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An Attractive Way of Developing the Concept of Systematic Titration Error of Visual Acid-Base Titrations (on the Basis of Logarithmic Acid-Base Diagrams)

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Abstract For any titration, the titration error is, by definition, the difference between the volume of titrant added to reach the end point and the volume of titrant necessary to reach a stoichiometrically defined equivalent point. A graphical approach is presented, which allows a smooth and far reaching quantitative discussion of the systematic titration error of Acid-Base titrations, on the basis of the Logarithmic Acid-Base Diagram representing the titrated solution. Considerations and relations are developed which connect this diagram to the titration error. Examples are fully developed, which show that the procedure suggested unavoidably goes beyond the technical or practical topic of evaluating the systematic titration error, and it can be especially rewarding from an educational point of view. Finally, for the reader's convenience, algebraic expressions and brief instructions to draw Logarithmic Acid-Base Diagrams (also known as Sillén's diagrams), by using a spreadsheet, are provided.

Keywords: *acid base titration, systematic error, acid base diagrams, amino acid, carbonate, bicarbonate*

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1. Introduction

Logarithmic Acid-Base Diagrams (in the following called, for brevity, LABD) were introduced in a pre computer era, [1], as an alternative to algebraic calculations, for the evaluation of pH and equilibrium concentrations of all species present in a specified (aqueous) solution of acids and/or bases.

In the computer era, there is no need for plots to calculate the equilibrium concentrations of species present in whatever solution (if the pertinent data are available).

However, graphical equilibrium calculations based on LABDs are still popular and very useful because of their recognized capabilities of transferring chemical knowledge and enhancing understanding of concepts related to Acid-Base reactions. Books are available which deal with this topic, [2,3,4]. Please note that, in reference [4], Logarithmic Acid-Base Diagrams are called Sillén's diagrams.

Then, we shall go beyond the subject of using LABDs for graphical pH calculations, in order to focus on the topic of systematic errors which can bias analytical results derived from Acid-Base titrations (especially visual Acid-Base titrations).

We shall discuss how LABD of the titrated solution can assist in the process of introducing, detecting, evaluating and, eventually, avoiding the systematic titration error for a specified Acid-Base titration, because we believe that this argument, if presented in an attractive way, is eminently suitable to promote a deep understanding of a broad range of concepts related to Acid-Base reactions and titrations.

In dealing with chemical equilibrium is fundamental to distinguish analytical concentrations of substances dissolved to prepare any given solution from equilibrium concentrations of species present in the solution.

Although there is an agreed and convenient symbol to indicate molar equilibrium concentrations (i.e., [X], where X symbolizes any species in the considered solution), there is no established symbol to indicate analytical molar concentrations. Therefore, we shall use the custom symbol [[Y]], to indicate the *molar analytical concentration* of any substance Y which has been dissolved to prepare the considered solution. By way of example, we can prepare a solution in which [[HCl]] = 0.1 M; however, because HCl is fully dissociated, in this solution [HCl] ≈ 0 and [Cl^-] = 0.1 M.

Furthermore, for the dissociation constants of weak acids, which are necessary to achieve our aims, we shall consistently use throughout the values at 25°C and zero ionic strength. These can, eventually, be substituted with practical or custom dissociation constants. The same applies to transition intervals of Acid-Base indicators.

2. Acid-Base Titrations, Logarithmic Acid-Base Diagrams and Systematic Titration Error

2.1. Acid-Base Titrations and Logarithmic Acid-Base Diagrams

Whatsoever solution of acids and/or bases can be represented by a Logarithmic Acid-Base Diagram (LABD), which is constructed by drawing in the plane log[j]→pH a curve for each species, j, present in the considered solution at the equilibrium concentration [j].

Instructions and algebraic expressions for developing a MS Excel file designed for drawing any required LABD are postponed, for convenience, to §4. In addition, a *Windows Forms* application for drawing appealing LABDs is supplied on a CD attached to reference [2].

For the present, it is sufficient to assume that the LABD representing any given solution is readily available.

LABD of pure water is the simplest one, since it is constituted by only two curves (actually two lines) representing log[H^+] and log[OH^-], respectively (see Figure 1). In Figure 1, line identified with label H has slope -1 and represents log[H^+] (= -pH); line with label OH has slope +1 and represents log[OH^-] (= - pK_w + pH). pK_w is the ion product of water. The two lines intersect at pH = 7.0, which is the pH of pure water at 25°C.

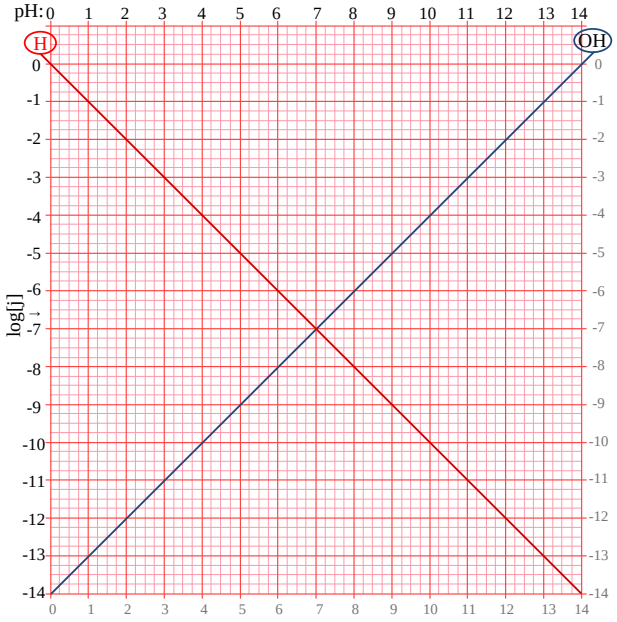

Figure 1. Logarithmic Acid-Base diagram of pure water at 25 °C. Line identified with label H represents log[H^+] and line with label OH represents log[OH^-] as functions of pH

As we add to water solutes having Acid-Base properties, additional curves must be added in order to represent the new species which are formed in the solution.

For instance, if we add a monoprotic acid, HA, of specified pK_a and *analytical concentration* [[HA]], two new curves will appear in the LABD representing the solution. These, curves represent log[HA] and log[A^-], respectively, and the LABD will expose four curves identified by labels H, OH, HA and A^-.

For instance, Figure 2 is a LABD which represents a solution 0.100 M of acetic acid. This means that, for Figure 2, [[CH_3COOH]] = 0.100 M. Curve with label CH_3COOH represents log[CH_3COOH] and curve with label CH_3COO^- represents log[CH_3COO^-]. The CH_3COOH curve meets CH_3COO^- curve at pH = pK_a = 4.75 (pK_a is the dissociation constant of acetic acid). The horizontal asymptote to the curves of CH_3COOH (or of CH_3COO^-) intersects the log[j] axis at log[[CH_3COOH]]. This diagram embodies the acetic acid dissociation equilibrium and mass balance, but not the charge balance. This implies that Figure 2. also represents a 0.100 M solution of acetate (i.e., [[CH_3COO^-]] = 0.100 M) or any other solution in which [CH_3COOH] + [CH_3COO^-] = 0.100 M.

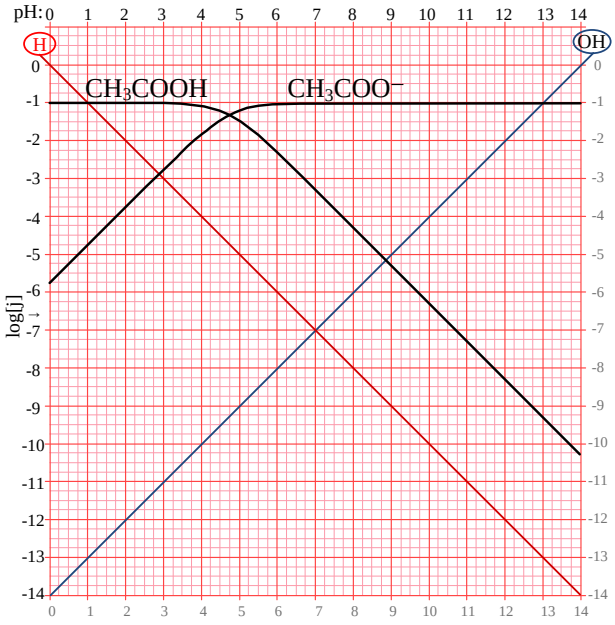

Figure 2. Logarithmic Acid-Base diagram of 0.100 M acetic acid, at 25°C. Curve with label CH_3COOH represents log[CH_3COOH] and curve with label CH_3COO^- represents log[CH_3COO^-] as a function of pH

In general, a LABD exposes as many curves as the number of species in the solution which it represents, becoming, by consequence, more and more crowded as the complexity of the considered solution increases.

In the following, we shall assume that the reader has a general knowledge of the significance of Logarithmic Acid-Base Diagrams as presented in references [1,2,3,4].

On the other side, the solution represented in a LABD can be titrated with the standard solution of a strong base (e.g., NaOH → *alkalimetric titrations*) or with the standard solution of a strong acid (e.g., HCl → *acidimetric titrations*).

As a matter of fact, a titration amounts, in a figurative way, to traversing the LABD of the titrated solution from its initial pH, pH_{in}, to a final pH, pH_{end}.

In practice, the evolution of the pH during an Acid-Base titration is caused by the stepwise addition of increasing volumes, V_t^{ml}, of the titrant solution to an initial volume, V_0^{ml}, of the titrated solution.

The target of an analytical Acid-Base titration is the determination of the equivalent volume, V_{eq}^{ml}, which, by definition, is the volume of titrant solution which contains a number of moles exactly equal (or stoichiometrically equivalent) to the number of moles of the titrated

substance in the titrated solution. In general, V_{eq}^{ml} is used to derive the analytical concentration or number of moles of the titrated substance by means of simple stoichiometric calculations presented in any standard general or analytical chemistry textbook, [5].

