Eliminating Measurement Dynamics
From Kinetic Data

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Abstract

When analyzing data to evaluate a rate model, the dynamics of the measuring device must be distinguished from the effects of the rate process. This is of special concern to chemical engineers because the time constants and time delays of instruments used to measure chemical composition can be as large or larger than the time constants of the chemical reactions being studied. Researchers may use sophisticated instruments to mitigate this problem but the cost of such instruments often prohibits their use in the undergraduate laboratory. This paper presents an alternative approach. By developing a transfer function to describe the dynamics of the instrument, the effect of the instrument can be removed from the data mathematically.

The specific application presented in this paper is the collection and analysis of kinetic data for the alkaline hydrolysis of methyl acetate. For this reaction, the rate can be monitored with an inexpensive pH meter. The transfer function for the meter was determined by fitting the constants in a second-order, lead-lag model to data from a series of step-change experiments. It was assumed that the pH in the batch reactor for each kinetic experiment could be described by a generic, four-parameter function $x(t)$; the expected form of the kinetic rate expression was not used in selecting this function. The choice of the function was based on the observed shape of the pH versus time curve and the need to have a function with a simple Laplace transform. The transform of $x(t)$ was multiplied by the transfer function for the meter and this product represents the transform of the observed pH. After taking the inverse of the product, the parameters in $x(t)$ were determined for each experiment by fitting the model to the pH data. The correlation coefficients for all of the experiments were quite good so it was concluded that $x(t)$ gave an accurate representation of pH in the reactor. The method was successful in eliminating the dynamics of the pH meter from the observed pH. Since the approach taken was not tailored to this specific application, the general methodology could be applied to other situations.

I. Introduction

In the kinetic experiment which is studied in our senior laboratory course, the students obtain time-dependent concentration data for a reacting mixture of liquids in a batch reactor and analyze the data to determine the order and specific rate constant of the chemical reaction. The reaction studied is the alkaline hydrolysis of methyl acetate; this irreversible reaction is first-order with respect to both reactants [1].

$$CH_3 \text{-} \overset{\overset{\displaystyle O}{\|}}{C} \text{-} COCH_3 + Na^+\, OH^- \Rightarrow CH_3 \text{-} \overset{\overset{\displaystyle O}{\|}}{C} \text{-} O^-\, Na^+ + CH_3OH$$

| Methyl Acetate | Sodium Hydroxide | Acetate Ion | Methanol |
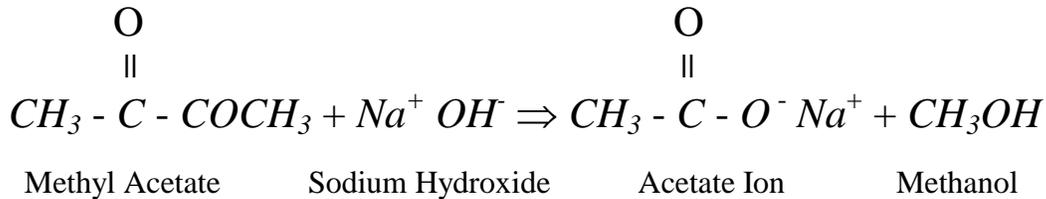
Presently, the concentration of OH⁻ is determined by titration and the other concentrations are then determined from the material balances.

To obtain a sufficient number of samples by titration, this reaction has to be slowed down either by operating the reactor below room temperature or by using low concentrations of reactants. The use of low concentrations is not desirable because the relative error is large when low concentrations are measured. Therefore, this reaction is operated at temperatures below ambient; the range of operating temperature for this experiment is typically five to ten degrees Celsius. Due to the slowness of the titration procedure, the error in the time measurement is significant and is estimated to be more than twenty seconds per data point.

Because the pH of the solution is determined by the concentration of sodium hydroxide only, a pH meter can be used to monitor the concentration of this reactant. A pH meter can acquire an experimental point every two to three seconds, and thus it is possible to collect more experimental data points than with titration. In addition, using a pH meter also makes it possible to conduct the experiment at higher temperature since a pH meter can acquire sufficient experimental data points even when the reaction rate is faster. Although a pH meter seems ideal for this experiment, the response time of pH meter has to be considered. If the response time of the pH meter is short relative to the reaction rate of the experiment, the time delay effect can be neglected. If on the other hand, the response time is significant relative to the reaction rate, then the time shift of the data caused by the meter must be considered. The dynamics of the meter can be represented by the transfer function G(s) that relates the observed pH to the pH in the reactor.

$$\boxed{} \quad \rightarrow\ X(s) \rightarrow \quad \boxed{\ G(s)\ } \quad \rightarrow\ Y(s)$$

Batch Reactor   pH meter
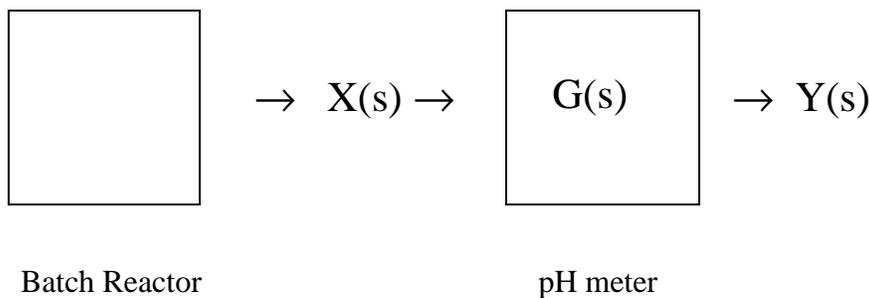
The input to the meter is represented by:

$$X(s) = \boldsymbol{L}\,[\ x(t) - x(0)\ ] \qquad\qquad (1)$$

where $\boldsymbol{L}$ is the Laplace transform operator. The output of the meter is represented by:

$$Y(s) = L \, [\, y(t) - y(0) \,] \qquad\qquad (2a)$$

and is related to the input by:

$$Y(s) = G(s) * X(s) \qquad\qquad (2b)$$

Deviation variables are used in both the input $X(s)$ and the output $Y(s)$ functions shown in equations (1) and (2). To calculate the input function $x(t)$ from $y(t)$, the transfer function $G(s)$ must be known. Therefore, a mathematical model for the transfer function $G(s)$ must be developed.

