CHEMICAL KINETICS, HEAT TRANSFER, AND SENSOR DYNAMICS REVISITED

in a Simple Experiment

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Since its beginnings, chemical engineering education has incorporated practical activities into the curricula (known as laboratory practices) in varying degrees (number of teaching hours, number of credits) according to the type of course or level of advancement in a given program. The historical evolution of this type of activity in chemical engineering programs has been recently discussed in literature.[1,2] It seems quite clear that, with the exception of certain courses and subjects directly involved with standard practical experiments (*e.g.*, general and instrumental analytic chemistry), there is ample choice in their design and implementation. On the other hand, new developments both in the processing of experimental data and in process control and automation techniques make it possible to design and implement laboratory practices in practically every area at any level of sophistication and scientific accuracy. This requires important investments in time and money that, unfortunately, many schools are not willing to undertake.

A valid alternative, then, is to redesign these practical activities to maximize the use of resources. This work describes a simple, inexpensive lab experiment that was originally designed for qualitative demonstration on the existence of "hot spots" in discontinuous reactors. It has been deeply modified from the viewpoint of the processing and interpretation of the data collected through the use of a relatively sophisticated mathematical model and the independent validation of certain parameters. With these modifications, the field of knowledge has been broadened (development and validation of mathematical models, heat transfer and sensor dynamics) at practically null costs (considering time and economic resources).

In what follows, both the experimental procedure and the development and validation of the model are described. Results illustrate this type of activities performed by students. The subject to which this activity belongs is Chemical Reac-

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tion Engineering I, which also has other practical activities of different design that range from pilot scale experiments with semi-industrial equipment to computational simulations of real processes.

CONTENTS: THEIR RELEVANCE AND DESCRIPTION

Several authors have reported studies with adiabatic reactors using the strongly exothermic reaction between sodium thiosulfate and hydrogen peroxide in aqueous media. At first, this reaction was used to experimentally assess theoretical predictions about hot spots in discontinuous or plug flow reactors and steady state multiplicity and hysteresis or oscillations in continuous stirred tank or recycle plug flow reactors.[3-7] More recently, this reacting system was used to evaluate some new techniques in control and optimization engineering and in risk management.[8-18]

Heat transfer in chemical reactors is an important topic both from theoretical and practical points of view. A common practice in chemical reaction engineering courses (which may be taken in parallel with energy transfer courses by the students) is to assume very simple models of this phenomenon to avoid further complications in the classical chemical reactor models.

Another aspect added to thermal kinetic data processing is the incorporation of the "time lag" concept in the temperature measurement. This concept naturally arises in the course of process control, which students take normally afterward, but may be easily modeled as a simple, first order heat transfer lag to help introduce students to the idea of non-instantaneous measurement. In this case, chemical reaction is very rapid, and we have chosen a sensor (digital thermometer) with a deliberately high thermal mass so the lag effect is more noticeable.

THEORETICAL FUNDAMENTALS AND MATHEMATICAL MODEL

The reaction between sodium thiosulphate and hydrogen peroxide in aqueous solutions is highly exothermic ($\Delta HR \cong$ 147 kcal/mol $Na_2S_2O_3$) and practically irreversible. The currently accepted stoichiometry for the reaction is:

$$2Na_2S_2O_3 + 4H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O \quad (1)$$

$$2A + 4B \rightarrow C + D + 4E$$

The kinetic behavior of this system has been well studied by several authors[3-6] and is first order with respect to each of the reagents:

$$r = k.C_A.C_B \qquad [r] = \text{gmol}\, Na_2S_2O_3 / cm^3.s \quad (2)$$

The dependence of k with T will be taken as the usual Arrhenius form:

$$k = A.e^{-E/R.T} \quad (3)$$

even though some slightly different form was reported in earlier studies.

For a batch reactor the mathematical model is made up of two differential equations resulting from mass and energy balances. Concentration of reagents sodium thiosulphate (C_A), hydrogen peroxide (C_B), and temperature (T) can be described by using these balances, the stoichiometry ratio between both reagents, and the initial conditions:

$$dC_A / d\theta = -k_{(T)}.C_A.C_B \quad (4)$$

$$V.Cp_v.(dT / d\theta) = k_{(T)}.C_A.C_B.(-\Delta H_R) - A_t.U.(T - t) \quad (5)$$

$$C_B = C_{B0} - 2.(C_{A0} - C_A) \quad (6)$$

$$T_{(0)} = 0 \qquad C_{A(0)} = C_{A0} \qquad C_{B(0)} = C_{B0} \quad (7)$$

The thermal mass of the beaker used as a reactor has been neglected in the energy balance (Eq. (5)), due to its low mass (less than 4g), to avoid further complications in the proposed model.