By definition, analytical results derived by using the equivalent volume are absolutely accurate and free from systematic error.

In addition, by definition, when a volume of titrant exactly equal to V_{eq}^{ml} has been added, the titrated solution's pH assumes a value which is the equivalent point pH, pH_{eq}.

However, during Visual Acid-Base Titrations (VABT), the colour change of an Acid-Base indicator is used as a signal to stop the titration. When a VABT is discontinued, the pH of the solution, indicated with pH_{end}, coincides with either pH value delimiting the transition interval of the indicator.

To be more specific, for an alkalimetric titration, pH_{end} coincides with the upper limit of the transition interval of the indicator. For an acidimetric titration, pH_{end} coincides with the lower limit of the transition interval.

Standard transition intervals for common Acid-Base indicators are readily available from analytical chemistry textbooks, [5], or from the Web.

The volume of titrant solution consumed to reach pH_{end} is the end point volume, V_{end}^{ml}, which can be read from the burette when the Acid-Base titration is ended.

It must be understood that, once we have specified the indicator, pH_{end} is automatically set and that, if not by chance, pH_{end} is different from pH_{eq}.

Of course, we can change pH_{end} by selecting a different indicator, but we have only a limited or no control on pH_{eq}, which is fixed by the analytical composition of the titrated solution.

2.2. Systematic Titration Error

Suppose that 25.00 ml of the 0.100 M solution of acetic acid represented in Figure 2 are titrated with a standard solution 0.1000 M of NaOH (i.e., [[NaOH]] = 0.1000 M), in presence of phenolphthalein as an indicator (transition interval {8.2, 9.5}).

This titration starts at $pH_{in} \approx 2.9$, which is the pH of a solution [[CH_3COOH]] = 0.1 M. This pH is easily read from Figure 2, because it corresponds to the pH at the intersection point between curves representing log[H^+] and log[CH_3COO^-]. By the way of example, this is a simple demonstration of how a LABD can help in pH calculations. From this point, we move towards higher pHs and we meet $pH_{eq} \approx 8.9$, which is the pH corresponding to the intersection point between the curve representing log[CH_3COOH] and the curve representing log[OH^-]. This is because, by neglecting the small change in volume of the titrated solution, pH_{eq} is, for our purposes, not significantly different from the pH of a 0.1 M solution of sodium acetate. By the way, changes in volume of the titrated solutions will be neglected throughout.

We should then stop the titration when pH_{eq} is reached and read V_{eq}^{ml} from the burette.

However, during the VABD with phenolphthalein, we do not stop at pH_{eq}, but continue to $pH_{end} \approx 9.5$, which is the upper limit of the phenolphthalein transition interval. After that, what we read from the burette is V_{end}^{ml}, which of course is, in abstract, larger than V_{eq}^{ml}.

For any specified VABT, we define the variables ΔpH_{tit} and ΔV_t^{ml} according to equations (1) and (2):

$$\Delta pH_{tit} = pH_{end} - pH_{eq} \quad (1)$$

$$\Delta V_t^{ml} = V_{end}^{ml} - V_{eq}^{ml} \quad (2)$$

In general, for whatever VABT, both, ΔpH_{tit} and ΔV_t^{ml}, will be different from zero.

ΔpH_{tit} is easily evaluated for a planned titration. In fact, pH_{end} is set by the chosen indicator and, on the other side, the evaluation of pH_{eq} is a standard pH calculation which is most readily performed graphically using the LABD of the titrated solution (as we have done above) or algebraically (as described in standard textbooks, [4,5]).

Although the fact that $\Delta pH_{tit} \neq 0$ is the primordial origin of the systematic titration error, the accuracy of a planned titration cannot be assessed simply on the basis of the value of ΔpH_{tit}.

Obviously, a lower ΔpH_{tit} value is not worse than a higher value, but not always it is better or necessary.

On the contrary, the most direct and physically significant measure of the titration accuracy is ΔV_t^{ml}.

In fact, in the following, we shall identify ΔV_t^{ml} with the systematic titration error and our target will be to show how it can be evaluated.

Obviously, the primordial systematic error, ΔV_t^{ml}, will propagate to the analytical results derived from the titration data.

Once ΔV_t^{ml} has been evaluated, it will be very easy to assess its effects on analytical results.

To this end, we note that to perform a titration we use a burette to deliver the titrant. Whatever burette has a limited precision which we shall indicate with δ_{bur}^{ml}.

This implies that V_{end}^{ml} is affected by an uncertainty (casual error) which is at least $\pm\delta_{bur}^{ml}$. For instance, a typical Class A burette might have $\delta_{bur}^{ml} = 0.05ml$, so that whatever volume read from this burette carries an uncertainty which is not less than ±0.05 ml.

The casual error on V_{end}^{ml} will then propagates as a casual error on the analytical results.

The key point is that we need to worry about the systematic error only in the case $\Delta V_t^{ml} > \delta_{bur}^{ml}$. In fact, in the opposite case, i.e., if $\Delta V_t^{ml} < \delta_{bur}^{ml}$, the effects of the systematic error will be embedded in the casual error of the burette and will not produce any practical effect on analytical results.

An obvious corollary of this is that it is of no use to make efforts to reduce ΔV_t^{ml} to the absolute zero; in fact,

it is only necessary, in practice, to reduce, if it is possible, ΔV_t^{ml} to a value lower than δ_{bur}^{ml}.

2.2.1. Evaluation of the Systematic Titration Error Expressed as ΔV_t^{ml}

Figure 3, which is the simulated titration curve of the above described titration of 25.00 ml of the acetic acid solution represented in Figure 2 (performed with a 0.1000 M standard solution of NaOH), shows the characteristic shape of a simple titration curve.

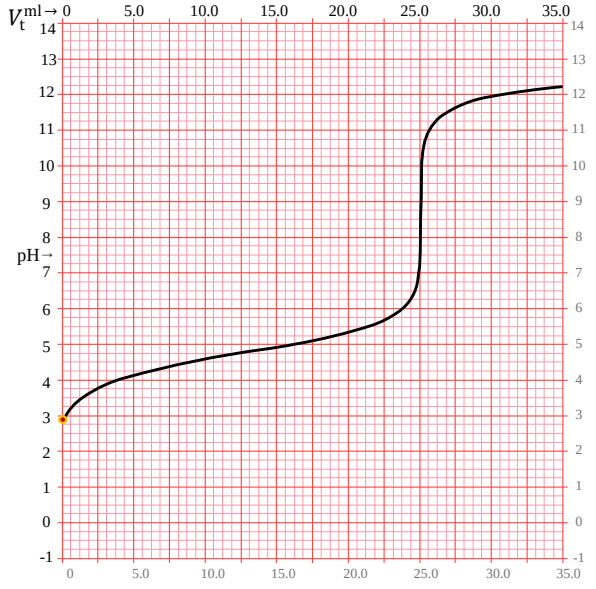

Figure 3. Alkalimetric titration curve of 25.00 ml of a solution 0.100 M acetic acid with a standard 0.1000 M solution of NaOH

In general, a titration curve has a slope which depends on the pH, and which we shall indicate with $\xi_{pH}\left(\overset{def}{=} d_{pH}/dV_t^{ml}\right)$. If the titration curve has been drawn in the plane $pH \rightarrow V_t^{ml}$, ξ_{pH} carries the dimensions of ml^{-1}.

For any specified titration, there is a relation between ΔpH_{tit} and ΔV_t^{ml}, which involves the slope of the titration curve and which, for the present purposes, can be formulated, in an approximate but very simple and useful way, as in equation (3):

$$\Delta V_t^{ml} \approx \frac{\Delta pH_{tit}}{\xi_{pH_{end}}} \quad (3)$$

In practice, $\xi_{pH_{end}}$, which is, by definition, the slope of the titration curve at the titration end point, can be regarded as a conversion factor, which converts the readily evaluated ΔpH_{tit} in the corresponding ΔV_t (which is a measure of the systematic error).

Obviously, for the use of equation (3), we need to evaluate $\xi_{pH_{end}}$ and, for this purpose, we shall use the LABD of the titrated solution.

To this end, it is necessary to select in the LABD representing the titrated solution the curve representing a particular species, which we shall call the *Slope Determining Species* (SDS).

At each selected pH, the curve representing the SDS, in a LABD, is the one that lays highest in the diagram and which at the selected pH has a non zero slope.

For instance, with reference to Figure 2, the SDS at pH = 1, 4, 8 and 10 coincides, in the order, with H^+, CH_3COO^-, CH_3COOH and OH^-. It is evident that the SDS will always be H^+, at sufficient low pH, and OH^- at sufficient high pH.

Actually, what we need for the use of equation (3) it is to pinpoint the SDS at the end point of the titration, that is to say when $pH = pH_{end}$. After that, $\log[SDS]_{pH_{end}}$ is readily read from the LABD of the titrated solution.

Finally, $\xi_{pH_{end}}$ can be evaluated from relation (4):

$$\log \xi_{pH_{end}} \approx -\log[SDS]_{pH_{end}} + \log \frac{[[TitrantConc]]}{2.3 \times V_0^{ml}} \quad (4)$$

In equation (4), [[*TitrantConc*]] stands for the known titrant analytical concentration (e.g., [[NaOH]] for alkalimetric and [[HCl]] for acidimetric titrations) and V_0^{ml}, is the initial volume of the titrated solution (usually between 10 and 50 ml).