Step change experiments were performed and the responses of the pH meter were analyzed to determine the transfer function $G(s)$. Three transfer function models were compared by fitting the response to a step change input. Since all the coefficients of the transfer function $G(s)$ may be temperature dependent, step change experiments were conducted at five different temperatures. The relationship between temperature and each coefficient of the transfer function was studied.

After a suitable transfer function for the pH meter is obtained, the data from a kinetic experiment can be analyzed. Theoretically the pH in the reactor could be calculated by the following equation:

$$x(t) - x(0) = L^{-1}[\, X(s) \,] = L^{-1}[\, Y(s) \, / \, G(s) \,] \qquad\qquad (3)$$

In fact, it's not practical to perform this inverse Laplace transform with a complicated transfer function. An alternative approach is to choose an appropriate mathematical form for $x(t)$. For the kinetics experiment, $x(t)$ represents the amount of reactant in an irreversible n^{th} order reaction and so $x(t)$ is known to be a smooth, monotonically decreasing function. For a specified $x(t)$, equation (2b) becomes:

$$y(t) - y(0) = L^{-1}[\, Y(s) \,] = L^{-1}[\, G(s) * X(s) \,] \qquad\qquad (4)$$

Note that the inverse Laplace transform of equation (4) is practical only when a relatively simple form of $x(t)$ is chosen. To determine whether the chosen form of $x(t)$ is suitable or not, $y(t)$ evaluated from equation (4) is fitted to the experimental pH data and the result is evaluated. After finding an appropriate form for $x(t)$ and determining the parameters by the fitting procedure, the resulting $x(t)$ represents the kinetic data without the time delay of the pH meter.

Since the experimental kinetic data obtained by this procedure can be obtained in a period of time shorter than the time required for the titration method, it is possible to get multiple sets of data at different temperatures in a single laboratory period. In addition, the number of data points acquired by pH meter is much larger than the number that can be obtained by titration and thus the analysis of the reaction rate is more reliable.

II. Modeling the pH meter

To determine the transfer function for the pH meter, step change experiments that cover the expected range of pH during the kinetic experiments were conducted. Since the pH value of the solution is temperature dependent, the probe of the pH meter was kept at the specified temperature during each step change experiment. The step change experiments were conducted at five different temperatures; the data for the minimum and maximum temperatures are shown at Fig. 1. The data for the other temperatures were similar and are not included to avoid a crowded figure. The initial value of pH in a step change experiment was calculated from the initial concentration which was determined by titration. Because the error in titration will become very large at lower concentrations [2], the final value of the pH was obtained directly from the pH meter. For the step change experiment, the input function X(s) is:

$$X(s) = \frac{\alpha}{s} \tag{5}$$

where α = final value of pH (11.52) - initial value of pH (13.07)

Figure 1. Step change data.
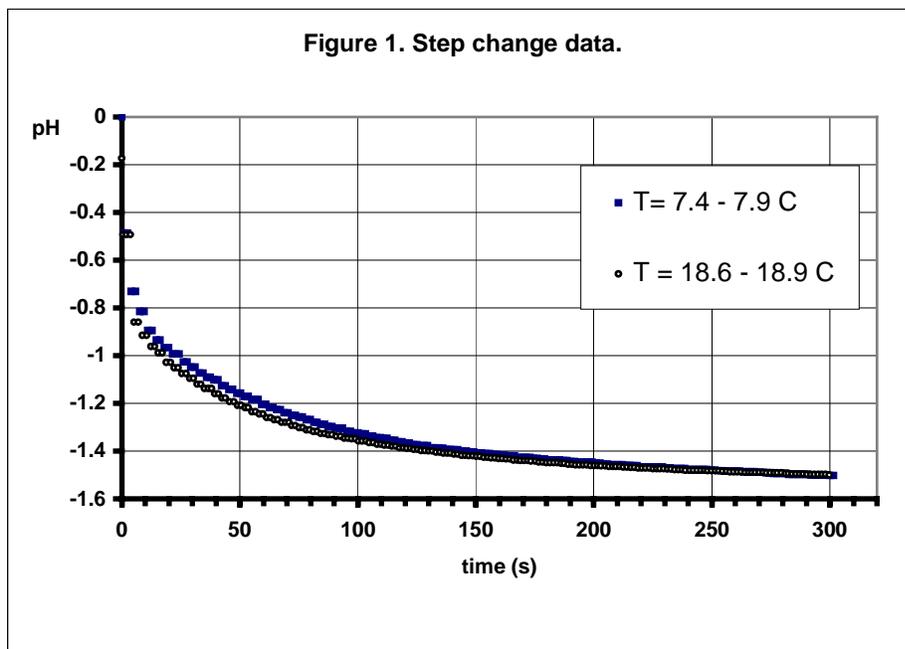
Three models were considered for the transfer function G(s). To find out which model is most suitable, the output function y(t) corresponding to the each model was obtained from equation (4) and fitted to the experimental data. The total error function E_1, defined as follow, was minimized:

$$E_1 (K_0, K_1, \tau_1, \tau_2) = \sum_{j=1}^{N} [y_j - y(t_j)]^2 \qquad (6)$$

where: N = the number of experimental data points
t_j = the sampling time of the jth data point
y_j = the experimental data at time t_j
$y(t_j)$ = the value of the model at time t_j

Because there is a lag of 1 to 2.5 seconds between the time the computer requests a value from the pH meter and the time the computer receives a value from the pH meter, the exact time of the pH meter reading is not known. The sample time t_j was taken to be the average of these two time values.

