

Determinaton of the Rate Constants from Phase Delay Effect in Chemical Reactions\textsuperscript{1}

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Abstract—A new method for the determination of rate constant $k$ of a reaction of the type $A + X \rightarrow P_1 + P_2$ is presented. The method is based on the phase delay between the oscillatory inflow of the parent substance X into the reaction medium and the concentration of the parent substance in the field changing as a result of the reaction, which can be expressed as $\tan\phi = \frac{2\omega}{kA}$. A method was used for the determination of the rate constant of the saponification of ethyl acetate (reactant A) with sodium hydroxide (reactant X) at 17°C. Reactant A was used in excess with respect to reactant X, which ensured its constant concentration.

INTRODUCTION

Chemical reactions are usually studied by determining changes in the concentrations of reactants in time, from which the reaction rate constant is found. The most common chemical methods for the determination of rate constants are stopping reaction flow, flow methods, mirror techniques, and others [1, 2]. The physical methods used for the same purpose are flash photolysis, relaxation techniques, the measurement of the total pressure of gas, and electric and optical methods [1, 2]. Moreover, some mixed techniques such as dilatometric, calorimetric, and thermal ones are used. Mass spectrometry and optical spectroscopy make it possible to study unstable reaction intermediates and the kinetics of complex systems [1]. For paramagnetic reactants, the EPR technique can be applied [3].

In chemical reactions, one or more reactants are constantly flowing into a reactor. If the inflow is oscillatory, concentrations of the reactants in the reaction medium can be expected to be oscillatory. However, because of the finite rate of the reaction, these oscillations will be delayed with respect to the inflow. The delay should depend on the rate of the reaction. This intuition and the ensuing possibility of determining the reaction rate constant on the basis of the delay have stimulated this work.

This study was aimed at checking if this intuitive point of view can be realized in practice. A detailed solution will be presented for a simple chemical reaction of the type $A + X \rightarrow P_1 + P_2$. We assume that reactant A is in great excess, and, therefore, its concentration does not change with the reaction time, while X is supplied to the system in an oscillatory manner. In this case, it is possible to get an exact solution to the kinetic equation from which a time dependence of the saponification of ethyl acetate with sodium hydroxide. Kinetic data on this reaction can be found, for example, in [2, 4]. This reaction occurs at a low rate and has been well recognized. We have chosen this reaction because reactant concentration can be determined in an easy way by conductivity measurements. For this reaction, the literature data on the rate constant most frequently refer to temperatures of 25°C [4, 5] or 30°C [2].

THEORY

The subject of our consideration will be a relatively simple irreversible chemical reaction of the type

\[ A + X \rightarrow P_1 + P_2. \] (I)

We assume that component A is in considerable excess and that the concentration of A is constant during the reaction. The reaction of the decomposition of X is characterized by the rate constant $k_j$. In the kinetic model, we assume that the inflow of the parent substance X into the reactor is periodically variable in time and expressed by the function

\[ I_X(t) = \alpha \cos^2 \omega t = \frac{1}{2} \alpha (1 + \cos 2\omega t), \] (1)

where $\alpha$ and $\omega$ are the amplitude and frequency of this inflow, respectively. The kinetic equation describing the
time changes of the $X$ concentration for simple reaction (I) is as follows:

$$\frac{dX}{dt} = -k_1AX + \alpha \cos^2 \omega t.$$  

(2)

Kinetic equation (2) can be solved analytically. After integration, Eq. (2) becomes the following equation for the concentration of parent substance $X$:

$$X(t) = \frac{\alpha}{2k_1A} + \frac{\alpha}{2(k_1A^2 + 4\omega^2)}(\cos 2\omega t + 2\omega \sin 2\omega t) + c \exp(-k_1At),$$  

(3)

where preexponential factor $c$ is

$$c = X_0 - \frac{\alpha}{2k_1A} - \frac{\alpha k_1A}{2(k_1A^2 + 4\omega^2)}.$$  

(4)

and $X_0$ is the initial concentration of the parent substance.