Equation (4) holds both for alkalimetric and acidimetric titrations. However, since acidimetric titration curves have negative slope, $\xi_{pH_{end}}$ must be, in such a case, interpreted as the absolute value of the slope. In other words, for an acidimetric titration, the sign of $\xi_{pH_{end}}$, calculated from equation (4), must be inverted.

For instance, for the above considered titration of 25.00 ml of [[CH_3COOH]] = 0.100 M with [[NaOH]] = 0.100 M, performed using phenolphthalein as an indicator, we need to pinpoint, from Figure 2, the SDS at $pH_{end} \approx 9.5$.

We see that $SDS \equiv OH^-$ and, by consequence:

$$\log[SDS]_{pH=9.5} = \log[OH^-]_{pH=9.5} = -4.5$$

Using this value and other titration data in equation (4), we calculate $\xi_{pH=9.5}$:

$$\log \xi_{pH=9.5} = -\log[OH^-]_{pH=9.5} + \log \frac{[[NaOH]]}{2.3 \times V_0^{ml}} \xrightarrow{yields}$$

$$\log \xi_{pH=9.5} = +4.5 + \log \frac{0.1}{2.3 \times 25} \xrightarrow{yields}$$

$$\log \xi_{pH=9.5} = +4.5 - 2.76 = 1.74$$

And finally:

$$\xi_{pH=9.5} = 10^{1.74} = 55.0 ml^{-1}$$

Since, from equation (1), we have:

$$\Delta pH_{tit} \approx 9.5 - 8.8 = 0.7$$

the systematic titration error of this titration is, from equation (3), evaluated to be:

$$\Delta V_t^{ml} \approx \frac{\Delta pH_{tit}}{\xi_{pH_{end}}} = \frac{0.7}{55.0} = +0.012 ml$$

The interpretation of this result is straightforward. If the titration is performed with a burette which can measure volumes within ± 0.05 ml, then the systematic titration error is negligible. The uncertainty on the concentration or

number of moles of acetic acid calculated from the titration data is governed by the precision of the burette and is calculated from relation (5):

$$\%Uncertainty = 100 \times \frac{\pm\delta_{bur}^{ml}}{V_{eq}^{ml}} \qquad (5)$$

For the current case relation (5) yields:

$$\%Uncertainty = 100 \times \frac{\pm 0.05}{25} \xrightarrow{yields} = \pm 0.2\%$$

In contrast with the above result, consider the titration of 25.00 ml of 0.100 M hypochlorous acid (i.e., [[HClO]] = 0.100 M) with [[NaOH]] = 0.100 M in presence of phenolphthalein as an indicator ($pH_{end} \approx 9.5$, as it was before).

The LABD of the titrated solution is presented in Figure 4, from which we can see that $pH_{eq} \approx 10.3$ (this is the pH corresponding to the intersection point of the curves representing log[HClO] and log[OH^-]).

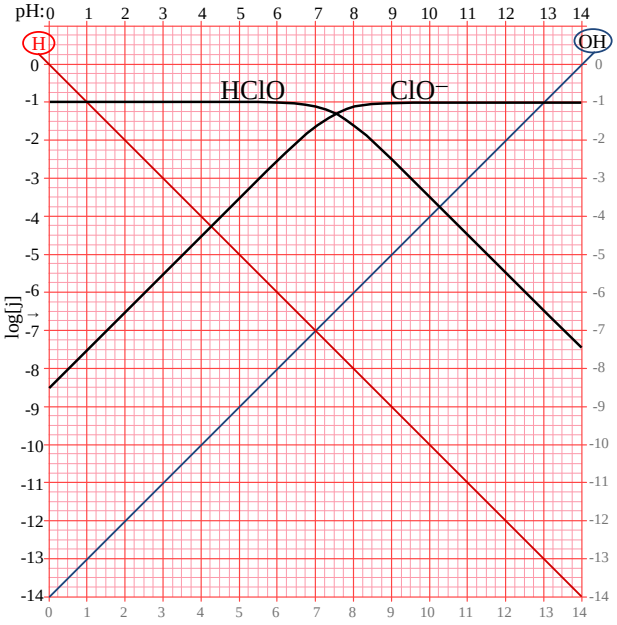

Figure 4. Logarithmic Acid-Base diagram of 0.100 M hypochlorous acid ($pK_a = 7.53$) at 25°C.

Therefore, $\Delta pH_{tit} = -0.8$, which means that the titration is ended before the equivalent point. In principle, we add less NaOH than required and this is an omen for a systematic error in defect on the concentration or number of moles of HClO determined from the titration.

However, as we have demonstrated in the previous example, this error will be practically important only if its absolute value exceeds δ_{bur}^{ml}.

For this reason we repeat the above procedure to evaluate the systematic error, ΔV_t^{ml}.

From Figure 4, we can smoothly see that the SDS at pH ≈ 9.5 is HClO and that log[HClO] = -3.0. Then, for $\xi_{pH=9.5}$ we have:

$$\log \xi_{pH=9.5} = 3.0 + \log \frac{0.1}{2.3 \times 25} \xrightarrow{yields} \xi_{pH=9.5} = 1.7 ml^{-1}$$

and finally:

$$\Delta V_t^{ml} \approx \frac{-0.8}{1.7} = -0.47 ml$$

It is obvious that this titration is affected by a systematic error which largely exceeds the uncertainty introduced by the precision of the burette.

In this case, the uncertainty introduced by the limited precision of the burette is irrelevant and the % systematic error on the concentration or number of moles of hypochlorous acid is calculated from relation (6):

$$\%SystematicError = 100 \times \frac{\Delta V_t^{ml}}{V_{eq}^{ml}} \qquad (6)$$

Equation (6), for the current case, yields:

$$\%SystematicError = 100 \times \frac{-0.47}{25} \approx -2\%$$

In practice, if we titrate, in the way we have described above, 25.00 ml of a solution in which [[HClO]] = 0.100 M, our experimental result will be: [[HClO]] ≈ 0.098 M.

2.2.2. The Exceptional Case of *StrongAcid* ↔ *StrongBase* Titrations

In the following we shall consider NaOH as a prototype for strong bases and HCl as a prototype for strong acids. This is made only for convenience, since whichever strong base can be substituted for NaOH and, analogously, any strong acid for HCl.

Then, under the label *StrongAcid* ↔ *StrongBase* titrations are included alkalimetric titrations of HCl solutions with standard solutions of NaOH, and, *vice versa*, acidimetric titrations of NaOH solutions with a standard solution of HCl.

Within the frame developed above for the systematic titration error, the LABD of the titrated solution serves both qualitative and quantitative purposes.

In a qualitative way, by observing the LABD at pH_{end}, the nature of the SDS can be established.

Then, the value of $\log[SDS]_{pH_{end}}$, to be used in equation (4), can promptly be read from the LABD.

Furthermore, the LABD of the titrated solution is used for the graphical evaluation of pH_{eq} (although this is outside the subject of this paper) which is needed to establish ΔpH_{tit}.

In general, pH_{eq} depends on the composition (i.e., the concentration of acid and/or base) in the titrated solution and so does ΔpH_{tit}. In addition, the LABD of the titrated solution and, by consequence, $\log[SDS]_{pH_{end}}$ depend on the composition of the titrated solution. The outcome is that, in general, the systematic titration error cannot be evaluated *a priori*, without an assumption on the analytical composition of the titrated solution.

The sense of the discussion on the systematic titration error is to show that the titration of a given acid or base can be performed with a negligible systematic error at least for a number of assumed values of its analytical concentration, so that one can be confident about the titration error when an actual sample, of unknown concentration, is titrated. Nevertheless, titrations of the same substance at different concentrations will have different systematic errors, even if all other titration data are kept unchanged.

Now, please consider the LABD in Figure 5, which represents a 0.05 M solution of HCl. The horizontal line at log[[HCl]] = log0.05 = -1.3 represents log[Cl^-]. The simplicity of the LABD of HCl depends on the fact that, being HCl a strong acid, [HCl] never assumes significant values (at least when we consider diluted solutions of the acid).

Analogously, the LABD of a NaOH solution exposes only a horizontal line, located at log[[NaOH]], which represents log[Na^+], since, [NaOH] is insignificant in any diluted solution of sodium hydroxide.

From this, we see that the plot of Figure 5 also represents a solution in which [[NaOH]] = 0.05 M, if the horizontal line is interpreted as representing log[Na^+].

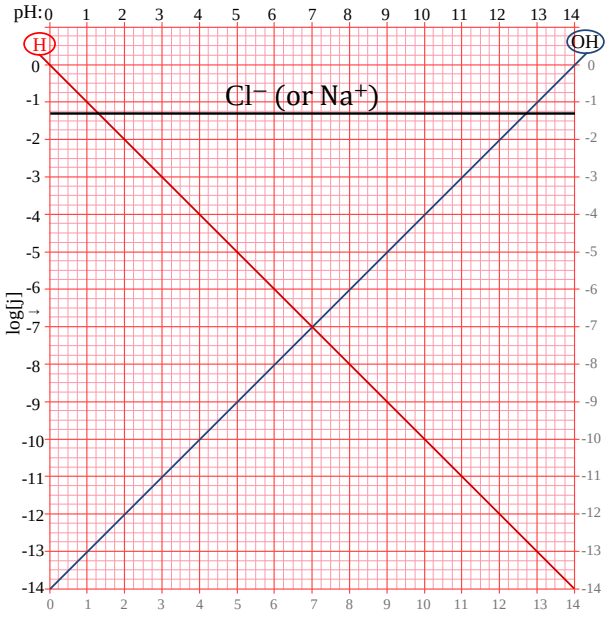

Figure 5. Logarithmic Acid-Base diagram of 0.05 M HCl (or 0.05 M NaOH) at 25°C

Many of the very special features of *StrongAcid* ↔ *StrongBase* titrations depend on the simplicity of the plot of the titrated solution.

