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NUMERICAL DESCRIPTION OF TITRATION

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Abstract. The analytical methods for qualitative and quantitative determination of ions in solutions are very flexible to automation. The process of titration is a recurrent process that can be observed by permanent measurement of a simple property such as mass, current intensity, tension, volume [1-2] or a complex property such as adsorption, heat of reaction [3-5], which needs a complex evaluation. The present work focuses on the modeling of the process of titration and shows a numerical simulation of acid-base titration. The titration parameter selected is the pH. The method allows us to observe the titration process and identify the equivalence point of titration.

Keywords: titration, acid-base, simulation, mathematical modeling of chemical processes

1. Introduction

Over the two billions of samples are currently sent to laboratories of medical clinics and their number is growing. Most of these tests include the determination of glucose, urea, proteins, sodium, calcium, HCO_3^-/H_2CO_3, uric acid and pH [6-8].

The environmental science focus on chemical, physical and biological changes by contaminating or modifying natural parameters of air, water, soil, alimentary products and residues [9-11]. Their analysis gives us the measure of human provoked changes and indicates the conditions that make them possible. Thus, by using science and technology we can control and ameliorate the quality of environment.

2. Analytical measurements

Even if the measurements are simple or complex, the measurements can be, the assurance, utility, precision, interpretation and achievement of them depends of the analyst, which must be concerned -by making analysis and in the same time by the laboratory management – by the scope and the place where the finally results of analysis are used. The analyst has the obligation to make determination based on sure, reproducible and verified procedures.

The first step in design of an analytical process is to establish the objective to be followed. Only by clear identification of proposed scope the analyst can imagine a logic way that lead to correct solving of the problem [12,13]. A big responsibility for the analyst is to choose an analytical method that is leading to best solving of final scope [14].

There exist cases when freedom of choosing is limited. The analysis of water or pharmaceuticals must be made through legal standard approved procedures [15].

If more than one similarly probe exists, such as quality control, the automation becomes possible.

3. Neutralization

A easy way to make an analytical method for quantitative determinations is trespassing from an acid solution to a basic one, known as neutralization. In this case, evolution of reaction can be watched through pH measurements, continuously, when a known volume of titrating solution is added.

Usually, a strong acid or a strong base, in solution, is added. The plot of the pH as function of added standardized solution forms the titration curve. Many data result from a titration curve. Most important for the quantitative determinations is the volume of titrating solution necessary for neutralization (pH = pOH = 7 at 25°C).

4. Modeled reaction

For obtaining a concrete model of titration, let consider the case of NH_3 ($K_b = 1.79\cdot10^{-5}$) solution titrate with CH_3COOH ($K_a = 1.76\cdot10^{-5}$). Remark that NH_3 is a typically soft base and CH_3COOH is a typically soft acid.

From chemical perspective, there exist following reactions and associated equilibrium equations:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-, \qquad (1)$$

$$K_b = \frac{[NH_4^+]\cdot[HO^-]}{[NH_3]} = 1.79\cdot10^{-5}; \qquad (2)$$

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-, \qquad (3)$$

$$K_a = \frac{[H_3O^+]\cdot[CH_3COO^-]}{[CH_3COOH]} = 1.79\cdot10^{-5}; \qquad (4)$$

where [·] is a concentration and, in this case, is the molar concentration operator.

Based on equations (2) and (4) a sequence of equations can be written that simulate real conditions of titration.

If we consider that initially there exist 100 mmol in the first solution (NH_3) and no reaction product (CH_3COONH_4) and we note with *a* letters quantity of mmols from first solution and with *b* the quantities of mmols from second solution, the initial conditions (IC) can be written as in equation (5):

$$\begin{bmatrix} bb_0 \\ aabb_0 \\ aa_0 \end{bmatrix} := \begin{bmatrix} 100 \\ 0 \\ 0 \end{bmatrix} \qquad (5)$$

where *aa* and *bb* is hypothetical concentration in assumption that there are not positively numbers.

Integer values of substances from solution let be evolve by steps of 1 mmol of added solution. The corresponding equation is:

$$\begin{bmatrix} bb_{n+1} \\ aabb_{n+1} \\ aa_{n+1} \end{bmatrix} := \begin{bmatrix} bb_n - 1 \\ aabb_n + 1 \\ aa_n + 1 \end{bmatrix} \qquad (6)$$

A correction is now necessary. The concentrations are of natural values (not negative numbers) and supplementary adding of one reactant in solution lead only to deplete the other one reactant. In conclusion, must reconsider (6) with following corrections for iteration *n*:

$$\begin{bmatrix} b_n \\ ab_n \\ a_n \end{bmatrix} := \begin{bmatrix} \text{if}(bb_n > 0, bb_n, c) \\ \text{if}(bb_n > 0, aabb_n, bb_0) \\ \text{if}(aa_n > 100, aa_n - 100, d) \end{bmatrix} \tag{7}$$

where

$$c = \frac{pH_{n-1} \cdot ab_{n-1}}{ka} \text{ and } d = \frac{pH_{n-1} \cdot ab_{n-1}}{kb} \tag{8}$$

In every moment of titration, the pH is given by:

$$pH_n := \text{if}\left(a_n > 0, -\lg\left(\frac{ka \cdot a_n}{ab_n}\right), 0\right) + \text{if}\left(b_n > 0, 14 + \lg\left(\frac{kb \cdot b_n}{ab_n}\right), 0\right) \tag{9}$$

where other environment condition was considered, the standard temperature, that make that pH + pOH = 14.

The following step is now simple. Fitting the dependencies pH_n, for n = 0, 1, …, 200, with MathCad (as example), a S shape graphic was obtained (see Fig.1):

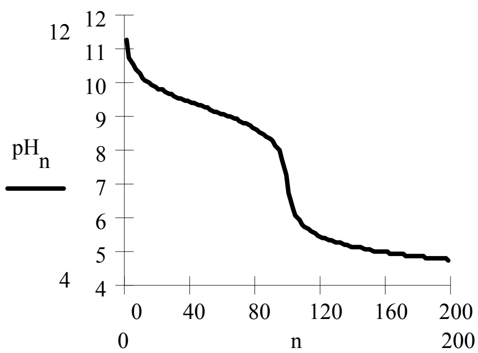

Fig. 1. Numerically fitted data in simulated titration of (1) with (3)

5. Conclusions and remarks

Although apparently simple, the titration process is in fact complex at a closer look. Unexpected difficulties may occur in the simulation process stage, even in a basic titration process, like that of a monobasic base, such as amonia, with a monoprotic acid, such as acetic acid. These difficulties mostly occur because there are no approximations used. The only so called ‘approximation’ used, is the sequential adding of the titrante which can be also used in laboratory practice.

The method permits to investigate more complex processes such as titration of poliprotic acids and polybasic bases. But without any approximation, more difficult equations need to be solved.

Anyway, the advantages of the method are higher than disadvantages resulted from complexity of calculus. Lack of approximations permits to express pH in all domain points with maximum accuracy.

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