

INDIRECT MEASUREMENT OF REACTION RATE

R. D. WILLIAMS
University of Arizona
Tucson, Arizona

This paper describes an experiment which can be used to study the kinetics of chemical reactions which are accompanied by measurable heat effects. An indirect method of data collection takes advantage of the fact that the rate of reaction is proportional to the rate of energy release or absorption.

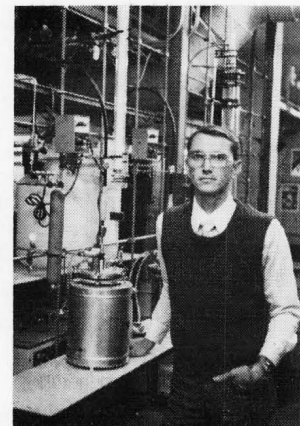
Laboratory experiments in chemical engineering curricula should be carefully selected according to the laboratory objective. Experiments which demonstrate several points are especially effective in the curriculum squeeze of today.

At the University of Arizona the undergraduate kinetics laboratory is used to give the student practical experience in the more important points covered theoretically in the lecture course the semester before.

The first three experiments of the lab are concerned with a demonstration of the differences in behavior of batch, continuous stirred and tubular reactors. The integral method of analysis is used in conjunction with isothermal batch kinetic data in order to determine the kinetics of the saponification reaction between ethyl acetate and sodium hydroxide. These kinetics are then used to predict behavior of the two continuous reactor types and these predictions are experimentally checked. The wet chemical method of data collection in these three experiments is tedious and by the end of the third the student is convinced that all kinetic determinations must be equally frustrating.

The fourth experiment was chosen in part for its comparative experimental simplicity. But more than this several important points from the theory course are well illustrated. These are enumerated below.

- An indirect data collection method is illustrated.
- An energy balance is required in addition to the material balance.
- The data cannot be conveniently analyzed by the integral method whereas the differential method can be used.
- Not only the kinetics, but also the stoichiometry and heat of reaction may be very simply determined.



Dick Williams received his undergraduate degree at Texas Tech University and his graduate degrees at Princeton University, all in Chemical Engineering. He has been at the University of Arizona since 1968 where his research has been involved primarily with chemical reaction engineering. Current research projects include design of a system to reduce automobile pollutants while increasing fuel economy and a study of hydrometallurgical leach recovery of minerals from their ores with emphasis on characterization of the underlying mechanisms involved.

This fourth experiment involves the determination, in an adiabatic-batch reactor, of the

TABLE 1: Possible Reactions between H_2O_2 and $Na_2S_2O_3$
 (From Reference 3)

Reaction	Reaction	v_A/v_B	theoretical $-dH_r/dt$ (cal/mole $Na_2S_2O_3$)
I	$2Na_2S_2O_3 + H_2O_2 \rightarrow Na_2S_2O_4 + 2NaOH$	0.5	39,000
II	$Na_2S_2O_3 + H_2O_2 \rightarrow Na_2S_2O_4 + H_2O$	1.00	41,400
III	$3Na_2S_2O_3 + 4H_2O_2 \rightarrow 2Na_2S_2O_6 + 2NaOH + 3H_2O$	1.33	122,500
IV	$Na_2S_2O_3 + 4H_2O_2 + 2NaOH \rightarrow 2Na_2SO_4 + 5H_2O$	4.00	210,000
V	$3Na_2S_2O_3 + 5H_2O_2 \rightarrow Na_2S_2O_6 + 2Na_2SO_4 + 5H_2O$	1.67	193,300
VI	$2Na_2S_2O_3 + 4H_2O_2 \rightarrow Na_2S_2O_6 + Na_2SO_4 + 4H_2O$	2.00	142,500
VII	$4NaOH + Na_2S_2O_6 + 4H_2O_2 \rightarrow 3Na_2SO_4 + 6H_2O$	----	-----

*stoichiometric ratio ($H_2O_2/Na_2S_2O_3$)

kinetics of the exothermic reaction between hydrogen peroxide and sodium thiosulfate. Glasser and Williams¹ have demonstrated a slightly more general technique using the acetic anhydride hydrolysis reaction. The former reaction has the pedagogical advantage of a non-obvious stoichiometry which can be experimentally determined. Several possible reactions between hydrogen peroxide and sodium thiosulfate are listed in Table 1.