As it is apparent from Figure 5, the SDS during the *StrongAcid* ↔ *StrongBase* titrations is either H^+ or OH^-. This is for the simple reason that there are no curves (or lines) with non zero slope in the LABD of the titrated solution, except lines representing log[H^+] and log[OH^-].

Then, SDS ≡ OH^-, and $-\log[SDS]_{pH_{end}} = 14 - pH_{end}$, if the *StrongAcid* ↔ *StrongBase* titration is ended a pH > 7.

By inserting this constraint in equation (4) we have:

$$\log \xi_{pH_{end}} \approx 14 - pH_{end} + \log \frac{[[TitrantConc]]}{2.3 \times V_0^{ml}} \quad (7)$$

On the other side, when the *StrongAcid* ↔ *StrongBase* titration is ended at pH < 7, then SDS ≡ H^+. In such a case $-\log[SDS]_{pH_{end}} = pH_{end}$ and equation (4) becomes:

$$\log \xi_{pH_{end}} \approx pH_{end} + \log \frac{[[TitrantConc]]}{2.3 \times V_0^{ml}} \quad (8)$$

From equations (7) and (8) we see that the slope of the *StrongAcid* ↔ *StrongBase* titration curve at pH_{end} is always the same, regardless of the analytical concentrations of the titrated StrongAcid or StrongBase, (e.g., [[HCl]] or [[NaOH]] in the titrated solution).

In practice, equation (7) applies to all titrations which are ended at alkaline pH, whenever the SDS coincides with OH^-. This happens to be the case for a number of alkalimetric titrations of weak acids, e.g., for the alkalimetric acetic acid titration presented in the previous paragraph (but not for the alkalimetric titration of hypochlorous acid).

Analogously, equation (8) applies to all titrations which are ended in the acidic range, whenever the SDS coincides with H^+. This often happens for acidimetric titrations of weak bases.

Nevertheless, *StrongAcid* ↔ *StrongBase* titrations have a unique feature which, strictly, is never found in titrations of weak acids or bases. We allude to the fact that *StrongAcid* ↔ *StrongBase* titrations have an invariant $pH_{eq} \approx 7$, independent on the concentration of the titrated StrongAcid or StrongBase. Within our framework, the consequence of this is that equation (1) becomes:

$$\Delta pH_{tit} = pH_{end} - 7$$

When all this (i.e., equations (3), (7), (8) and (9)) is considered, we deduce that any *StrongAcid* ↔ *StrongBase* titration has a constant systematic error, ΔV_t^{ml}, which is independent on the concentration of the titrated StrongAcid or StrongBase. ΔV_t^{ml} only depends on variables that are under the full control of the operator, i.e., the chosen indicator, the titrant concentration and the initial volume of titrated solution. The implication of this is that, unlikely all other cases, the systematic titration error of *StrongAcid* ↔ *StrongBase* titrations can be evaluated *a priori*, without knowledge of the amount of StrongAcid or StrongBase in the titrated solutions.

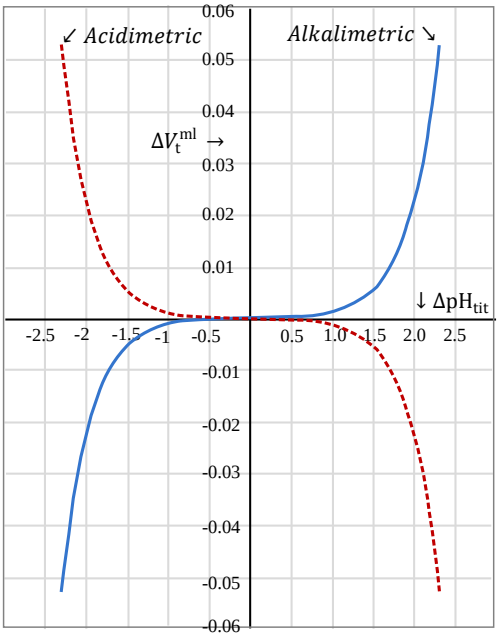

Figure 6. Plot of the systematic titration error V_0^{ml} for *StrongAcid* ↔ *StrongBase* titrations calculated for V_0^{ml} = 50 ml and $[[TitrantConc]]$ = 0.1000 M. $[[TitrantConc]]$ symbolizes [[NaOH]] in alkalimetric titrations and [[HCl]] in acidimetric titrations

Plots of ΔV_t^{ml} as a function of ΔpH_{tit} for alkalimetric and acidimetric *StrongAcid* ↔ *StrongBase* titrations are presented in Figure 6 (which has been calculated from the above relations assuming $[[TitrantConc]]$ = 0.1000 M and V_0^{ml} = 50 ml, which are typical values).

If we assume for the burette a precision of ± 0.05 ml, which is a very common case, from Figure 6 we see that *StrongAcid* ↔ *StrongBase* titrations can be ended (under the assumed conditions) anywhere in the range $-2.3 \lesssim \Delta pH_{tit} \lesssim 2.3$ without the systematic error exceeding the precision of the burette.

This implies that almost all the common indicators (except a few) are suitable for the *StrongAcid* ↔ *StrongBase* titration.

For instance, whichever indicator with an upper limit of its transition interval falling between pH ≈ 4.7 ad pH ≈ 9.3 (e.g., bromocresol green, methyl red, bromothymol blue, phenol red, phenolphthalein, etc..) is a suitable indicator for the alkalimetric titration of a StrongAcid.

Phenolphthalein, which strictly corresponds to $\Delta pH_{tit} \approx 2.5$, is on the border, since, as can be easily evaluated, yields $\Delta V_t^{ml} \approx +0.09$ ml. This is a small systematic error which can be tolerated for many purposes and which, in practice, can altogether be avoided by stopping the titration in correspondence of the legendary *phenolphthalein's pale red*.

Although, strictly, the value of ΔV_t^{ml} depends on the particular indicator chosen, from the practical viewpoint, all the mentioned indicators will produce the same results, which are dominated by the uncertainty introduced by the burette limited precision.

3. Attractive Examples

3.1. Acid-Base Titrations of Amino Acids

In this paragraph, we consider the problem of evaluating, within the framework developed above for the systematic titration error, the utility of Acid-Base titrations as a method for determining accurately the amount of an amino acid in a given solution.

Although this may appear a matter of mere academic interest, it offers, on the one side, a beautiful chance to expose a number of general questions which can arise (or may intentionally be raised) while coping with Acid-Base reactions and titrations. On the other side, it is a way to penetrate deeply in the Acid-Base chemistry of amino acids, which is a worthy undertaking because amino acids are ubiquitous in biology and biochemistry.

As it is well known, natural amino acids are described by the general formula $H_2NCHRCOOH$, in which R represents the amino acid side chain bonded to the alpha carbon atom, which also bears the basic amino group (—NH_2) and the acid carboxylic group (—COOH).

Simple amino acids which do not bear in the side chain additional functional groups with Acid-Base properties will be called *GlycineType* amino acids (this group includes several natural amino acids, e.g., Alanine, Valine, Leucine, etc.). Natural amino acids bearing an additional acidic function in the side chain are classified below as *AsparticAcidType* amino acids (for instance, Glutamic acid). Finally, natural amino acids with a basic group in the side chain are classified as *LysineType* amino acids (for instance, Ornithine).

3.1.1. GlycineType Amino Acids

Two dissociation constants (respectively, pK_{a1} and pK_{a2}) are associated with GlycineType amino acids. pK_{a1} and pK_{a2} connect three different species according to the scheme in Figure 7.

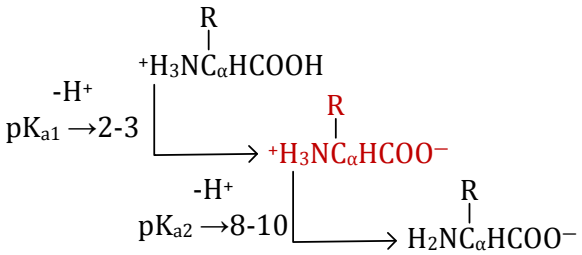

Figure 7. Schematic presentation of the Acid-Base properties of GlycineType amino acids

For instance, for Alanine, pK_{a1} = 2.31 and pK_{a2} = 9.7. pK_{a1} and pK_{a2} are much the same for all natural GlycineType amino acids.

From the above scheme, it must result that, in water, the neutral species, i.e., $H_2NCHRCOOH \equiv {}^+H_2NCHRCOO^-$, is amphiprotic and can react both with acids or bases.

In the context of Acid-Base titrations, this must be interpreted to signify that, in abstract, an amino acid can be titrated either alkalimetrically or acidimetrically. The question is: *of the two possible titration modes, which one would provide more accurate results*?

Of course, the answer is incorporated in the pK_{a1} and pK_{a2} values characterizing the Acid-Base behaviour of the amino acid, but it requires an extra bit of thinking.

We take Alanine as representative of GlycineType natural amino acids and consider a solution containing 0.05 M Alanine (i.e., [[Alanine]] = 0.05 M).

LABD of this solution is exposed in Figure 8. The neutral amino acid is denoted HAla, to show that Alanine has an acidic proton which can be dissociated. The dissociation of the proton from Alanine produces the conjugated base, Ala^-. H_2Ala^+ is the conjugated acid of HAla formed upon protonation of the neutral species. In Figure 8, the curves representing H_2Ala^+ and HAla intersect at pH = pK_{a1} = 2.31, while curves of HAla and Ala^- intersect at pH = pK_{a2} = 9.7.

To solve the above dilemma, we observe that the initial pH of the Alanine solution is about 6, which graphically corresponds to the point where the curve of H_2Ala^+ meets the curve of Ala^-.

