Evaluation of Reaction Kinetics Constants from Calorimetric Data

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Information about the reaction kinetics of a chemical process is vital for both process safety and process optimization in the scale-up of batch and semibatch reactions. In process safety studies it is obviously important to ascertain the rates of heat and gas evolution under potential reaction conditions so that the adequacy of the plant cooling and venting capacity may be determined before carrying out chemical reactions on a large scale. Neither rapid nor very slow reactions usually cause problems since rapid reactions are normally controlled by the addition rate of a key reagent, and in very slow reactions, the rate of reaction and hence the heat (or gas) output is slow and easily controlled by reactor cooling. Intermediate reactions that have rates comparable with the desired addition rate or that are nonisothermal are more problematic and require some determination of the reaction heat evolution rate so that an appropriate reactor may be used. Reaction kinetics has several applications in the field of process optimization; these include the need to favor the desired reaction, minimize competing reactions, maximize yield and minimize cycle times.

Theory

The measurement made in a calorimetry experiment is related to the rate of reaction as expressed in the following equation (see appendix for symbol definitions):

\[ \frac{dQ}{dt} = \sum (Q_i \cdot d[R_i]) / dt \]

This heat output is usually integrated to obtain an overall heat output. This overall heat evolution is related to the extent of the reaction (degree of conversion). However, the relationship is only simple for straightforward reaction systems. With more complex systems it becomes difficult to unravel the contributions made by individual reactions. Nevertheless, it is possible to obtain important information about reaction kinetics from the results of a reaction calorimetry experiment. This paper deals with isothermal systems. Although methods do exist for determining reaction kinetic constants for nonisothermal systems, working isothermally reduces the complexity of the calculations since the temperature dependence of the reaction rate constants does not need to be taken into account. One of the significant advantages of using a reaction calorimeter for reaction kinetics work is the facility for close control of reaction mixture temperatures.

The way in which the rate of the heat evolution varies with the total heat evolved is dependent on the reaction kinetics. For simple reaction kinetic systems it is possible to derive an analytical expression for the relationship between the heat evolution rate and the total heat evolved. This may be illustrated by some models of reaction kinetic systems:

**Reaction (1):** \( A \rightarrow B \)
Rate of reaction = \( k[A] \)
\[ \frac{dQ}{dt} = kQ - kQ_t \]

**Reaction (2):** \( A \leftrightarrow B \)
\( k_1 \) forward, \( k_2 \) reverse
Rate of reaction = \((k_1[A]) - (k_2[B])\)
\[ \frac{dQ}{dt} = k_1 Q - (k_1 + k_2)Q_t \]

**Reaction (3):** \( A \rightarrow B \) \( k_1, Q_1 \)
\( A \rightarrow C \) \( k_2, Q_2 \)
\[ [B]_0, [C]_0 = 0 \]
Rate of reaction = \( k_1[A] + k_2[A] \)
\[ \frac{dQ}{dt} = k_1 Q_1 + k_2 Q_2 - (k_1 + k_2) Q_t \]

**Reaction (4):** \( A + B \rightarrow C \)
\[ [A]_0 < [B]_0 \]
Rate of reaction = \( k[A][B] \)
\[ \frac{dQ}{dt} = kQ[B]_0 - k([A]_0 + [B]_0)Q_t + k[A]_0 Q_t^2/Q \]
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**Reaction (5):** \( A + B \leftrightarrow C + D \)

\[ k_1 \text{ forward, } k_2 \text{ reverse} \]
\[ [A]_0 < [B]_0; [C]_0, [D]_0 = 0 \]
\[ \text{Rate of reaction} = k_1 [A][B] - k_2 [C][D] \]
\[ \frac{dQ}{dt} = k_1 Q [B]_0 - k_1 ([A]_0 + [B]_0)Q_t \]
\[ + [A]_0 Q_t^2 / Q(k_1 - k_2) \]

**Reaction (6):** \( A + B \leftrightarrow C \)

\[ k_1 \text{ forward, } k_2 \text{ reverse} \]
\[ [A]_0 < [B]_0; [C]_0 = 0 \]
\[ \text{Rate of reaction} = k_1 [A][B] - k_2 [C] \]
\[ \frac{dQ}{dt} = k_1 Q [B]_0 - (k_1 ([A]_0 + [B]_0) + k_2)Q_t \]
\[ + k_1 [A]_0 Q_t^2 / Q \]

**Examples**

**Reaction of benzyl chloride with sodium methoxide**

This reaction was carried out by the rapid addition of benzyl chloride to a solution of sodium methoxide in methanol. A graph of heat output rate against heat evolution was obtained (figure 1).