The average error, defined as E_1 divided by N, was used as one measure of the goodness of the fit. The correlation coefficient, R is also employed as an indicator of the fitting and is defined by:

$$R = \sqrt{\frac{S-E_1}{S}} \qquad (7a)$$

S is defined as:

$$S = \sum_{j=1}^{N} (y_j - \bar{y})^2 \qquad (7b)$$

where $\bar{y}$ is the mean value for all the experimental data points. A comparison of the different transfer functions is shown in Table 1.

Table 1. Comparison of different transfer functions						
	First-order plus $G(s) = \dfrac{K_0 e^{-\tau_2 s}}{\tau_1 s + 1}$		Second-order model $G(s) = \dfrac{K_0}{(\tau_1 s + 1)(\tau_2 s + 1)}$		Lead-lag model $G(s) = \dfrac{K_0 + K_1 s}{(\tau_1 s + 1)(\tau_2 s + 1)}$	
Temp.(°C)	E_1/N	R	E_1/N	R	E_1/N	R
7.4 to 7.9	0.00465	0.902	0.00455	0.924	0.00032	0.994
10.1	0.00559	0.875	0.00533	0.882	0.00020	0.996
12.1 to 12.3	0.00515	0.902	0.00505	0.916	0.00022	0.996
15.0 to 15.1	0.00555	0.890	0.00530	0.904	0.00018	0.996
18.6 to 18.9	0.00723	0.865	0.00714	0.8712	0.00047	0.991

The fit for the lead-lag model is good; the correlation coefficient is close to one and its average error is small. For this G(s), the observed pH of a step change experiment is given by:

$$y(t) - y(0) = \alpha \left[\frac{K_1 - K_0 \tau_1}{\tau_1 - \tau_2} e^{(-t/\tau_1)} - \frac{K_1 - K_0 \tau_2}{\tau_1 - \tau_2} e^{(-t/\tau_2)} \right] \qquad (8)$$

The results of fitting this model to the experimental data at one temperature (12°C) are shown in Fig. 2. Note that only one data point was drawn for every twenty data points in Fig. 2 to make it possible to distinguish the experimental data points from the fitted line. The results at the four other temperatures also showed very good agreement between the model and the data.

Figure 2. Fitting the step change data.
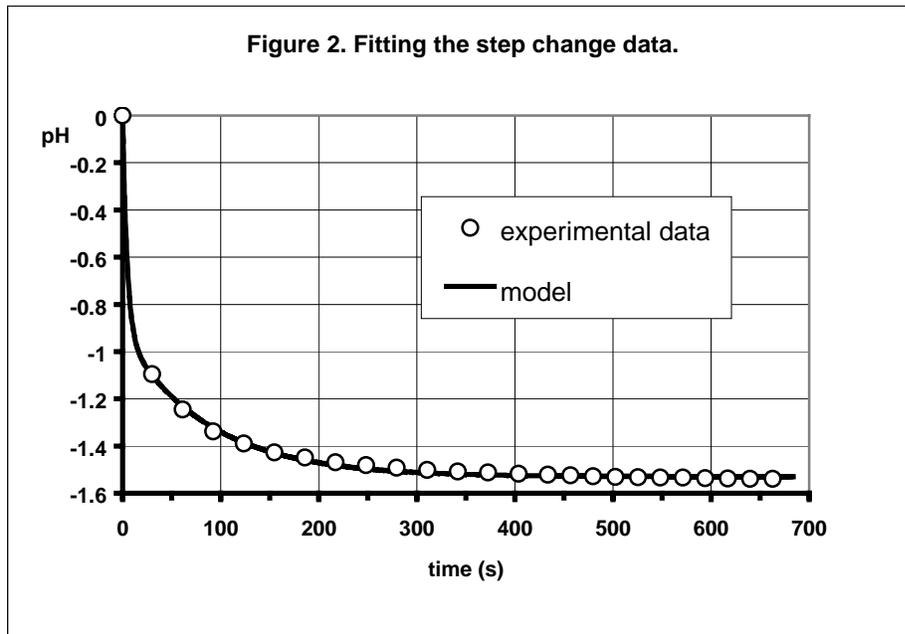
The four parameters of the transfer function K_1, K_2, τ_1 and τ_2 corresponding to different temperatures are listed in Table 2. Since there is no simple theoretical basis for the temperature dependence of these parameters, the natural log of each parameter was plotted against the inverse of temperature. The results are shown in Fig. 3, 4, 5 and 6 and lead to the following equations:

$$K_0 = 0.7416 \, e^{(82.95/T)} \qquad (9)$$
$$K_1 = 0.2408 \, e^{(1522/T)} \qquad (10)$$
$$\tau_1 = 0.02490 \, e^{(2312/T)} \qquad (11)$$
$$\tau_2 = 3.518 \qquad (12)$$

where T is in Kelvin. τ_2 is given as a constant since no correlation with temperature was observed in Fig. 6. Although the mean value of this parameter was used in this case, it does not affect the accuracy of the temperature dependent model because y(t) is relatively insensitive to τ_2 since the

third term of equation (8) decreases much faster than the other two terms. For example, at T = 10.1°C and t = 15 seconds, the third term of equation (8) contributes only about 2% to the value of y(t). To make sure that the parameters obtained from equations (9) to (12) are accurate in the temperature range over which the step change experiments were conducted, y(t) was recalculated and compared to the observed data in Fig. 7. Comparison of Fig. 2 with Fig. 7 shows that using the parameters generated by equation (9) to (12) does not cause a significant loss of accuracy. The results were similar at the other temperatures.