An acidimetric titration amounts to traversing the Alanine LABD, from $pH_{in} \approx 6$, towards lower pH. In this journey we meet $pH_{eq1} \approx 1.9$ (which graphically corresponds to the crossing point between curves representing H^+ and HAla).

Symmetrically, an alkalimetric titration starts at $pH_{in} \approx 6$ and reaches the equivalent point at $pH_{eq2} \approx 11.2$ (which graphically corresponds to the crossing point between curves representing HAla and OH^-).

Even a superficial consideration of these statements, within the frame of Figure 8, will show that an alkalimetric titration is, of the two, the more convenient.

In fact, from the LABD in Figure 8, we see at a glance that, if our target is the acidimetric equivalent point, the SDS must be selected between H^+, HAla and H_2Ala^+. On the other side, if our target is the alkalimetric equivalent point, the SDS will be either OH^- or HAla. Since any possible SDS around the acidimetric equivalent point has an higher concentration than that of any possible SDS around the alkalimetric equivalent point, $\xi_{pH_{end}}$ will be higher, and the systematic error lower, if we select an end point around $pH_{eq2} \approx 11.2$ rather than around $pH_{eq1} \approx 1.9$.

Furthermore, we can easily predict that even the alkalimetric titration (although certainly more favourable than the acidimetric) will not produce very accurate results because of the rather large concentrations of HAla and OH^- (which are the potential SDS around pH_{eq2}). This prognosis can easily be verified.

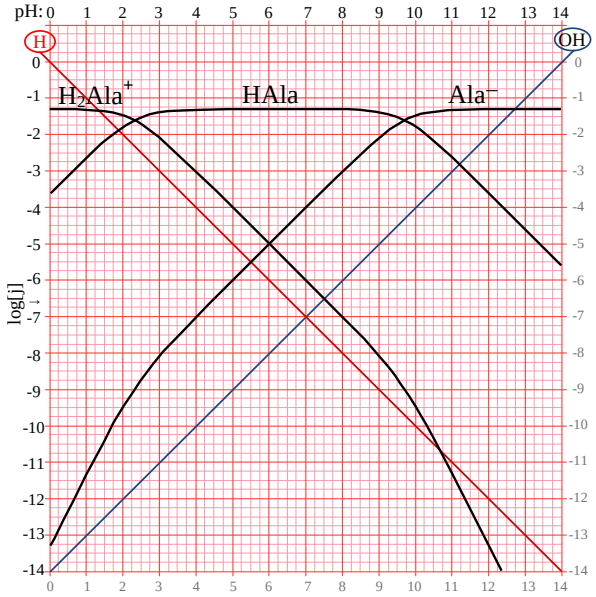

Figure 8. Logarithmic Acid-Base diagram of 0.05 M Alanine, at 25 °C. Label HAla stands for the neutral amino acid

To this end, the most appropriate indicator (among common Acid-Base indicators), is thymolphthalein (transition interval {9.4, 10.6}).

This choice amounts to fixing $pH_{end} \approx 10.6$ and $\Delta pH_{tit} \approx 10.6 - 11.2 = -0.6$ (which is an omen for a systematic error in defect).

In any case, by taking for the NaOH titrating solution [[NaOH]] = 0.1000 M and $V_0^{ml} = 50$ ml for the initial volume of titrated solution, calculations are as it follows:

$$\log[SDS]_{pH=10.6} = \log[HAla]_{pH=10.6} = -2.3$$

$$\log \xi_{pH=10.6} \approx 2.3 + \log \frac{0.1}{2.3 \times 50} \underrightarrow{yields} \xi_{pH=10.6} \approx 0.18 ml^{-1}$$

$$\Delta V_t \approx \frac{-0.6}{0.18} = -3.3 ml$$

Since in the titration are consumed about 25 ml of NaOH, this amounts to a % systematic error, on the concentration or number of moles of Alanine, of about -13%.

The limitations of visual Acid-Base titrations with respect to the determination of GlycineType amino acids (e.g., Glycine, Valine, Leucine, etc.) are quite evident.

However, the above described Alanine titration is eminently suitable for a laboratory experiment aimed to demonstrate impressively the effects of systematic error.

Suppose that we weight accurately, at the analytical balance, an amount of pure Alanine (which is easily available) close to ≈ 0.0025 moles (for the evaluations below we assume a weight of 0.2227 g, which correspond exactly to 0.0025 moles of Alanine). After that, we transfer the weighted sample to a titration flask with about 50 ml distilled water. After adding the thymolphthalein indicator, the Alanine solution is titrated, with standard 0.1000 M NaOH, until the full blue colour of the indicator has been developed.

The stoichiometric equivalent volume corresponding to 0.0025 moles of Alanine is calculated to be 25.00 ml. However, on the basis of the above evaluations, we shall measure a smaller end point volume: $V_{end}^{ml} \approx V_{eq}^{ml} - \Delta V_t^{ml}$ ≈ 22 ml. By using 22 ml to calculate the number of moles of Alanine we obtain ≈ 10^{-3}×22×[[NaOH]] = 0.0022 moles (instead of 0.0025). Finally, the molecular weight of Alanine, $MW^{Alanine}$, is calculated by dividing its weight (0.2227 g) by ≈ 0.0022 moles. The result will be: $MW^{Alanine} \approx 0.2227/0.0022 = 101$ u.m.a.. When this value is compared to the real one (i.e., $MW^{Alanine} = 89.09$ u.m.a.), one is memorably impressed that the difference between the two amounts about to adding a carbon atom to the Alanine formula.

3.1.2. AsparticAcidType Amino Acids

However, as it happens, thinks may change if the amino acid side chain contains an additional acidic functional group, which implies that the neutral molecule bears two dissociable protons according to the scheme in Figure 9.

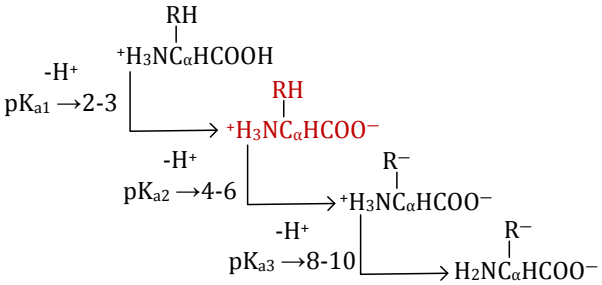

Figure 9. Schematic presentation of the Acid-Base properties of AsparticAcidType amino acids.

In this case, four species, which differ in the number of bonded protons, are produced in the solution.

Aspartic acid itself ($pK_{a1} = 1.94$, $pK_{a2} = 3.7$ and $pK_{a3} = 9.62$) is a good representative of this class of amino acids.

In abstract, a solution of the neutral amino acid not only could be titrated acidimetrically or alkalimetrically, as in the case of Alanine (in fact, Aspartic acid is, as all the amino acids, an amphiprotic substance). But a further question can be raised which attains to the fact that Aspartic acid is *de facto* a diprotic acid. Then, in principle, an alkalimetric titration of Aspartic acid can be performed up to a first stoichiometric equivalent point or continued to a second stoichiometric equivalent point (this dilemma arises with all multiprotic acids).

After excluding the acidimetric titration (on the basis of what we have seen for Alanine), the question is: an alkalimetric Aspartic acid titration yields more accurate

results if targeted at the first or at the second equivalent point?

For evaluations below, we assume the usual typical values (i.e., [[AsparticAcid]] = 0.05 M, [[NaOH]] = 0.1000 M, V_0^{ml} = 50 ml).

LAMD of the titrated solution is presented in Figure 10, in which H_2Asp symbolizes the neutral amino acid. By consequence, the conjugated acid of H_2Asp is H_3Asp^+, while the bases derived from the stepwise dissociation of the two acidic protons from the neutral species are $HAsp^-$ and Asp^{2-}. The curves representing H_3Asp^+ and H_2Asp intersect at pH = pK_{a1} = 1.94; curves of H_2Asp and $HAsp^-$ intersect at pH = pK_{a2} = 3.7; curves of $HAsp^-$ and Asp^{2-} intersect at pH = pK_{a3} = 9.62.

In order to discuss the raised question, we begin locating in the LABD the initial pH of the titrated solution, pH_{in}.

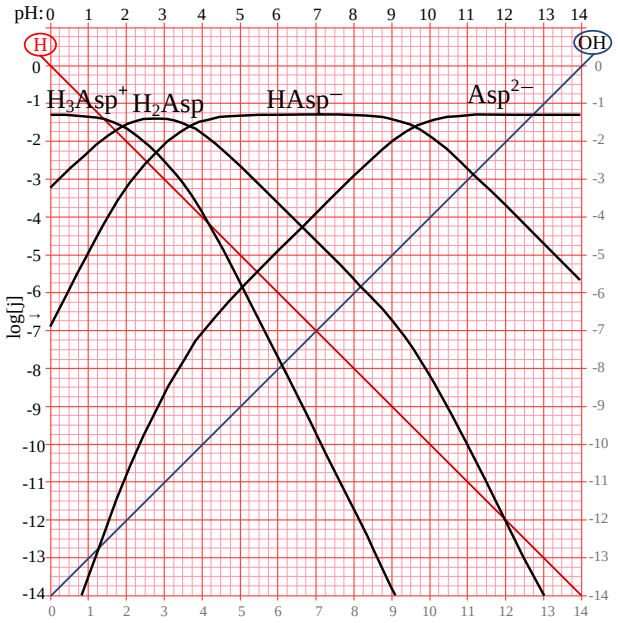

Figure 10. Logarithmic Acid-Base diagram of 0.05 M Aspartic acid, at 25 °C. Label H_2Asp stands for the neutral amino acid

At a glance we obtain $pH_{in} \approx 2.8$, corresponding to the crossing point between curves representing H_3Asp^+ and $HAsp^-$.

