ChE letter to the editor

Dear Editor:

Ten years ago, Sanders and Sommerfeld[1] published an interesting article presenting a laboratory experiment on combined mass transfer and kinetics. Specifically, the increase of the pH in an aqueous solution of acetic acid was followed with a digital pH-meter during neutralization with commercial antacid tablets. This experiment was selected mainly because its cost is very low and because it allows an interesting process to be studied.

Since approximately 1989, we have implemented this experiment in our undergraduate laboratory on mass transfer and kinetics, following all the instructions, including the experimental system, procedure, theory, and the data analysis, as presented in the above-mentioned paper.

Nevertheless, a closer study of the discussion presented by these authors revealed important inconsistencies that cannot be obviated, and the argument of the authors that the model provides a good fitting of the pH (though the constants reported are not correct) involving a very simple data reduction procedure seems to be not acceptable.

The authors represent the system by a very simple overall reaction:

$$2\,H_3O^+ + CO_3^{2-} \rightarrow 3\,H_2O + CO_2$$

and they assume that the instantaneous rate, measured as the rate of disappearance of the hydronium ion, is proportional to the remaining surface area, a, of the tablets and the hydronium ion concentration, with the order of the latter as yet unspecified.

Nevertheless, the fact that the material balances and the equilibrium between the acetic acid and the acetate, as well as the dissolved CO_2 were not considered in their model, would lead to the nonsense conclusion that the $CaCO_3$ and acetic acid are almost not consumed during the experiment reported, which is, obviously, contrary to reality.

According to the previous considerations, we suggest to our students the following model to explain the dissolution (and neutralization) of antacid tablets:

1. *Reactions involved:*

$$2\,H_3O^+ + CaCO_3 \xrightarrow{k_1} CO_2\uparrow + 3\,H_2O + Ca^{2+}$$

$$H_2CO_3{*} + CaCO_3 \xrightarrow{k_2} Ca^{2+} + 2\,HCO_3^-$$

2. *The pH of the solution and the acid concentration are the result of the equilibrium of the non-reacted acetic acid, the acetate anion (formed as a consequence of the reaction between the acetic acid and the $CaCO_3$ of the tablet), and the carbonic acid, which is in equilibrium with the carbon dioxide of the surrounding atmosphere and the bicarbonate anion. The concentration of these species are related by the corresponding chemical equilibrium, and the acid dissociation of the HCO_3^- can be neglected, since the pH of the reaction medium is, during all the experiment, low enough so as to assure the practical absence of $CO_3^=$ anions. To calculate the instantaneous ratio of the tablet, we use the same equation, shown by Sander and Sommerfeld.*

3. *We represent the rate of dissolution by the rate of disappearance of calcium carbonate (dN_B/dt), and obviously*

$$\frac{1}{V}\frac{dN_B}{dt} = \frac{1}{2}\frac{d\left[H_3O^+\right]}{dt} = -k_1 a^{n_1}\left[H_3O^+\right]^{n_2} - k_2 a^{n_3}\left[H_2CO_3^*\right]^{n_4} =$$
$$-k_1 a^{n_1}\left[H_3O^+\right]^{n_2} - k_2' a^{n}$$

where

$$k_2' = k_2\left[H_2CO_3^*\right]^{n_4}$$

and can be considered as constant, since the concentration of dissolved carbonic acid has been considered as constant.

In order to estimate the validity of the model, the previous equation must be numerically integrated in combination with the equations corresponding to the equilibrium of the acetic and carbonic acids, which requires the knowledge of the concentration of all the species involved at any time. To solve this problem, we use the charge balance and the material balance for the acetic acid and the acetate. We have implemented several improvements to the model in order to obtain a better fit, and only the consideration of a time delay in the response of the pH meter produces a significant improvement of the fitting.

Nevertheless, the main objective of this letter is to bring attention to the type of models in our undergraduate laboratories; excessive simplifications can only be appropriate when the simplified model is able to explain adequately the whole experiment. In this case, a very simple model was applied, but was incapable of explaining the concentration variations of the different chemical species with time. On the other hand, the increasing knowledge of our students about different computer tools permits application to more complex models, with more complex equations, while keeping the time for data reduction and analysis—thus allowing teachers to emphasize the importance of developing better and more complete models.

Sincerely:

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1. Sanders, A.A., and J.T. Sommerfeld, "A Laboratory Experiment on Combined Mass Transfer and Kinetics," *Chem. Eng. Ed.*, **23**(2), 86 (1989) ❒