Table 2. The transfer function parameters at different temperatures.				
Temp.(°C)	K_0	K_1 (sec)	τ_1 (sec)	τ_2 (sec)
7.4 to 7.9	1.000	54.3	95.2	2.57
10.1	0.990	52.6	86.4	3.96
12.1 to 12.3	0.990	53.1	86.0	4.56
15.0 to 15.1	0.992	41.9	70.3	2.20
18.6 to 18.9	0.985	46.9	71.5	4.30

Figure 3. The temperature dependence of K_0.
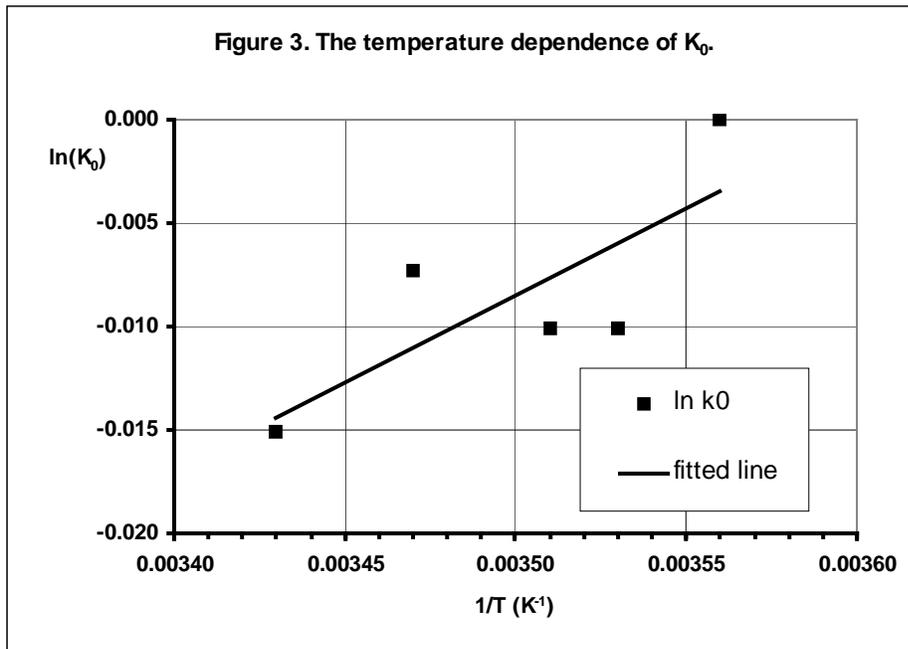
Figure 4. The temperature dependence of K_1.
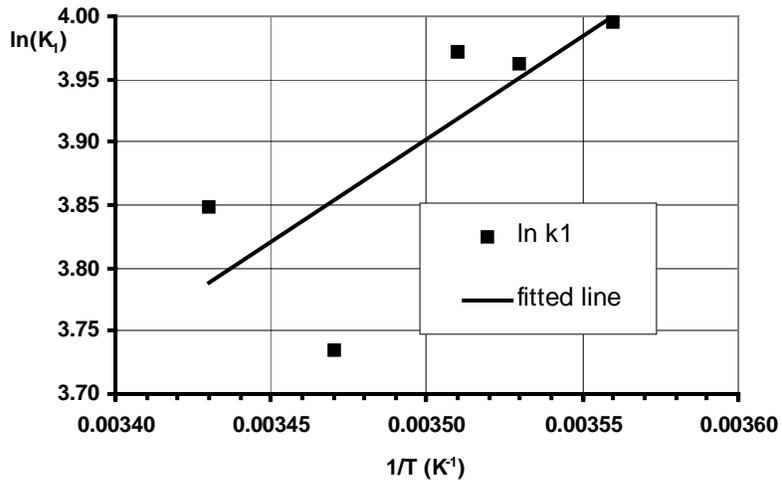
Figure 5. The temperature dependence of τ_1.
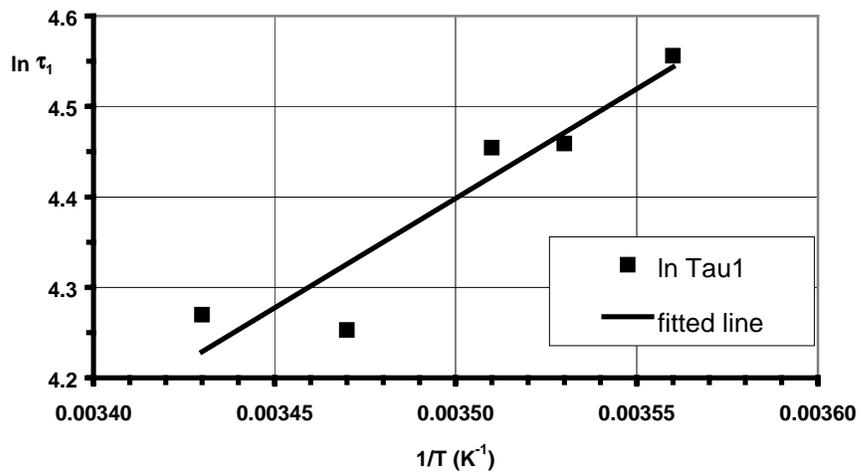
Figure 6. The temperature dependence of τ_2.
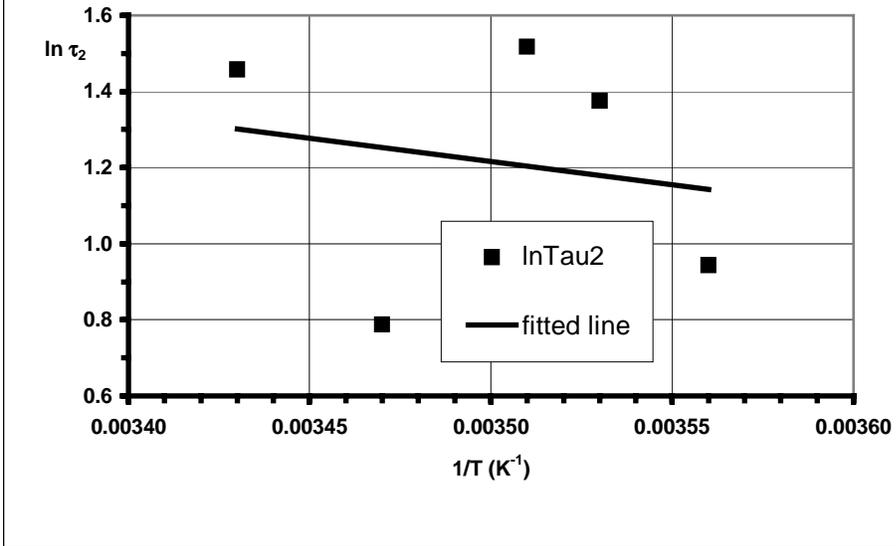
Figure 7. Fit of the temperature depenedent model.
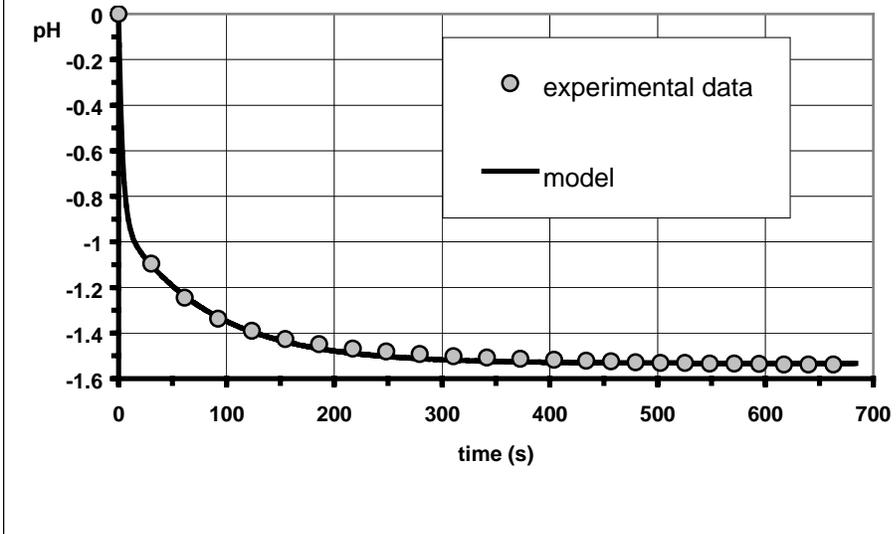
III. Determination of real time data