The sum of the two trigonometric functions in brackets can be replaced by a single trigonometric function after introducing an auxiliary angle $\phi$ defined as

$$\tan \phi = \frac{2\omega}{k_1A}.$$  

(5)

After substitution into Eq. (3) and some mathematical transformations, we obtain

$$X = \frac{\alpha}{2k_1A} + \frac{\alpha k_1A}{2(k_1A^2 + 4\omega^2)} \frac{1}{\cos \phi}$$  

$$\times \cos (2\omega t - \phi) + c \exp(-k_1At),$$  

(6)

where the angle

$$\phi = \arctan \left( \frac{2\omega}{k_1A} \right)$$  

(6a)

is called the shift angle.

The concentration of $X(t)$ changes from the initial value $X_0$ to the equilibrium value $\frac{\alpha}{2k_1A}$. The time of reaching equilibrium depends on the time constant $\tau = \frac{1}{k_1A}$, which is called the relaxation time. Putting $\tau$ into Eq. (6), we obtain

$$X(t) = \frac{\alpha \tau}{2} + b \cos (2\omega t - \phi) + c \exp\left( -\frac{t}{\tau} \right),$$  

(7)

where $b$ is the amplitude of oscillations which, after the elimination of $\cos \phi$ by means of the trigonometric relation $\cos^2 \phi = \frac{1}{2} \cdot \frac{1}{1 + \tan^2 \phi}$, can be written as

$$b = \frac{\alpha}{2\sqrt{k_1^2A^2 + 4\omega^2}} = \frac{\alpha \tau}{2\sqrt{1 + 4\omega^2 \tau^2}}.$$  

(7a)

and $c$ from (4) as

$$c = X_0 - \frac{\alpha \tau}{2} \left( 1 + \frac{1}{1 + 4\omega^2 \tau^2} \right).$$  

(7b)

The time dependence of the concentration of the parent substance inflow $I_x(t)$ according to (1) and changes in the parent substance concentration $X(t)$ in the reactor forced by the inflow and described by Eq. (7) are shown in Fig. 1. Instead of the frequency $\omega$, we introduced the oscillation period $T$ which is related to $\omega$ through the relation $T = \frac{2\pi}{\omega}$. We assume that the variable inflow is described by the amplitude $\alpha = 6$ and $T = 10$ (Fig. 1, I) or 5 (Fig. 1, II) in arbitrary units. The time dependences of the parent substance concentration are shown in Fig. 1, Ib and Fig. 1, Ic, or Fig. 1, IIb and Fig. 1, IIc. According to Eq. (7), the oscillations of the parent substance concentration $X(t)$ of the amplitude $b$ and frequency $\omega$ take place with respect to the average value which changes from the initial value $X_0 = 1$ to a steady state value of $\frac{\alpha \tau}{2}$. The time of the stabilization of the oscillations depends on the relaxation time of the system $\tau$ and is relatively long and well perceptible when $\tau$ is comparable to the oscillation period $T$ (Fig. 1, Ib and Fig. 1, IIb). When $\tau \ll T$ (Fig. 1, Ic and Fig. 1, IIc), the oscillations are stabilized immediately. As follows from Fig. 1, the most interesting fact is the shift (delay) of the concentration $X(t)$ of the parent substance in the reaction medium compared to the same inflow $I_x(t)$ of $X$ to the system. It is easily seen from a comparison of the maximum or minimum values of $X(t)$ and $I_x(t)$. After reaching a maximum, $I_x(t)$ decreases, whereas the parent substance concentration $X(t)$ still increases for some time before it reaches a maximum. The time of this delay $\delta$ is related to the shift angle $\phi$ through $\delta = \frac{T}{2\pi} \phi = \frac{\phi}{\omega}$. Because according to Eq. (5), $\phi$ cannot exceed $\frac{\pi}{2}$, $\delta$ must be less than $\frac{T}{4}$. The time delay of the system response to the oscillatory inflow of the parent substance is determined by the shift angle $\phi$, which is related to the $\frac{\tau}{T}$ ratio as $\phi = \arctan \frac{4\pi \tau}{T}$. This is evidenced by a comparison of the curves Ib and Ic or IIb and IIc in Fig. 1. For $T \gg \tau$, the shift angle is low, and for $T = \tau$, $\phi = 85^\circ 27'$ (Fig. 1, IIb). Thus we conclude that the angle $\phi$ takes high values when $T$ is comparable with $\tau$. The amplitude $b$ (see Eq. (7a)) depends on the frequency of oscillations $\omega$ and the relaxation time $\tau$. 

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