2A + B(OH)_2 \rightleftharpoons A^{2-} + B^{2+} + 2H_2O$; B^{2+} is an extremely weak Lewis acid unable to react with the excess of titrant);

(2) on the titration of H_2A having only one analitically useful acid function with strong $B(OH)_2$ base (e.g.: $C_{H_2A} = 0.1 M$, $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-20}$, $C_{B(OH)_2} = 0.1 M$, $K_{b1} = 10^{-3}$, $K_{b2} = 10^{-4}$; occurring reaction: $2H_2A + B(OH)_2 \rightleftharpoons 2HA^- + B^{2+} + 2H_2O$, stochiometric ratio $n_{H_2A}/n_{B(OH)_2} = 2/1$);

(3) on the titration of strong acid H_2A with $B(OH)_2$ having only one analitically useful reactive function (e.g.: $C_{H_2A} = 0.1 M$, $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-4}$, $C_{B(OH)_2} = 0.1 M$, $K_{b1} = 10^{-3}$, $K_{b2} = 10^{-20}$; occurring reaction: $H_2A + 2B(OH)_2 \rightleftharpoons A^{2-} + 2B(OH)^+ + 2H_2O$, stochiometric ratio $n_{H_2A}/n_{B(OH)_2} = 1/2$).
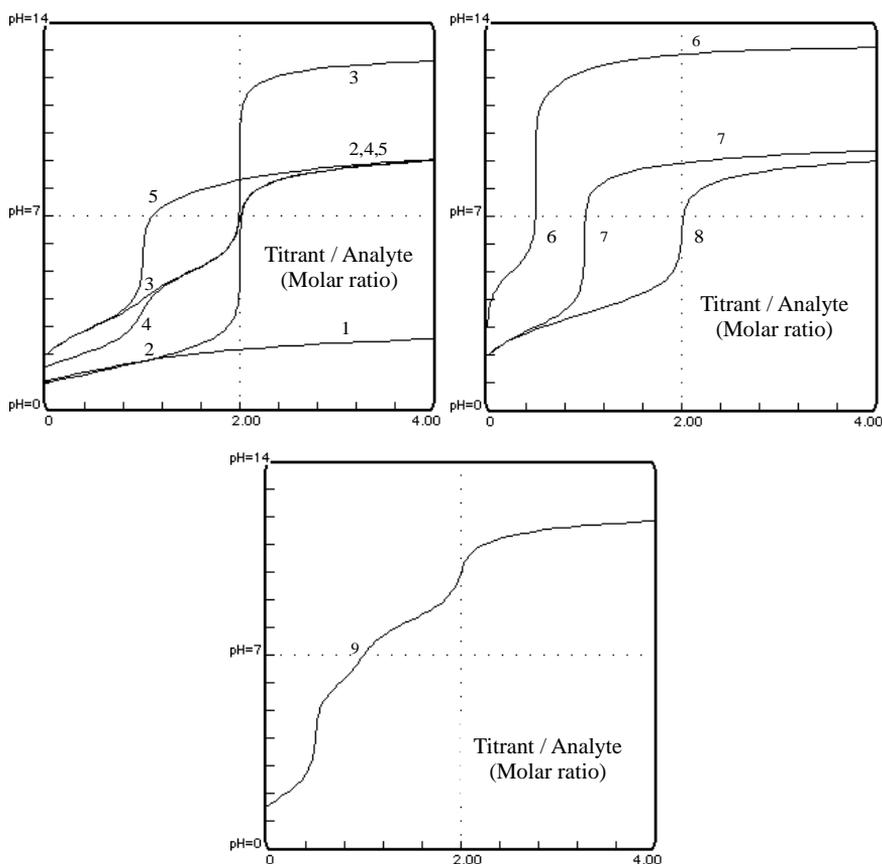
Figure 3. Titration curves of di-protic acids H_2A $10^{-1}M$ with base BOH (curves 1-5) or $B(OH)_2$ (curves 6-9) $10^{-1}M$. Curve 1: $K_{a1} = 1$, $K_{a2} = 10^{-4}$, $K_b = 10^{-12}$. The curve shows no usefull elements to identify the equivalence point. Curve 2: $K_{a1} = strong$, $K_{a2} = 10^{-5}$, $K_b = 10^{-5}$. Curve 3: $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-5}$, $K_b = 10^{-5}$. The curves 2 and 3 show single equivalence point at $n_{H_2A}/n_{BOH} = 1/2$. Curve 4: $K_{a1} = 10^{-2}$, $K_{a2} = 10^{-5}$, $K_b = 10^{-5}$. The curve shows two equivalence points for the stepwise reactions. Curve 5: $K_{a1} = 10^{-2}$, $K_{a2} = 10^{-15}$, $K_b = 10^{-5}$. The curve shows single equivalence point. Curve 6: $K_{a1} = 10^{-2}$, $K_{a2} = 10^{-15}$, $K_{b1} = strong$, $K_{b2} = strong$. The curve shows single equivalence point at $n_{H_2A}/n_{BOH} = 2/1$. Curve 7: $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-15}$, $K_{b1} = 10^{-5}$, $K_{b2} = 10^{-15}$. The curve shows single equivalence at $n_{H_2A}/n_{B(OH)_2} = 1/1$ for the reaction $H_2A + B(OH)_2 \rightleftharpoons HA^- + BOH^+ + H_2O$. Curve 8: $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-4}$, $K_{b1} = 10^{-5}$, $K_{b2} = 10^{-15}$. The curve shows single equivalence at $n_{H_2A}/n_{B(OH)_2} = 1/2$. Curve 9: $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-6}$, $K_{b1} = 10^{-3}$, $K_{b2} = 10^{-6}$. The curve shows three equivalence points for the successive reactions $2 H_2A + B(OH)_2 \rightleftharpoons 2 HA^- + B^{2+} + 2 H_2O$, $2 HA^- + B(OH)_2 \rightleftharpoons 2 A^{2-} + B^{2+} + 2 H_2O$ and $2 B^{2+} + 2 B(OH)_2 \rightleftharpoons 4 BOH^-$.
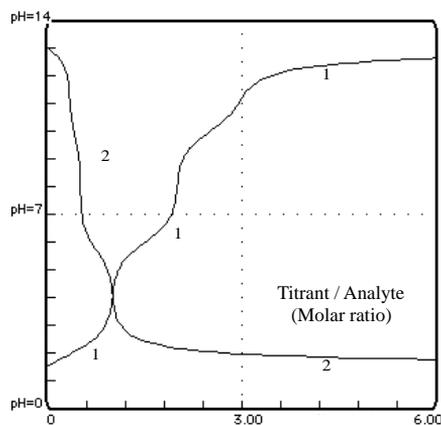
Figure 4. Titration curves of three-protic weak acid ($K_{a1} = 10^{-2}$, $K_{a2} = 10^{-6}$, $K_{a3} = 10^{-10}$) with strong base (curve 1) and viceversa (curve 2).