This set of differential equations can be solved using an appropriate numerical method (Euler, Runge-Kutta, etc.) in order to obtain the evolution of products concentration and temperature with time. It must be noted that this system may exhibit a "stiff"[17,18] behavior, so the numerical integration method should be a robust one.[19]

For exothermic reactions such as this one, with heat exchange resulting from an external cooling media, the temperature vs. time profile has a maximum value ("hot spot"). At this point:

$$k_{(T)}.C_A.C_B.(-\Delta H_R) = A_t.U.(T - t) \Rightarrow dT / d\theta = 0 \quad (8)$$

After this point the temperature will decrease with a diminishing slope, as the reaction rate tends asymptotically to zero. At infinite time, the temperature within the reactor will be the same as that of the surrounding media:

$$[k_{(T)}.C_A.C_B.(-\Delta H_R)]_{\theta \to \infty} = 0 \quad (9)$$

$$[dT / d\theta]_{\theta \to \infty} = (A_t.U / V.Cp_v).(T - t) \Rightarrow T_{\theta \to \infty} = t \quad (10)$$

This behavior at sufficiently high times is useful to "independently" estimate the value of U (from At.U/V.Cp_v) using values of temperature/time in this time domain. For the vessel used as a reactor, values of V and A_t were 100 cm^3 and ca. 120 cm^2. The value of Cp_v was 1 cal/g.K.[8] These values were used to estimate the heat transfer coefficient.

The "time lag" of the sensor (digital thermometer) was taken into account through the simple first-order model:[22-24]

$$dT_R / d\theta = (1 / \tau).(T - T_R) \quad (11)$$

which may result from the finite heat transfer rate between the fluid, which is at the "real" temperature T, and some internal point in the sensor probe, which is at the read temperature T_R. Both the high chemical reaction rate and the deliberate choice of a sensor with high thermal mass justifies the incorporation of the new dependent variable T_R in the model with its additional differential equation and a new parameter (τ).

EXPERIMENTAL

The equipment used is simple, inexpensive and is comprised of the following elements: a 100 mL disposable, lightweight polystyrene beaker, a magnetic stirrer, a digital thermometer of the type used for frozen meat control at cold-storage plants (273 K/423 K range, 0.1K resolution) and a 500 mL crystallizer to be used as an ice bath. A few millimeters of clearance was left between the bottom of the beaker and the stirrer plate to achieve a more homogeneous external heat transfer environment. The chemical reactants employed are of analytical grade, but commercial hydrogen peroxide (10-20 vol, with stabilizer) or commercial thiosulfate have been used with no substantial result alteration.

A series of experiments is synthetically described below, for typical work performed by students that can be easily modified from operating conditions or sequencing.

EXPERIMENT #1

Chemical reaction involving heat exchange with the environment (kinetic experiment)

This experiment consists of loading the reactor with 50 mL of a $Na_2S_2O_3$ ~ 0.8M solution, placing the thermometer in an adequate fixed position, and stabilizing the stirring rate to finally add 50 mL of H_2O_2 ~1.2M as rapidly as possible. Then, temperature readings should immediately start at appropriate time intervals. Figure 1 shows typical results obtained by students conducting this experiment at 303 K (room temperature).

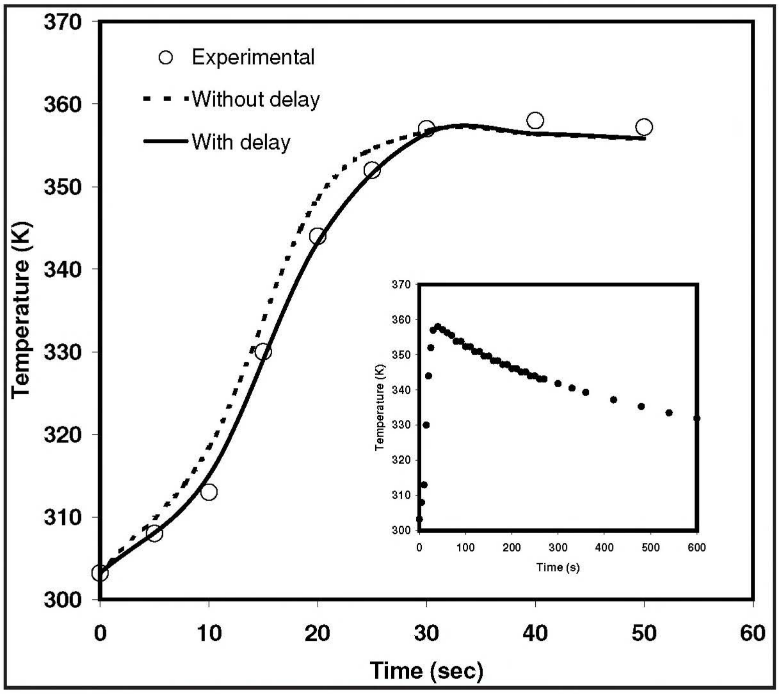

Figure 1. Reaction between $Na_2S_2O_3$ and H_2O_2 in a batch reactor with heat exchange by natural convection (room temperature: 300 K).