Unless an expression for the reaction rate is specified, the form of x(t) can not be determined. However, it is known that as the reaction proceeds, the reactants are consumed and the reaction rate will decrease. When the value of pH is plotted as a function of time, the magnitude of the slope should decrease as time increases as shown in Fig. 8. It is reasonable to expect that the following function with two exponential terms could be used to represent the reactant data:

$$x(t) = c_1\, e^{(-t/b_1)} + c_2\,{}^{(-t/b_2)} \qquad (13)$$

where c_1, c_2, b_1 and b_2 are parameters to be determined by fitting the model to the data. The transfer function of the pH meter has been determined previously so that the output of the pH meter y(t) can be represented by:

$$y(t) - y(0) = L^{-1}[\, G(s)X(s)\,] =$$

$$[\,\frac{K_1 - \tau_1 K_0}{\tau_1 - \tau_2}\,]\,[\,\frac{c_1 b_1}{b_1 - \tau_1} + \frac{c_2 b_2}{b_2 - \tau_1} - (\,c1 + c2\,)\,]\,e^{(-t/\tau_1)}$$

$$-\,[\,\frac{K_1 - \tau_2 K_0}{\tau_1 - \tau_2}\,]\,[\,\frac{c_1 b_1}{b_1 - \tau_2} + \frac{c_2 b_2}{b_2 - \tau_2} - (\,c1 + c2\,)\,]\,e^{(-t/\tau_1)}$$

$$+\,[\,\frac{b_1{}^2 K_0 c_1 - K_1 c_1 b_1}{(b_1 - \tau_1)(b_1 - \tau_2)}\,]\,e^{(-t/b_1)} + [\,\frac{b_2{}^2 K_0 c_2 - K_1 c_2 b_2}{(b_2 - \tau_2)(b_2 - \tau_1)}\,]\,e^{(-t/b_2)}$$

$$-\,K_0(\,c_1 + c_2\,) \qquad (14)$$

Since the parameters K_0, K_1, τ_1 and τ_2 have already been determined, only four parameters c_1, c_2, b_1 and b_2 were adjusted to minimize the total error E_2 defined by the following equation:

$$E_2(\,c_1, c_2, b_1, b_2\,) = \sum_{j=1}^{N} [\,y_j - y(t_j)\,]^2 \qquad (15)$$

where: N   = the number of experimental data points
        t_j = the sampling time of jth data point
        y_j = the experimental kinetic data at time t_j
       $y(t_j)$ = the value of the model from equation (14) at time t_j