By traversing the LABD from pH_{in} towards higher pH we must meet two stoichiometric equivalent points.

The first equivalent point corresponds to the conversion $H_2Asp \rightarrow HAsp^-$ and is reached at $pH_{eq1} \approx 6.7$ (corresponding to the crossing point between curves representing H_2Asp and Asp^{2-}).

The second equivalent point corresponds to the conversion $H_2Asp \rightarrow Asp^{2-}$ and is reached at $pH_{eq2} \approx 11.1$ (corresponding to the crossing point between curves representing $HAsp^-$ and OH^-).

Then, if we target the titration at the first equivalent point, an indicator must be chosen with an upper limit of its transition interval close to pH_{eq1}. Otherwise, an indicator with its upper limit of its transition interval around pH_{eq2} must be employed.

From Figure 10, it is seen at a glance that the alkalimetric titration of Aspartic acid must be targeted at $pH_{eq1} \approx 6.7$, simply because, around pH_{eq1}, any possible SDS (i.e., H_2Asp and Asp^{2-}) has a much lower concentration than that of any possible SDS (i.e., $HAsp^-$ and OH^-) around $pH_{eq2} \approx 11.1$.

Then, the answer to the above question is that Aspartic acid is best titrated as a monoprotic acid fixing pH_{end} as close as possible to $pH_{eq1} \approx 6.7$.

A suitable indicator for this titration is methyl red (transition interval: {4.4, 6.3}). This implies $pH_{end} \approx 6.3$ and $\Delta pH_{tit} \approx 6.3 - 6.7 = -0.4$ (which is a warning for a systematic error in defect).

However, from Figure 10, evaluations are as it follows:

$$\log[SDS]_{pH=6.3} = \log[H_2Asp]_{pH=6.3} = -3.9$$

$$\log \xi_{pH=6.3} = 3.9 + \log \frac{0.1}{2.3 \times 50} \xrightarrow{yields} \xi_{pH=6.3} = 6.9 ml^{-1}$$

$$\Delta V_t \approx \frac{-0.4}{6.9} = -0.06 ml$$

From this we can smoothly see that, unlike Alanine and congeners, Aspartic acid can be determined alkalimetrically, practically without the systematic error exceeding the precision of the burette.

The above titration has another favourable feature, which relates to the fact that, for a selected indicator, ΔpH_{tit} is independent on the concentration of Aspartic acid and, by consequence, can be calculated *a priori*. This is because pH_{eq1}, in a broad range of concentrations, is independent on the concentration of Aspartic acid.

For instance pH_{eq1} would still be ≈ 6.7 for the alkalimetric titration of a 0.005 M solution of Aspartic acid.

This can be seen considering that the LABD of a solution, in which [[AsparticAcid]] $\neq$ 0.05 M, can be generated from the one in Figure 10, by translating, as a single group, the curves representing H_3Asp^+, H_2Asp, $HAsp^-$ and Asp^{2-} either upward or downward. Obviously, whatever simultaneous vertical translation of these curves does not modify the abscissa of the intersection point between the curves of H_2Asp^+ and Asp^{2-}, which determines pH_{eq1}.

It is also useful to mention that chemically, the independence of pH_{eq1} from the Aspartic acid concentration is due to the fact that $HAsp^-$, which is produced at the first equivalent point, is an amphiprotic species. This rule can be extended to all titrations in which the species produced by the Acid-Base reaction between the titrant and the titrated substance is amphiprotic.

3.1.3. LysineType Amino Acids

Acid-Base properties of LysineType amino acids are described by scheme in Figure 11.

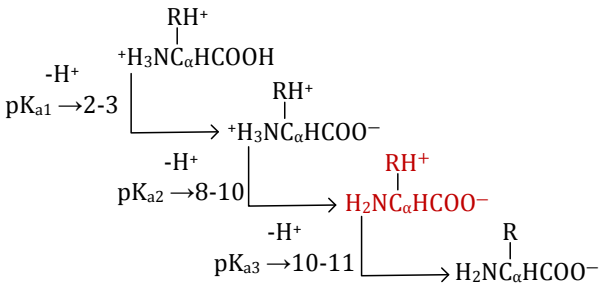

Figure 11. Schematic presentation of the Acid-Base properties of LysineType amino acids

We take Lysine as representative of its own class. The neutral species will be indicated by HLys to expose its acidic dissociable proton. Dissociation of the HLys proton produces the singly charged base Lys^-. HLys can accept up to two protons producing the acidic species H_2Lys^+ and then the fully protonated and double charged species H_3Lys^{2+}.

With respect to Acid-Base titrations, we can raise for Lysine questions analogous to those raised above for GlycineType and AsparticAcidType amino acids.

They are formulated as it follows:

Must we titrate a Lysine solution acidimetrically or alkalimetrically?

If, for a given choice of the titration mode, it exists more than one stoichiometric equivalent point, which one should we target at?

For evaluations below, we assume as usual the typical value, i.e., [[Lysine]] = 0.05 M, for the amino acid solution to be titrated. LABD of this solution is presented in Figure 12. Curves representing H_3Lys^{2+} and H_2Lys^+ intersect at pH = pK_{a1} = 2.19; curves of H_2Lys^+ and HLys intersect at pH = pK_{a2} = 9.12; curves of HLys and Lys^- intersect at pH = pK_{a3} = 10.68.

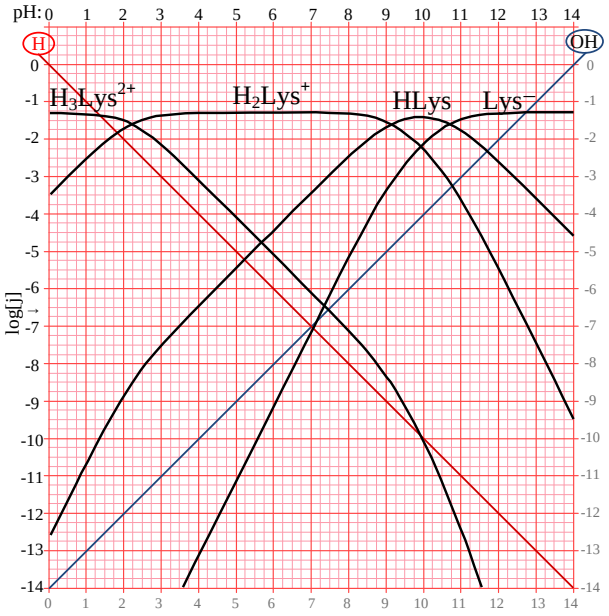

Figure 12. Logarithmic Acid-Base diagram of 0.05 M Lysine, at 25 °C. Label HLys stands for the neutral amino acid

We start by observing that a lysine solution has an alkaline pH, which can easily be found graphically since it corresponds to the intersection point between curves of H_2Lys^+ and Lys^-. From the diagram we read $pH_{in} \approx 9.9$, and this high initial pH, *per se*, excludes the alkalimetric titration. Then, we consider the acidimetric titration and find that there are, in abstract, two stoichiometric equivalent points corresponding to the conversions HLys→H_2Lys^+ and HLys→H_3Lys^{2+}. When the first equivalent point has been reached HLys has been stoichiometrically converted to H_2Lys^+. So pH_{eq1} is the pH of an H_2Lys^+ solution, which graphically corresponds to the point where the curve of H_3Lys^{2+} intersects the curve of HLys (i.e., $pH_{eq1} \approx 5.7$). pH_{eq1} does not depend on the concentration of Lysine since species H_2Lys^+ is amphiprotic.

The second equivalent point is reached when the initial HLys has been stoichiometrically converted to the fully protonated H_3Lys^{2+} acid and it corresponds to the intersection point between curves of H_2Lys^+ and H^+ (i.e., $pHe_{q2} \approx 1.8$).

From LABD in Figure 12, we see at a glance that the acidimetric titration of Lysine is by far more accurate if stopped around pH_{eq1}. This is because, around the first acidimetric equivalent point ($pH_{eq1} \approx 5.7$), the SDS is either H_3Lys^{2+} or HLys; while around the second acidimetric point ($pHe_{q2} \approx 1.8$) the SDS is either H_2Lys^+ or H^+; then it can be seen that the concentration of the SDS will be lowest if we select an end point around $pH_{eq1} \approx 5.7$. Furthermore, around pH ≈ 5.7, [H_3Lys^{2+}] and [HLys] are so low that we can predict very accurate results.

Between the common indicators, bromothymol blue (transition interval: {6.0, 7.0}) is an appropriate choice. In fact, this corresponds to $pH_{end} \approx 6$ and $\Delta pH_{tit} \approx 6.0 - 5.7 = 0.3$. At pH ≈ 6.0, SDS ≡ HLys and evaluations are as it follows:

$$\log[SDS]_{pH=6} = \log[HLys]_{pH=6} = -4.45$$

$$\log \xi_{pH=6} \approx 4.45 + \log \frac{0.1}{2.3 \times 50} \underrightarrow{yields} \xi_{pH=6} \approx 24.5 ml^{-1}$$

$$\Delta V_t \approx \frac{0.3}{24.5} \approx +0.01 ml$$

There is no doubt that this titration is capable of great accuracy and that the uncertainty on the results will be fully controlled by the precision of the burette.

This conclusion extrapolates to all LysineType natural amino acids.

Please note that Lysine and its congeners are very often sold in the form of the corresponding hydrochloride salts.

What we have demonstrated above does not apply to a solution of Lysine×HCl (Lysine hydrochloride).

A 0.05 M solution of Lysine×HCl is still represented by the LABD of Figure 12, but the key point is that $pH_{in} \approx 5.7$. Then, from Figure 12, we see that a Lysine hydrochloride solution cannot be accurately titrated neither acidimetrically nor alkalimetrically.