It was observed that the temperature increased rapidly at the beginning, went through a well-marked maximum for about one minute, and then decreased increasingly at a slower pace. This results were obtained because when the limiting reactant is practically exhausted, the reaction rate becomes negligible and the system behaves as a simple vessel with fluid at a temperature close to room temperature, where it exchanges heat by convection (internally forced, externally natural) with low heat transfer coefficients.[20,21]

EXPERIMENT #2

Natural cooling of the vessel with no chemical reaction

This experiment consists of following the liquid cooling (preferably using the same solution used in Experiment #1 after its completion) under the same conditions previously analyzed, from a temperature of about 353-363 K. The final liquid from the previous experiment, preheated up to that temperature level, is left to evolve spontaneously under the same stirring conditions. Many time/temperature values are then registered (10 – 15 values) to estimate a value of the U global exchange coefficient under conditions similar to those of the kinetic experiment. To do so, it suffices to use the asymptotic integrated form of the energy balance differential Eq. (5):

$$\ln\left[(T_0 - t)/(T - t)\right] = (A_t.U/V.Cp_v).\theta = \alpha.\theta \qquad (12)$$

The slope of a straight line in the graph of $\ln[(T_0 - t)/(T - t)]$ vs.θ is the value of α. Figure 2 (next page) shows the results of an experiment of this type together with statistical analysis of the data.

EXPERIMENT #3

Determination of the thermometer time lag (time constant)

This experiment should also be performed with the liquid sample of the first experiment, preheated to a convenient temperature level (343-353 K) and existing under the same conditions (stirring, etc.). In this case, the thermometer (previously in thermal equilibrium at room temperature) is introduced and fixed as quickly and as smoothly as possible and the registered temperature evolution is read as a function of time (given the ordinary response times of tools such as the thermometer employed, the readings should be carried out at a frequency of about 2-5 s). An essential condition for this experiment is that the temperature of the liquid mass be constant during the experiment. Since the time consumed is short, this condition is practically accomplished. The integrated form of differential Eq. (11) yields the classical step input time response for a first order system:

$$\ln\left[\left(T_{R0}-T_F\right)/\left(T_R-T_F\right)\right]=(1/\tau).\theta \qquad (13)$$

from which the value of time constant, τ, can be estimated by regression of the experimental data. The value of T_F is the "final" value shown in the display when it varies no longer ($T_F = T_R|_{\theta\to\infty}$). Figure 3 shows typical results as well as the estimation of τ.

Analysis of the data: Models and interpretation of results

The results obtained with a typical kinetic experiment may be correlated using a simple model (Model I) integrated by the mass balance (Eq. (4)) and energy (Eq. (5)) differential equations with proper boundary conditions and parameters A, E and U (or α). They can also be correlated by a more sophisticated model (Model II) including the differential equation accounting for thermometer time response with the additional τ parameter. On the other hand, the number of parameters (and hence the error associated with its determination) are reduced to 2 in both models if values of α and τ, obtained from the analysis of the results of Experiments # 2 and 3, are taken as known. Figure 1 shows the adjustment of both types of models (with its associated floating parameters), and Table 1 summarizes the results obtained as well as the comparison between the parameters obtained and those from independent experiments or reported in the literature. Notice the better adjustment of the model in Figure 1, including the time lag of the thermometer readings. Likewise, in Table 1, a good correspondence can be observed between the parameters determined from the kinetic experiment, those from independent experiments, and those reported in the literature. This correspondence is more marked in the case of the model including the thermometer time lag. The interpretation and analysis of the results is usually performed using any available software capable of performing the regression of the temperature-time experimental values, by way of numerical integration of the differential equations (with methods adequate for "stiff" systems) using any parameter search engine such as simplex, steepest descent, Monte Carlo, etc. There is a lot of general software available for these ends (Matlab, Matematica, MathCAD, to mention just a few) and some direct-oriented free applications (such as Scientist from Micromath) to solve the problem of statistical determination