Figure 8. Data from kinetic experiments at 18⁰C
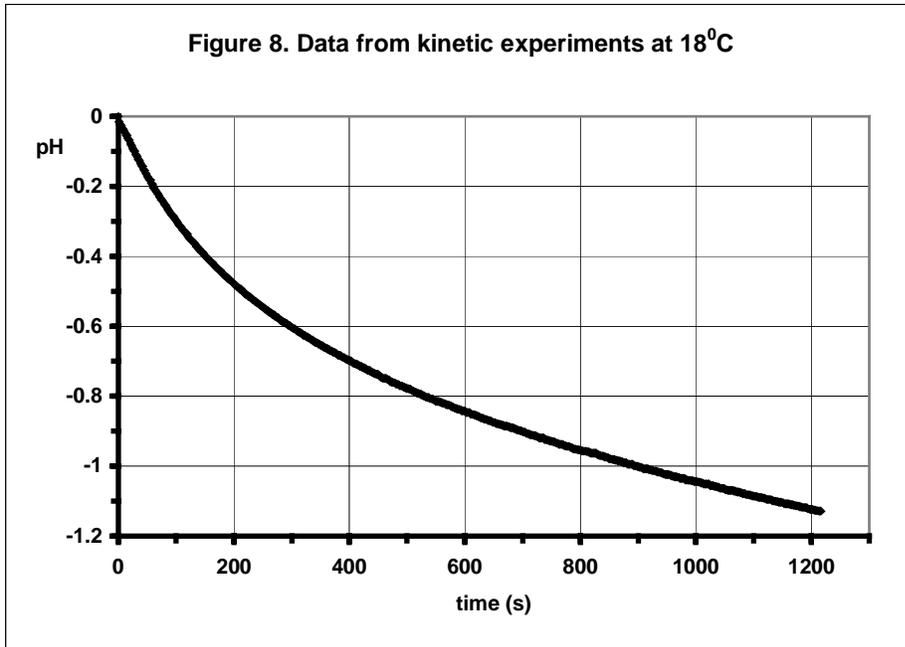
As before, the average error and the correlation coefficient were employed as indicators of the goodness of the fit. Kinetic experiments were conducted at three different temperatures. For one of the temperatures, the observed experimental data, the fitted line for the observed data $y(t_j)$ and the line for the adjusted $x(t_j)$ are shown in Fig. 9. As in Fig. 2, only one experimental data point was drawn for every twenty data points to make it possible to distinguish the experimental data from the fitted line. The agreement between the model from equation (14) and the experimental data is excellent, indicating that the form of $x(t)$ provides an accurate representation of the experimental data during the kinetic experiment. Similar results were observed at the other two temperatures.

Figure 9. Actual and adjusted data at 18^0C.
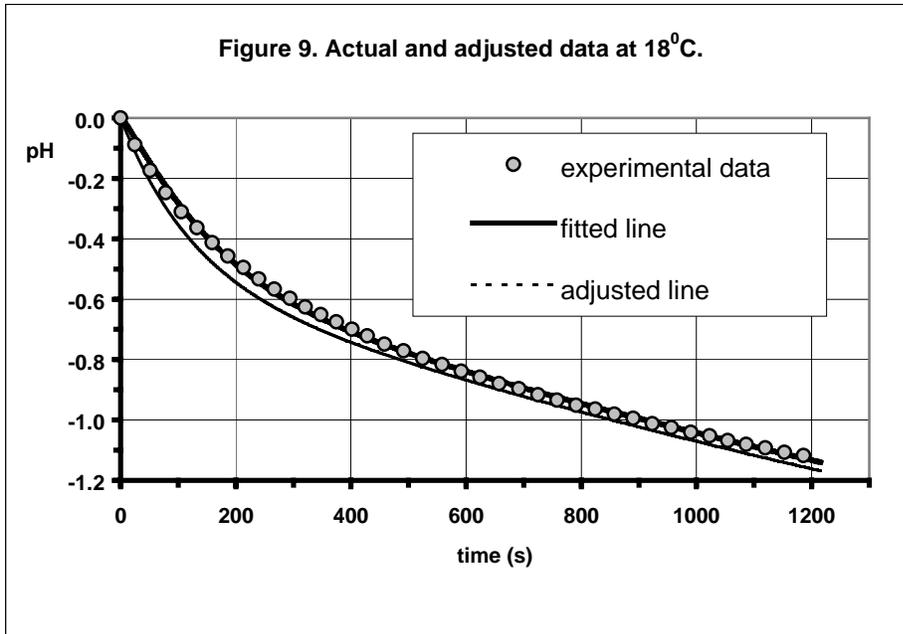
IV. Sample analysis of kinetic data

The flow chart of the computer program to be used in the laboratory course is shown in Fig. 10. As shown in the flow chart, the program will give the students a set of data at the end of each kinetic experiment. The concentration of sodium hydroxide in the solution is obtained from the pH value by the following equation:

$$C(t) = 10^{(pH - K_w)} \qquad (16)$$

where K_w is the ionic product constant of water. K_w is dependent only on temperature; the relationship between K_w and temperature is given by:

$$\ln (K_w) = 2.70291 - 2.61054 * 10^{-3} T \qquad (17)$$

where T is in Celsius [3]. The order of the reaction can be determined from the concentration data $C(t_j)$. The chemical reaction studied is an irreversible reaction and the stoichiometric coefficients for all the reactants and products are one. When all the initial concentrations of reactants are kept the same, the relationship between reaction order, reaction rate and concentration of reactants is given by:

$$-r(t_j) = k [C(t_j)]^n \qquad (18)$$

where k is the rate constant for the reaction and n represents the reaction order. This can be plotted as:

$$\ln [-r(t_j)] = \ln (k) + n \ln [C(t_j)] \qquad (19)$$

Fig. 10 Flow chart of the computer program.