3.2. Titrations of Bicarbonate and Carbonate Mixtures with the "*Two Indicators Method*"

The Acid-Base titration of solutions containing mixtures of carbonate and bicarbonate is a classical experiment suggested in many analytical textbooks.

The very elegant *two indicators method* for the determination of carbonate and bicarbonate consists in the acidimetric titration of their mixtures (usually with an HCl standard solution).

First, phenolphthalein is added to the titrated solution, which at the beginning appears intensely red, and the acidimetric titration is interrupted when the red colour disappears. After reading the volume of titrant delivered (i.e., V_{end1}^{ml}), the solution is coloured in blue by adding bromocresol green and the titration continued until the blue colour turns yellow. The volume of the HCl solution consumed to reach the bromocresol end point is V_{end2}^{ml}.

Consequently, two end points volumes are elegantly collected in a single titration, which are then used, with

other titration data, to evaluate the concentrations (i.e., $[[CO_3^{2-}]]$ and $[[HCO_3^-]]$) or the number of moles of carbonate and bicarbonate in the titrated solution.

The moles of HCl consumed to reach the phenolphthalein end point ($pH_{end1} \approx 8.2$) are assumed to convert the carbonate to bicarbonate. Then we have:

$$mol CO_3^{2-} = 10^{-3}\left[\left[HCl\right]\right] \times V_{end1}^{ml} \quad (10)$$

At the bromocresol end point (($pH_{end2} \approx 4$), carbonate and bicarbonate have been converted to carbonic acid. Then, the number of moles of HCl consumed is related to the number of moles of carbonate and bicarbonate by the obvious relation (11):

$$mol HCO_3^- + 2mol CO_3^{2-} = 10^{-3}\left[\left[HCl\right]\right] \times V_{end2}^{ml} \quad (11)$$

By combining relations (10) and (11), one obtains relation (12), from which the number of moles of bicarbonate can be calculated:

$$mol HCO_3^- = 10^{-3}\left[\left[HCl\right]\right] \times \left(V_{end2}^{ml} - 2V_{end1}^{ml}\right) \quad (12)$$

Although the *two indicators method* appears very simple and elegant, it is not the method of choice and various authors, [5], suggest alternative methods (which require more manipulations and reactants). The question is: *what is the problem with the two indicator method?*

In the following we shall answer within the framework of the systematic titration error.

For convenience, for evaluations below, we assume that 50.0 ml of a solution containing $[[CO_3^{2-}]] = [[HCO_3^-]] = 0.025$ M, are titrated with standard 0.1000 M HCl.

LABD representing the assumed carbonate + bicarbonate solution is presented in Figure 13.

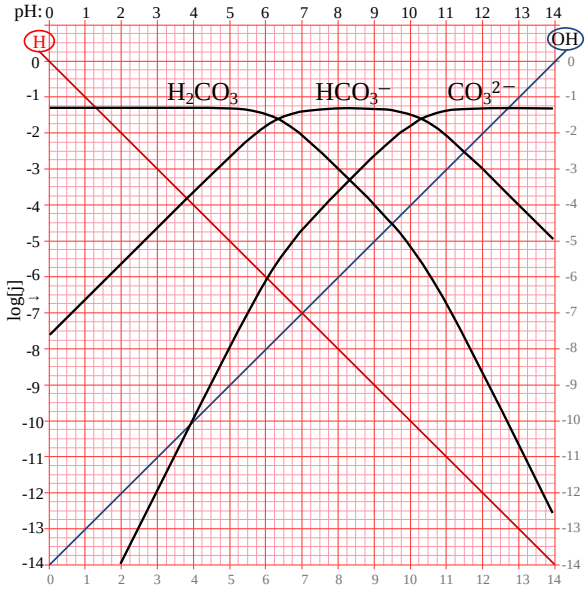

Figure 13. Logarithmic Acid-Base diagram of 0.05 M carbonic acid, at 25°C. Curve representing carbonic acid (H_2CO_3) intersects curve representing bicarbonate (HCO_3^-) at pH = pK_{a1} = 6.35; bicarbonate curve and carbonate (CO_3^{2-}) curve intersect at pH = pK_{a2} = 10.33

On the basis of the titration data and of Figure 13, we deduce the following stoichiometric values:

→*First stoichiometric equivalent point*↓:

$pH_{eq1} \approx 8.4$ (→crossing point between curves of H_2CO_3 and CO_3^{2-});

$$V_{eq1}^{ml} = \left[\left[CO_3^{2-}\right]\right] \times V_0^{ml} / \left[\left[HCl\right]\right] = 12.50\text{ml};$$

→→Second stoichiometric equivalent point↓:

$pH_{eq2} \approx 3.8$ (→crossing point between curves of HCO_3^- and H^+);

$$V_{eq2}^{ml} = \left(2\left[\left[CO_3^{2-}\right]\right] + \left[\left[HCO_3^-\right]\right]\right) * V_0^{ml} / \left[\left[HCl\right]\right] = 37.50\text{ml};$$

It can be appreciated that the phenolphthalein end point at $pH_{end1} \approx 8.2$, is, in effect, very close to pH_{eq1} (ΔpH_{tit1} = 8.2 - 8.4 = - 0.2), and so does the bromocresol end point at $pH_{end2} \approx 4$ (ΔpH_{tit1} = 3.8 – 4 = - 0.2).

From Figure13, evaluations for ΔV_{t1}^{ml} are as it follows:

$$-\log[SDS]_{pH=8.2} = \log[H_2CO_3]_{pH=8.2} = -3.2$$

$$\log \xi_{pH=8.2} \approx 3.2 + \log\frac{0.1}{2.3\times 50} \underrightarrow{yields} \xi_{pH=8.2} \approx -1.4\text{ml}^{-1}$$

$$\Delta V_{t1} \approx \frac{-0.2}{-1.4} \approx +0.15\text{ml}$$

Analogously, evaluations for ΔV_{t2}^{ml} are as it follows:

$$-\log[SDS]_{pH=4.0} = \log[HCO_3^-]_{pH=4.0} = -3.7$$

$$\log \xi_{pH=4.0} \approx 3.7 + \log\frac{0.1}{2.3\times 50} \underrightarrow{yields} \xi_{pH=4.0} \approx -4.4\text{ml}^{-1}$$

$$\Delta V_{t2} \approx \frac{-0.2}{-4.4} \approx -0.05\text{ml}$$

Obviously, there is a systematic error on the number of moles of carbonate which, from equation (6), is evaluated at about + 1.2%.

On the other side, the number of moles of bicarbonate depends on $\left(V_{end2}^{ml} - 2V_{end1}^{ml}\right)$. This difference carries a negative systematic error which is about -0.4 ml $(= \Delta V_{t2} - 2\Delta V_{t1})$. This implies that the concentration or number of moles of bicarbonate is affected by a % systematic error of about -3%.

These evaluations are based on Figure 13 (which has been drawn by using values at 25° and zero ionic strength for the dissociation constants of carbonic acid, i.e., pK_{a1} = 6.35 and pK_{a2} = 10.33), on standard transition ranges for the indicators and on the specified titration data.

In practice, changes on the assumed values can have effects on the accuracy (in either direction). Nevertheless, it is evident that the original sin of the two indicators method is the systematic error in excess on the carbonate which then propagates unfavourably to the bicarbonate through equation (12).

Some authors, [6], suggest the use of methyl red instead of bromocresol green in the above procedure. This amounts to taking $pH_{end2} \approx 4.4$. From Figure 2, we see that this choice makes the error on V_{end2}^{ml} more negative and, by consequence cannot, in general, be justified (unless much lower concentrations of total carbonate are considered than assumed in the present example).

Although bicarbonate cannot be determined very accurately when carbonate is present in a given solution, the acidimetric titration of bicarbonate to the bromocresol end point produces very accurate results. This is easily seen as a special case of the two indicators method, in

which the cause of inaccuracy (i.e., the large error on V_{end1}^{ml}) is removed since, by definition, $V_{end1}^{ml} = 0$, in absence of carbonate.

The same can be said for the determination of carbonate in absence of bicarbonate, since in such a case V_{end2}^{ml} can be directly connected to the number moles of carbonate through relation (13):

$$moles CO_3^{2-} = \frac{1}{2} \times 10^{-3} \left[\left[HCl\right]\right] \times V_{end2}^{ml} \qquad (13)$$

which is obtained from equation (11) when it can be assumed that $mol HCO_3^- = 0$.

4. Using MS Excel for Drawing Logarithmic Acid-Base Diagrams

Table 1 provides algebraic expressions needed for drawing LABDs for solutions containing monoprotic (HA), diprotic (H_2D) and triprotic (H_3T) acids.