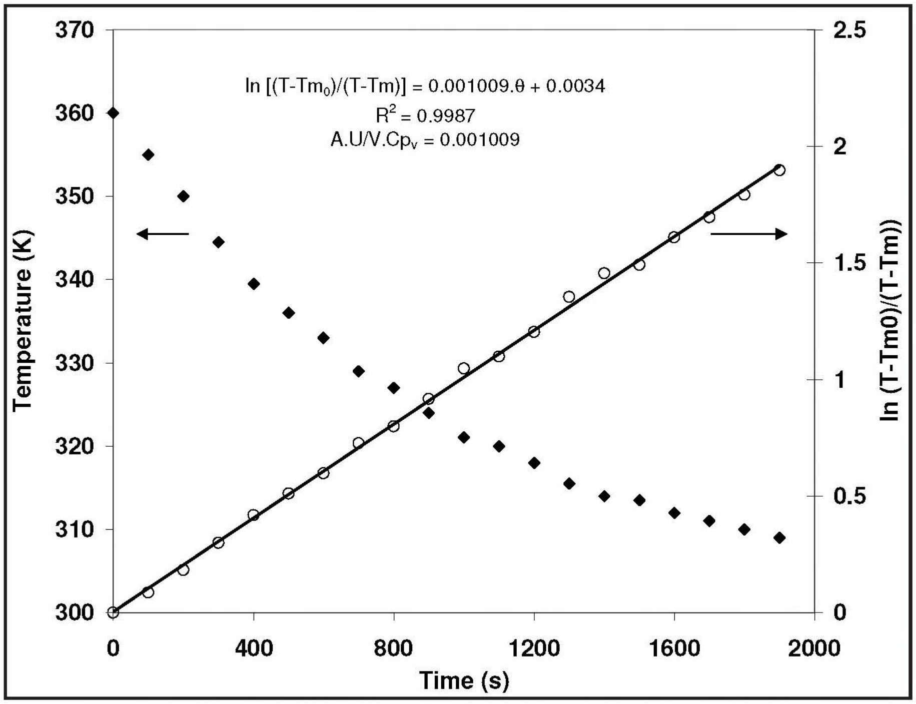

***Figure 2**. Determination of parameter α defined in Eq. (12).*

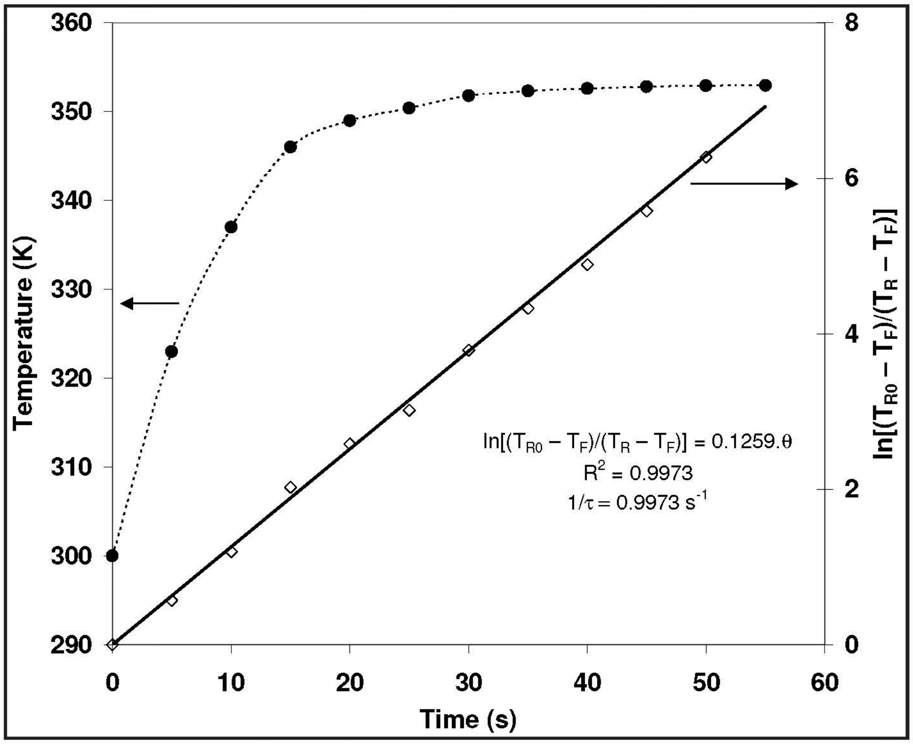

***Figure 3**. Determination of the thermometer time lag.*

of the parameters and/or to simulate the system. It is not the aim of this work to approach the wide field of mathematical and statistical methods employed in the correlation and modeling of experimental data, so only the results are shown as long as alumni are not compelled to use any particular software. The analysis of data presented in this paper was done using software with Episode (stiff) integrator, which includes the analytical calculus of the Jacobian matrix and a least square method (minimizing relative error) for the parameter adjustments.