From the relationship between the heat output rate and the heat evolved, a reaction rate constant of \( 3.3 \times 10^{-4} \text{dm}^3\text{mol}^{-1}\text{s}^{-1} \) was obtained. Calculated values of heat output rate using this rate constant are also drawn on figure 1.

Using an isothermal technique reduces the number of variables involved and thus the resulting data are more likely to be reliable. To obtain information about the temperature dependence of the reaction parameters, it is necessary to repeat the experiments at a range of suitable temperatures.

**Experimental**

Some experimental considerations need to be noted in this type of reaction calorimetry work.

The reactions that are studied tend to be relatively slow and thus the heat output rate may be low, especially toward the end of the reaction. As a consequence, the method is susceptible to inaccuracies due to variation in ambient temperatures. For this reason, better results are obtained with a reasonably exothermic reaction. Experimental noise may also be more noticeable when the heat output rate is low, and this may be an additional source of error. Because of the protracted nature of the experi-

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**Figure 1: Heat evolution profile of benzyl chloride/sodium methoxide reaction.**
ment and the generally low heat output rates, calori-
metrics need to be done very carefully to avoid accumulative errors.

These considerations have an effect on the useful temperature range for the technique since the rate of reaction must be such as to give a heat output that falls between the limits of detectability and controllability.

When complex reaction kinetics are involved it becomes difficult or impossible to derive an analytical solution for the relationship between the heat output rate and the heat evolved. An example of this is the case of a pair of simultaneous reversible reactions:

\[
\begin{align*}
A & \leftrightarrow B \\
A & \leftrightarrow C
\end{align*}
\]

Rate of reaction = \(k_1[A] - k_2[B] + k_3[A] - k_4[C]\)

A plot of heat output rate against heat evolved for one example of this system is shown in figure 2.

A second example is the case of an autocatalytic reaction. In this case the rate of heat evolution is observed to increase as the reaction progresses (figure 3).

Figures 1-3 show that even though an analytical solution is not available, plotting the values of heat output rate against heat evolved does give some insight into the type of reaction involved. The plot obtained should be consistent with the predicted reaction mechanism and thus it may be used to eliminate some of the likely reaction pathways.

Reaction rate constants may be obtained readily from the simpler types of reaction systems by means of curve fitting and extracting the rate parameters from the expressions as given. Different systems can give similar results, and some independent check such as chemical analysis to identify a reversible reaction needs to be made.

\[
\begin{align*}
\text{Heat Evolution Rate} & \quad \text{Heat Evolved} \\
\text{Heat Evolution Rate} & \quad \text{Heat Evolved}
\end{align*}
\]
For a more complex reaction system, more elaborate techniques are required to establish a mechanism and to extract reaction rate constants. The observed data may be compared with those predicted by computer simulation of the proposed reaction mechanism using trial values of rate constants. By altering these (usually according to a standard optimization routine) it is possible to obtain a fit to the observed data and thus the reaction rate constants. However, a good fit to the experimental data is not conclusive proof of a reaction kinetic model and additional corroborative evidence is required. This would normally take the form of reagent and product concentrations obtained by analytical chemical means.

Appendix

\[ [N] = \text{concentration of species N, mol/dm}^3 \]
\[ [N]_0 = \text{initial concentration of species N} \]
\[ \frac{dQ}{dt} = \text{rate of heat evolution, W/mol} \]
\[ Q_t = \text{heat evolved at time t, J/mol} \]
\[ Q_n = \text{heat of reaction of nth reaction of scheme, J/mol} \]
\[ k_n = \text{reaction rate constant of nth reaction of scheme, s}^{-1} \text{ (1st order), dm}^3\text{mol}^{-1}\text{s}^{-1} \text{ (2nd order).} \]

Reaction of acetic anhydride with methanol

This reaction was carried out by the rapid addition of methanol to acetic anhydride in the absence of solvent. Figure 4 illustrates heat output rate plotted against heat evolved.

This shows that the uncatalyzed reaction between methanol and acetic anhydride follows somewhat complex reaction kinetics. From the forth of the graph in figure 4, it may be inferred that the reaction is either autocatalytic in nature or that it proceeds via an intermediate stage.

Conclusions

Reaction calorimetry may be used to obtain information about the kinetics of the reaction under study. With simple reaction systems it is possible to obtain values for the reaction kinetic constants.