Collect pH data, $y(t_j)$, at all sampling times t_j.

Determine the four parameters c_1, c_2, b_1 and b_2 from the experimental data.

Calculate $x(t_j)$ from equation (13).

Convert $x(t_j)$ to concentration and record $C(t_j)$.
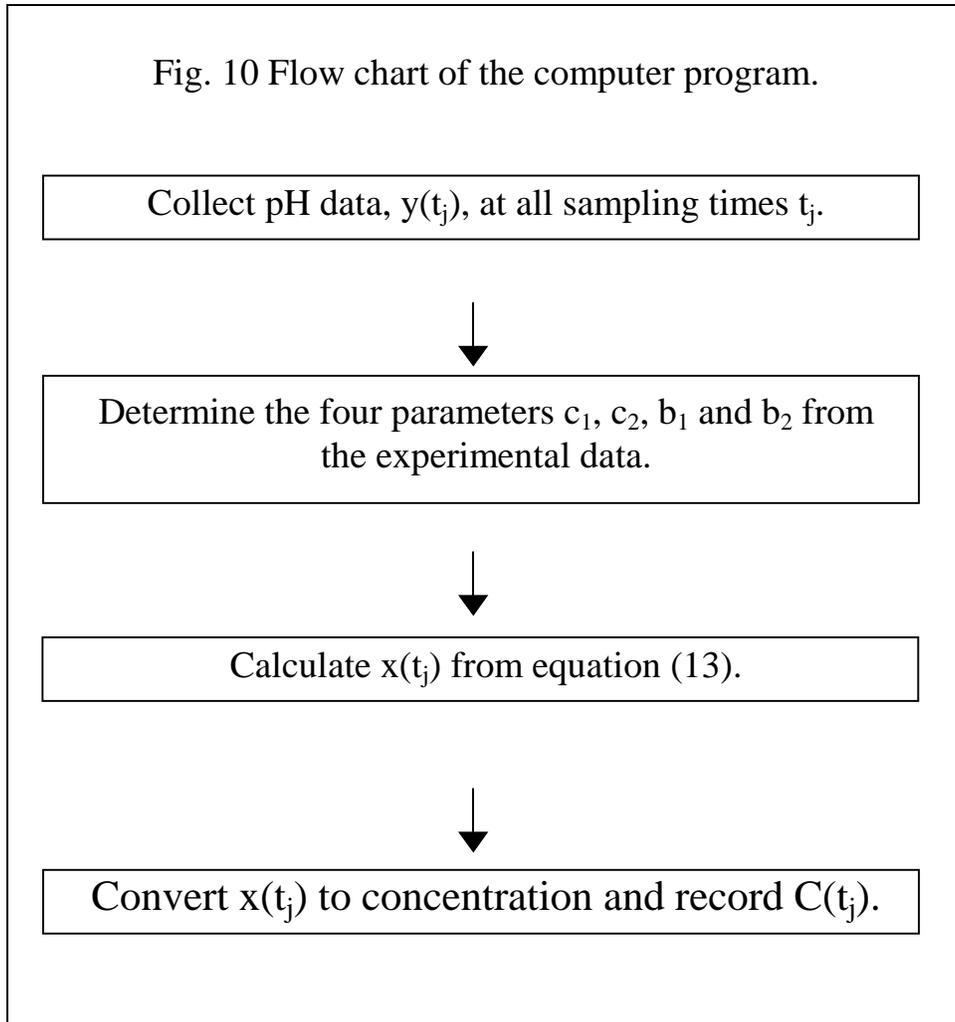
The slope of the plot is the reaction order n and the rate constant can be calculated from the intercept. The reaction rate at time t_j is calculated from the concentration data by the following equation:

$$r_j = \frac{(t_j - t_{j-1})\dfrac{C(t_{j+1}) - C(t_j)}{t_{j+1} - t_j} + (t_{j+1} - t_j)\dfrac{C(t_j) - C(t_{j-1})}{t_j - t_{j-1}}}{(t_{j+1} - t_{j-1})} \qquad (20)$$

where: t_j = the sample time of jth data point
r_j = the reaction rate at time t_j
$C(t_j)$ = the concentration at time t_j

As shown in Fig. 11, the overall order of the reaction is close to two (1.980). The values of the

slope at the other temperatures were also close to two (2.047 at 12°C and 1.833 at 15°C). With n = 2 in equation (19), the rate constants are recalculated as shown in Fig. 12.

The temperature dependence of the rate constant [4] is typically given by:

$$\ln (k) = -\frac{E}{RT} + \ln (A_0) \qquad (21)$$

where:

T = absolute temperature
R = gas constant
E = activation energy
A_0 = frequency factor

Consequently, when ln k is plotted versus 1 / T, a straight line with slope - E / R is expected. The temperature dependence of the rate constant (for n=2) is shown in Fig. 13. In comparison to the reference point ($k = 0.184$ $M^{-1}s^{-1}$ at T = 25 ^{0}C) [1], the rate constant obtained from the analysis above is $k = 0.199$ $M^{-1}s^{-1}$.

Note that when the range of the temperatures for the sets of kinetic data is too small, this analysis would not be accurate because the differences between the rate constants would be small relative to the experimental error. Therefore, a wide range of temperatures is necessary to obtain an accurate representation of the temperature dependence. Certainly, a large number of data points is also necessary to accurately evaluate $\frac{dC}{dt}$ used in the relationship between rate constant and temperature. Unfortunately, when students use titration to acquire experimental data, they cannot obtain a sufficient number of data points for each experiment and they have to conduct the experiment within a very limited temperature range (5 ~ 10°C). With a pH meter, the students will be able to analyze the kinetic data with greater accuracy and reliability.