Root and Schmitz² utilized this reaction in demonstrating reactor instability in an adiabatic loop reactor. Their analysis did not require a detailed knowledge of the kinetics. Cohen and Spencer³ have calorimetrically studied this system to obtain the kinetic details.

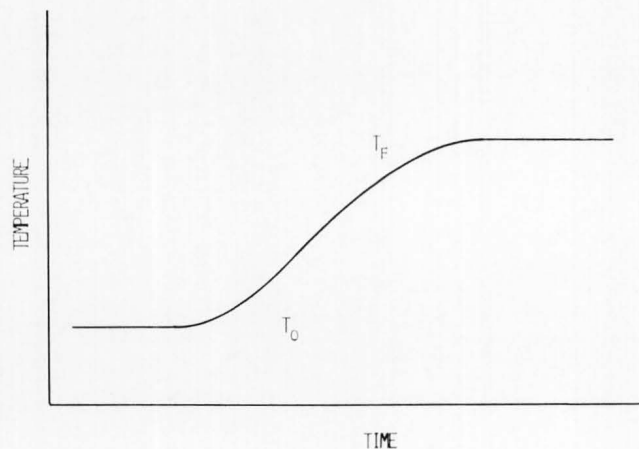


FIGURE 1: TYPICAL TEMPERATURE - TIME TRACE.

EXPERIMENTAL

The experimental apparatus consists of a 500 ml beaker, a magnetic stirrer, and a thermocouple-strip chart recorder arrangement. Volumes of two molar solutions of each of the reactants are mixed in the beaker and the temperature is recorded as the reaction progresses. An s-shaped curve such as shown in Figure 1 is obtained. If the total reaction mixture volume is held constant while varying the relative amounts of each reactant, then the temperature rise will go through a maximum when the reactants are mixed in their stoichiometric ratio. A graph of ΔT versus initial concentration ratio will exhibit this behavior. A typical result is shown in Figure 2. It can be seen

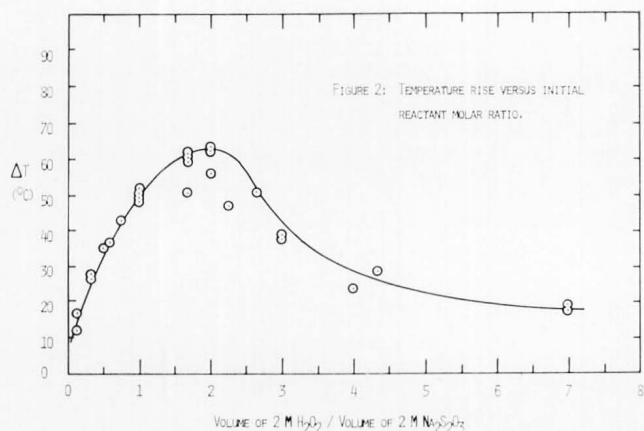


FIGURE 2: TEMPERATURE RISE VERSUS INITIAL REACTANT MOLAR RATIO.

An indirect method of data collection takes advantage of the fact that the rate of reaction is proportional to the rate of energy release or absorption.

that the maximum occurs near a reactant ratio of two implying that the major reaction occurring is VI in Table 1. A check on this result can be made by calculating the theoretical heat of reaction and comparing this value with values obtained from the experimental data using Equation 1. These results are given in Table 2.

$$\frac{\Delta H_R}{v_A} = \frac{\overline{\rho C} \Delta T}{a_0} \quad (1)$$

	v_A/v_B	$-\Delta H_r/v_B$ kcal/mole $\text{Na}_2\text{S}_2\text{O}_3$	E kcal/mole	k_0 liters/mole-sec
student	2	142 ± 7	18.7	7.33×10^{11}
literature (ref. 3)	2	142.5	18.28 ± .3	6.85×10^{11}

THEORETICAL

The kinetic data can be analyzed in light of the theoretical temperature-time relationship. The material and energy balances for an adiabatic, constant volume batch reactor are given below.

$$\frac{da}{dt} = v_A R \quad (2)$$

$$\overline{\rho C} \frac{dT}{dt} = (-\Delta H_R) R \quad (3)$$

These are subject to the initial conditions,

$$a(0) = a_0; T(0) = T_0.$$

Equation 2 can be divided by Equation 3 in order to eliminate the nonlinear rate term. Integration of this result gives a relationship between reactant concentration and temperature.