Table 1. Algebraic expressions for drawing Logarithmic Acid-Base Diagrams*

1	↓***Water***: $H_2O \xrightarrow{K_W} H^+ + OH^-$
2	$[OH^-] = \frac{K_W}{[H^+]}$
3	↓***Monoprotic acid***: $HA \xrightarrow{K_a} A^-$
4	$[HA] = \frac{C_{HA}[H^+]}{\left[H^+\right] + K_a}$
5	$[A^-] = \frac{C_{HA}K_a}{\left[H^+\right] + K_a}$
6	↓***Diprotic acid***: $H_2D \xrightarrow{K_{a1}} HD^- \xrightarrow{K_{a2}} D^{2-}$
7	$\left[H_2D\right] = \frac{C_{H_2D}[H^+]^2}{\left[H^+\right]^2 + K_{a1}\left[H^+\right] + K_{a1}K_{a2}}$
8	$\left[HD^-\right] = \frac{C_{H_2D}K_{a1}[H^+]}{\left[H^+\right]^2 + K_{a1}\left[H^+\right] + K_{a1}K_{a2}}$
9	$\left[D^{2-}\right] = \frac{C_{H_2D}K_{a1}K_{a2}}{\left[H^+\right]^2 + K_{a1}\left[H^+\right] + K_{a1}K_{a2}}$
10	↓***Triprotic acid***: $H_3T \xrightarrow{K_{a1}} H_2T^- \xrightarrow{K_{a2}} HT^{2-} \xrightarrow{K_{a3}} T^{3-}$
11	$[H_3T] = \frac{C_{H_3T}[H^+]^3}{\left[H^+\right]^3 + K_{a1}\left[H^+\right]^2 + K_{a1}K_{a2}\left[H^+\right] + K_{a1}K_{a2}K_{a3}}$
12	$\left[H_2T^-\right] = \frac{C_{H_3T}K_{a1}[H^+]^2}{\left[H^+\right]^3 + K_{a1}\left[H^+\right]^2 + K_{a1}K_{a2}\left[H^+\right] + K_{a1}K_{a2}K_{a3}}$
13	$\left[HT^{2-}\right] = \frac{C_{H_3T}K_{a1}K_{a2}\left[H^+\right]}{\left[H^+\right]^3 + K_{a1}\left[H^+\right]^2 + K_{a1}K_{a2}\left[H^+\right] + K_{a1}K_{a2}K_{a3}}$
14	$\left[T^{3-}\right] = \frac{C_{H_3T}K_{a1}K_{a2}K_{a3}}{\left[H^+\right]^3 + K_{a1}\left[H^+\right]^2 + K_{a1}K_{a2}\left[H^+\right] + K_{a1}K_{a2}K_{a3}}$

* C_{HA}, C_{H_2D} and C_{H_3T} represent total analytical concentrations.

Species which differ only in the number of bonded protons constitute an *Acid-Base group*. For instance there are four different species in the Acid-Base group of any triprotic acid. The variables C_{HA}, C_{H_2D} and C_{H_3T} which appear in Table 1, are *analytical group concentrations*.

For instance, $C_{H_2CO_3}$, would represent the total concentration of carbonic acid Acid-Base group. So, in abstract, if a solution is prepared dissolving specified analytical concentrations of H_2CO_3, $NaHCO_3$ and Na_2CO_3, $C_{H_2CO_3}$ is interpreted as:

$$C_{H_2CO_3} = [[H_2CO_3]] + \left[\left[NaHCO_3\right]\right] + [\left[Na_2CO_3\right]]$$

However, in most cases an Acid-Base group is introduced in the solution through a single substance, so that only one of the analytical concentrations, i.e., [[...]], in the group is different from zero. For instance, a solution of sodium bicarbonate has: $C_{H_2CO_3} = \left[\left[NaHCO_3\right]\right]$; but for a mixture of sodium carbonate and bicarbonate (as the one described in the previous paragraph) we have: $C_{H_2CO_3} = \left[\left[NaHCO_3\right]\right] + [\left[Na_2CO_3\right]]$. In practice, in a given solution, the analytical concentration of an Acid-Base group coincides with the sum of the equilibrium concentrations, [...], of all species belonging to the group. Naturally, analytical group concentrations are deduced from the amount of the various substances employed to prepare the considered solution.

In a given solution, each Acid-Base group is considered independently and its analytical concentration and acid dissociation constants (which connect the species in a group) are fixed. Then, the equilibrium concentration of any species in the considered group can be calculated as a function of $[H^+]$ (or, which is the same, of pH) from the appropriate expression in Table 1.

If a solution contains several Acid-Base groups, the above procedure is repeated for all Acid-Base groups, since the LABD representing such a solution is simply the superposition of the LABDs of each Acid-Base group.

Then, a MS Excel .xlxs file, which we shall call myLABD.xlxs, for drawing the logarithmic Acid-Base diagram representing any solution containing one or several Acid-Base groups is readily developed using functions in Table1.

One can start with an Excel file exposing four sheets which, for convenience, are renamed: Sheet1 → MonoproticAcid, Sheet2 → DiproticAcid, Sheet3 → TriproticAcid, Sheet4 → myPlot.

In the MonoproticAcid sheet the first row is reserved to labels. Cells from A1 up to I1 are labelled in the order: pH, log[H^+], [H^+], log[OH^-], [OH^-], [HA], log[HA], [A^-], log[A^-], pK_w, pK_a, C_{HA}.

Under cell labelled pK_w (i.e., cell J2) we input the water self dissociation constant, pK_w (e.g., 14 at 25 °C); then, in cell K2, under label pK_a, we input the value of pK_a (for instance, 9.25 for an ammonia solution). It is useful also to have values for K_w and K_a, which are readily obtained inserting in cells J3 and K3, respectively, the functions 10^{-pKw} (=10^-J2) and 10^{-pKa} (=10^-K2).

In column A (starting with cell A2) of the MonoproticAcid sheet we generate 140 pH values, from 0

to 14, spaced 0.1 pH units. Under label log[H^+], cell B2, we input the function –pH (=-A2). In cell C2 (under label [H^+]) we input the function 10^{-pH} (i.e., =10^-A2). Then, we extend the functions in cells, B2 and C2 up to cells B142 and C142. Under cell log[OH^-], cell D2, we input the function pH - pK_w (=A2-$J$2); please note the absolute reference to cell J2, written $J$2. Then, we extend the content of cell D2 up to cell D142.

Under the cell [OH^-], cell E2, we input the function 10^{logOH} (i.e., = 10^D2) and extend its contents up to cell E142.

In cell F2 (under the label [HA]) we now input the [H^+] function in row 4 of Table 1. To do so we need a value for the Acid-Base group concentration, which is written in cell L2 under cell labelled C_{HA}. For instance we use C_{HA} = 0.1(→in cell L2).

Specifically, in cell F2 we write: =($L$2*C2)/(C2+$K$3) and extend its content up to cell F142. Then, in cell G2 (under label log[HA]), we input function $\log_{10}$[HA] (=LOG10(F2)) and its content is extended up to cell G142.

In cell H2 (under label [A^-]) we input function in row 5 of Table 1 (=($L$2*$K$3)/(C2+$K$3)) and extend the function up to cell H142. Then, under label log[A^-] (cell I2), we input the function $\log_{10}$[A^-] (=LOG10(H2)) and we extend the function up to cell I142.

Finally, we have in the MonoproticAcid sheet values necessary for drawing curves for log[H^+], log[OH^-], log[HA] and log[A^-]. Changing pK_a in cell K2 and/or C_{HA} in cell L2 will automatically update all values in the sheet.

In order to visualize the LABD, an empty dispersion plot is inserted in the myPlot sheet. Then, data to be plotted are selected from the MonoproticAcid sheet. Values in the first column of the MonoproticAcid sheet (i.e., pH) represent the abscissa for all the curves to be drawn. Then, for each curve to be drawn we select the appropriate column in the MonoproticAcid sheet, i.e., columns with labels log[H^+], log[OH^-], log [HA], log[A^-]. The Excel plot appears like the one in Figure 14.

It represents a solution in which the Acid-Base group myHA/myA^-, characterized by pK_a = 9.25 has a 0.1 M total analytical concentration.

The coordinates, (pH, log[j]) of any point on any curve in the original LABD, exposed in the myPlot sheet, can be read within 0.1 log units by positioning the mouse pointer on the selected point.

The procedure we have shown above for the monoprotic acid can be easily extended, introducing the appropriate changes, to develop the sheet DiproticAcid, using [H^+] functions in rows 7, 8 and 9 in Table 1. Finally, one can develop the sheet TriproticAcid on the basis of functions in rows 11, 12, 13 and 14 (of Table 1).

LAMD of any solution of acids and bases are drawn in myPlot sheet selecting the appropriate columns in MonoproticAcid, DiproticAcid and TriproticAcid sheets, with the usual Excel operations.

Obviously, there are infinite ways to personalize plots using the standard Excel tools.

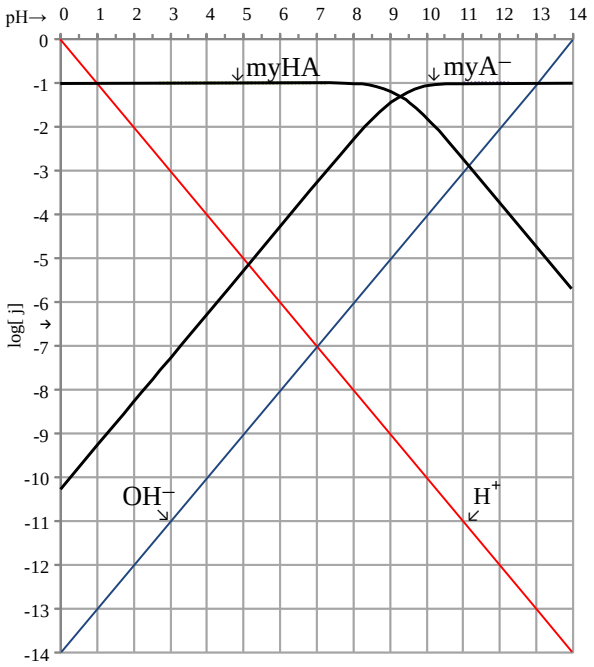

Figure 14. Logarithmic Acid-Base diagram representing the 0.1 M solution of a monoprotic acid (having pK_a = 9.25) drawn in MS Excel

5. Conclusions

If an Acid-Base titration is considered within the frame of the Logarithmic Acid-Base Diagram of the titrated solution, the topic of systematic titration error, which is generally treated in a qualitative way, can smoothly be transferred at the quantitative level, without lengthy algebraic manipulations which would otherwise be required.

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