Testing the predictive power of the model: Ice bath experience

An additional experiment to assess the usefulness of the model to predict the behavior of the system can be done by modifying the heat transfer scenario (*i.e.*, using an ice bath as external transfer medium). In this case the values of kinetics parameters (A and E) and the sensor time constant are taken as the previously determined ones, and the heat transfer parameter is separately determined in an individual cooling experience as described before (as heat exchange coefficient value is expected to change for the ice bath surrounding media) or estimated from temperature-time values for higher times. Typical results of such experiences are not shown here, but in Fig. 4 a good concordance can be seen between predicted and measured temperature vs. time profiles in this case, confirming the usefulness of the model for predictive purposes.

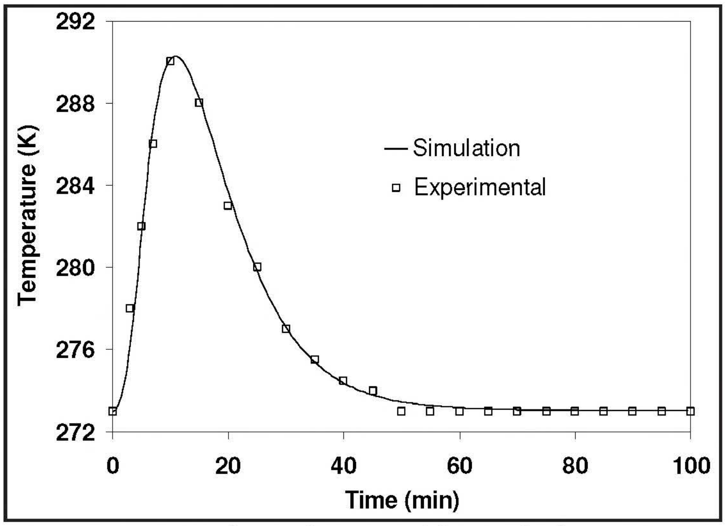

Figure 4. *Testing the predictive model in ice bath experience.*

CONCLUSIONS

Some very simple laboratory experiments can be inexpensively modified to obtain higher pedagogical output through a more open analysis and correlation of obtained data and some minor operative modifications, including concepts and methods that strictly pertain to another (but closely related) area of knowledge. Modeling and simulation, two fundamental tools in chemical engineering, should be used despite the modest quality of equipment and obtained data to illustrate important aspects of the formulation and validation of models, design of complementary experiences for estimation of parameters, and the utilization of current numerical analysis and statistical procedures and software. Rather surprisingly in this case, as long as only one variable is measured, the results of parameter estimation and simulation are good and constitute an additional stimulus for students.

NOMENCLATURE

A	Arrhenius preexponential factor [cm^3/mol^{-1}/s^{-1}]
A_t	Effective heat transfer area [cm^2]
C	Molar concentration [mol/cm^{-3}]
Cp_v	Volumetric heat capacity [cal/cm^{-3}/K^{-1}]
E	Activation energy [cal/mol^{-1}]
k	Kinetic constant [cm^3/mol^{-1}/s^{-1}]
r	Reaction rate [mol/cm^{-3}s^{-1}]
R	Gas constant [cal/mol^{-1}/K^{-1}]
T	Temperature of system, real [K]
t	Temperature of surrounding media [K]
T_0	Initial temperature [K]
T_F	Constant temperature of medium in Experiment #3 [K]
T_R	Digital thermometer temperature reading [K]
T_{R0}	Initial digital thermometer temperature reading [K]
U	Global heat transfer coefficient [cal/s^{-1}/cm^{-2}/K^{-1}]
V	Reactor volume [cm^3]
θ	Time [s]
τ	Thermometer time constant [s]
α	Parameter defined as A_t.U/V.Cp_v [s^{-1}]
ΔH_R	Enthalpy change of reaction [cal.mol^{-1}]

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TABLE 1
Comparison of Parameter Values

PARAMETER	VALUE OBTAINED MODEL I	VALUE OBTAINED MODEL II	VALUE OBTAINED INDEPENDENT EXPERIMENT	VALUE REPORTED IN THE LITERATURE
A	2.10^{10}	2.10^{10}	—	2.10^{10} - 6.85.10^{11}
E (Cal/mol)	8120	8238	—	8238-9200
U (KCal/s m^2 K)	0.0031	0.0035	0.0036	0.002-0.02
τ (s^{-1})	—	0.1259	0.1259	—

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