$$a = a_0 - \frac{\bar{\rho}C_p}{\Delta H_R / \nu_A} (T - T_0) \quad (4)$$

Assuming the reaction to be irreversible and first order with respect to each reactant the kinetic rate expression becomes,

$$R = k a b \quad (5)$$

where

$$b = b_0 + \frac{\nu_B}{\nu_A} (a - a_0) \quad (6)$$

or when reactants are initially present in the stoichiometric ratio,

$$b = \frac{\nu_B}{\nu_A} a. \quad (7)$$

Assuming Arrhenius temperature dependence for k , Equations 4, 5 and 7 can be inserted into Equation 3 to give a single nonlinear ordinary differential equation giving the temperature-time dependence,

$$\frac{dT}{dt} = \gamma (T_f - T)^2 e^{-E/R_g T} \quad (8)$$

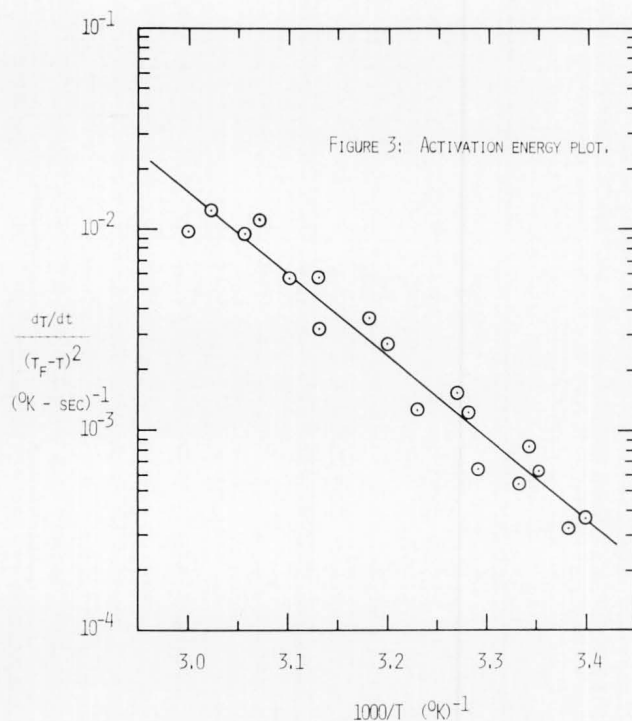
This suggests that a plot of $\log \left(\frac{dT/dt}{(T_f - T)^2} \right)$ versus

$1/T$ should give a straight line of slope $-E/R_g$ if the assumptions made with regard to the rate expression are correct. The pre-exponential factor can then be calculated from Equation 8. The temperature derivative is easy to determine in this experiment since a continuous temperature—time trace is obtained. Typical student results are plotted in Figure 3. As was the case in Figure 2 these data are from experiments run by several different groups on different days. Values of E and k_0 from Figure 3 are given in Table 2. \square

REFERENCES

1. Glasser, David and Williams, Don F., "The Study of Liquid-Phase Kinetics Using Temperature as a Measured Variable," *I&E.C. Fund.*, **10**, 516 (1971).
2. Root, R. B. and Schmitz, R. A. "An Experimental Study of Steady State Multiplicity in a Loop Reactor", *AIChE J.*, **15**, 670 (1969).
3. Cohen, W. C. and Spencer, J. L., "Determination of Chemical Kinetics by Calorimetry," *Chem. Engr. Prog.*, **58**, 40 (1962).

... the exothermic reaction between hydrogen peroxide and sodium thiosulfate has the pedagogical advantage of a non-obvious stoichiometry which can be experimentally determined.



NOMENCLATURE

a, b	reactant concentrations, moles/liter
C_p	solution mean heat capacity, calories/gm-°K
E	activation energy, kcal/mole
ΔH_R	heat of reaction for a given stoichiometry, kcal/mole
k	reaction rate constant, liter/mole-sec
k_0	pre-exponential factor, liter/mole-sec
R	reaction rate for a given stoichiometry, mole/liter-sec
R_g	gas constant, calories/mole-°K
t	time, sec
T	temperature, °K
ΔT	temperature rise, °K

Greek Letters

γ	a constant
ν	stoichiometric coefficient
ρ	solution density, gm/liter

Subscripts

A, B	denote different reactant species
O	denotes an initial condition
f	denotes a final value