Two equivalence points occur when:

(1) both acid functions react simultaneously with both the base functions and the titrant excess reacts with its conjugated species (e.g.: $C_{H_2A} = 0.1\,M$, $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-4}$, $C_{B(OH)_2} = 0.1\,M$, $K_{b1} = 10^{-3}$, $K_{b2} = 10^{-7}$; occurring reactions: $H_2A + B(OH)_2 \rightleftharpoons A^{2-} + B^{2+} + 2\,H_2O$, stochiometric ratio $n_{H_2A}/n_{B(OH)_2} = 1/1$ followed by $B^{2+} + B(OH)_2 \rightleftharpoons 2\,B(OH)^+$; B^{2+} is moderately strong Lewis acid);

(2) the first acid function reacts with both functions of the base $B(OH)_2$ and B^{2+} reacts with the excess of titrant (e.g.: $C_{H_2A} = 0.1\,M$, $K_{a1} = 10^{-3}$, $K_{a2} = 10^{-7}$, $C_{B(OH)_2} = 0.1\,M$, $K_{b1} = 10^{-3}$, $K_{b2} = 10^{-4}$; occurring reactions: $2\,H_2A + B(OH)_2 \rightleftharpoons 2\,HA^- + B^{2+} + 2\,H_2O$ followed by $2\,HA^- + B^{2+} + 3\,B(OH)_2 \rightleftharpoons 2\,A^{2-} + 4\,BOH^+ + H_2O$; HA^- is not too weak protic acid and B^{2+} is moderately strong Lewis acid);

Titration curves with three equivalent points occur when the acid functions of H_2A and the conjugate functions (B^{2+}) of the titrant base react separately with the titrant base (e.g.: $C_{H_2A} = 0.1\,M$, $K_{a1} = 10^{-2}$, $K_{a2} = 10^{-6}$, $C_{B(OH)_2} = 0.1\,M$, $K_{b1} = 10^{-2}$, $K_{b2} = 10^{-6}$; occurring reactions: $2\,H_2A + B(OH)_2 \rightleftharpoons 2\,HA^- + B^{2+} + 2\,H_2O$ followed by $2\,HA^- + B(OH)_2 \rightleftharpoons 2\,A^{2-} + B^{2+} + H_2O$ followed by $2\,B^{2+} + 2\,B(OH)_2 \rightleftharpoons 4\,BOH^+$; the 2nd and the 3rd reaction can occur inverted depending on the acid strength of HA^- and B^{2+}).

2.4. Reversing the titration. On reversing the titration (instead of acid titrated with base, base titrated with acid) very often it is said that specular curves result. This is fairly true in the titration of strong acid with strong bases. In Fig. 4, the titration of three-protic acid H_3PO_4 with mono-functional strong bases and its reversed are reproduced. It is well known that the titration of H_3PO_4 has equivalence points for its stepwise neutralization of the 1st and 2nd and scarcely evident for the 3rd hydrogen acid . The reverse titration of NaOH with H_3PO_4 has three equivalent points corresponding to the following reactions:

$$3\,OH^- + H_3PO_4 \;\; \rightleftharpoons \;\; PO_4^{3-} + 3\,H_2O$$
$$PO_4^{3-} + H_3PO_4 \;\; \rightleftharpoons \;\; H_2PO_4^- + HPO_4^{2-}$$
$$HPO_4^{2-} + H_3PO_4 \;\; \rightleftharpoons \;\; 2\,H_2PO_4^-.$$
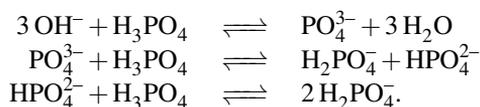
Both the shapes of the curves and the corresponding chemical reactions are surely mutually related but no specular.

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