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NUMERICAL DESCRIPTION OF TITRATION

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Abstract. The analytical methods of qualitative and quantitative determination of ions in solutions are very flexible to automation. The process of titration is a recurrent process that can be watched by permanent measurement of a simple property such as mass, current intensity, tension, volume [1-3] or a complex property such as adsorption, heat of reaction [4-6], which need a complex evaluation. The present work is focused on modeling the process of titration and presents a numerical simulation of acid-base titration. Titration parameter selected is the pH. The method permits to observe the titration process and identify the equivalence point of titration.

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

1. Introduction

Currently, over the two milliards of probes are sent to laboratories of medical clinics and this number growing. Most of these tests include the determination of glucose, urea, proteins, sodium, calcium, HCO_3^-/H_2CO_3, uric acid and pH [7-9].

The science of environment are focused on chemical, physical and biological changes through contaminating or modifying natural parameters of air, water, soil, alimentary products and residues [10-12]. The analysis of these can give the measure of human provoked modifications and can indicate the conditions that make them possible. Thus, the applying of science and technology can control and ameliorate the quality of environment.

2. Analytical measurements

Any simple or complex the measurements can be, the assurance, utility, precision, interpretation and achievement of them depend of the analyst, that must be preoccupied -by making analysis and in same time by the how - why and where are the finally results of analysis 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 it can imagined a logic way that lead to correct solving of the problem [13,14]. A big responsibility for the analyst is to choose an analytical method that is leading to best solving of followed scope [15].

There exist cases when freedom of choosing is limited. The analysis of water or pharmaceuticals must be made through legal standard approved procedures [16]

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

3. Neutralization

An 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 is solution added. The plot of the pH as function of added standardized solution is the titration curve. Many data result from a titration curve. Most important for the quantitative determinations is 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:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-, \tag{1}$$

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

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-, \tag{3}$$

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

where [·] is a concentration and in considered case is 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 mmols of the first solution (NH_3) and no reaction product (CH_3COONH_4) and we note with "*a*" letter quantities from first solution and with "*b*", the quantities from second solution, initial conditions (IC) can be written as in equation (5):

$$\begin{bmatrix} bb_0 \\ aabb_0 \\ aa_0 \end{bmatrix} := \begin{bmatrix} 100 \\ 0 \\ 0 \end{bmatrix} \tag{5}$$

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

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

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*:

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

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

$$pH_n := \text{if}\left(a_n > 0, -\lg\left(\frac{ka \cdot a_n}{ab_n}\right), 0\right) + \text{if}\left(b_n > 0, 14 + \lg\left(\frac{kb \cdot b_n}{ab_n}\right), 0\right) \qquad (8)$$

where another environment condition was considered, the normal 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) will be obtain a graphic in form similarly with fig. 1:

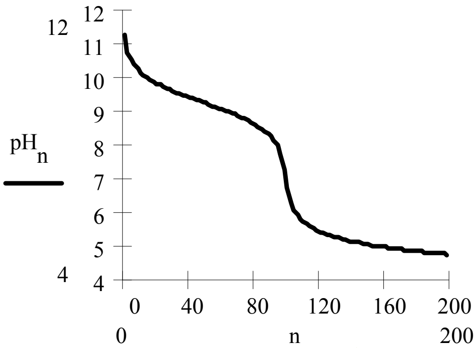

Fig. 1. Numerically fitted data in simulated titration of (1) with (3)

5. Conclusions and remarks

The titration process is simple in appearance but shows to be complex in details. Even the simple case of titration of monobasic base ammonia with a monoprotic acid, such as acetic acid, hangs up unexpected difficulties in simulation process. The difficulties exists especially because is no approximations in model. Only one (so called) approximation is sequent adding of titrate, that are also perfectly possible in practice.

The method permits to investigate more complex processes such as titration of polyprotic acids and polybasic bases. If no approximation will be made, more complex equations will be necessary and superior rank equations will appear 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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