Figure 11. Analysis of reaction order.
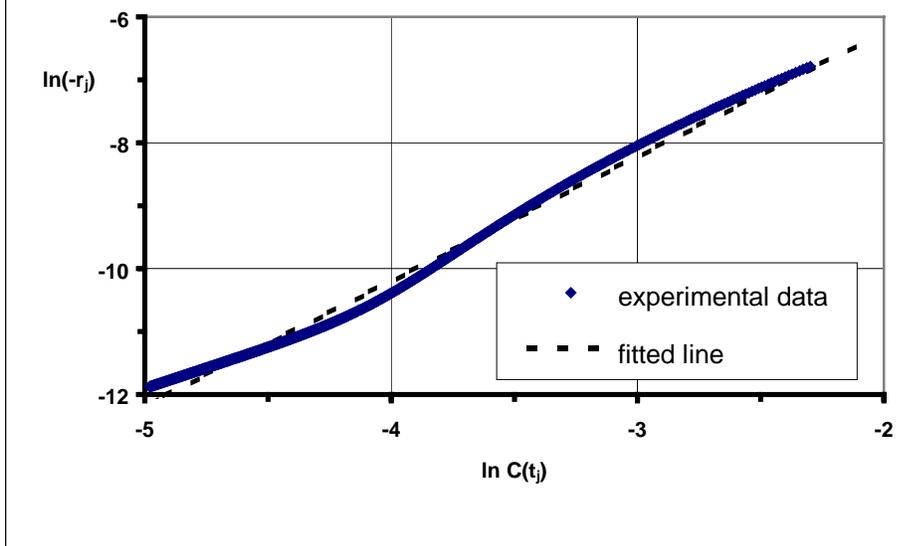
Figure 12. Determination of reaction rate constant.

Figure 13. Temperature dependence of the rate constant.
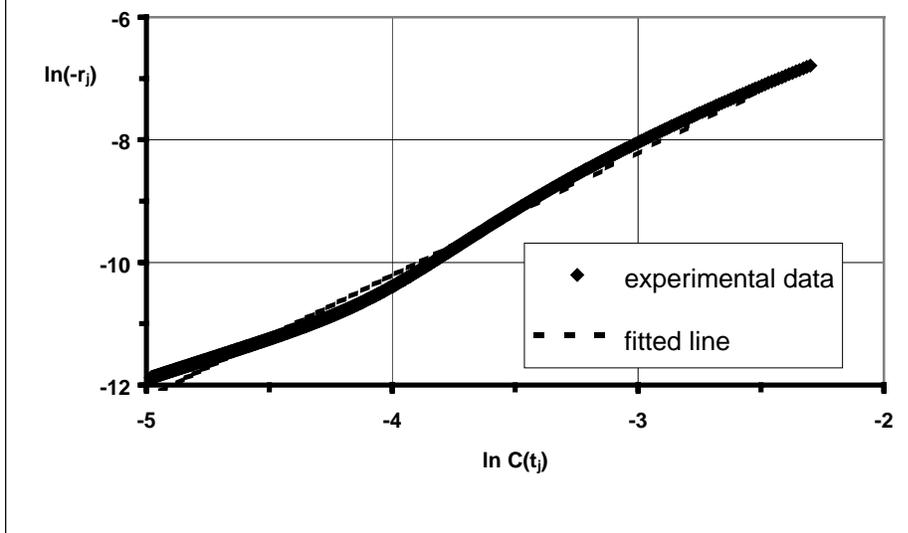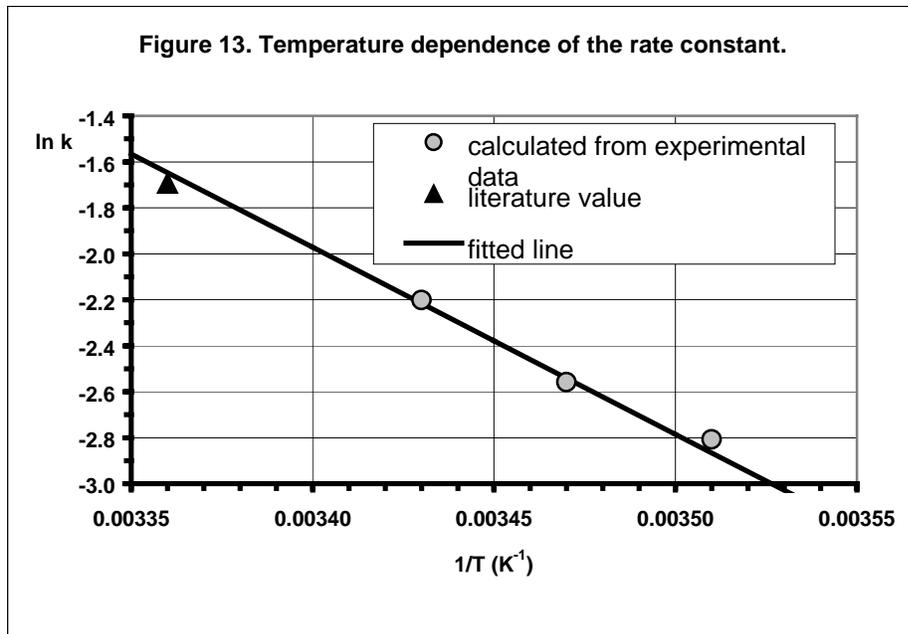
V. Conclusion

Using a pH meter coupled to a computer can provide a large number of experimental data points and the experiment can be conducted over a wide range of operating temperature. In addition, this method is easier to use and more accurate than titration. For this reaction, the pH meter is a better way to acquire kinetic data.

A similar methodology could be employed to correct experimental data obtained with other measuring devices for which the time shift of the data is significant.

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