

Lecture 7 Collection and Analysis of Experimental Data: Methods for Evaluating Kinetics

Goal of the lecture: To study the principles and methods of collecting, processing, and analyzing experimental data for determining kinetic parameters and evaluating reaction mechanisms.

Brief lecture notes: This lecture discusses the experimental foundation of chemical kinetics — how data are obtained, processed, and used to evaluate rate laws and mechanisms. It introduces the steps of kinetic data acquisition, including measurement of concentration, temperature, and pressure over time. The analysis methods covered include differential and integral techniques, graphical approaches, and nonlinear regression for rate constant estimation. Special attention is given to experimental accuracy, error analysis, and validation of kinetic models.

Main part

Understanding reaction kinetics requires reliable experimental data on the rate of reaction and the concentration changes of reactants and products over time. The data collection process involves monitoring key variables such as concentration, pressure, or absorbance, depending on the system's physical state. Kinetic data can be obtained using techniques like spectrophotometry, gas chromatography, calorimetry, or manometry.

Types of Kinetic Experiments

Kinetic experiments can be conducted under batch, semi-batch, or continuous conditions.

- Batch reactors provide concentration-time data directly.
- CSTRs provide steady-state data suitable for rate evaluation at fixed conditions.
- PFRs give conversion as a function of position, from which rates can be derived.

In batch experiments, data typically appear as a concentration–time curve $C_A(t)$, while for continuous systems, conversion–flow relationships $X_A(F_A)$ are used.

Methods for Evaluating Kinetic Parameters

Two major categories of data analysis are used: differential and integral methods.

(a) Differential Method

This approach requires calculation of the instantaneous rate from the slope of the concentration–time curve:

$$r_A = -\frac{dC_A}{dt}$$

By plotting r_A versus C_A , one can determine the order of the reaction and estimate the rate constant k .

This method is sensitive to experimental noise since numerical differentiation amplifies errors, thus requiring smooth data or curve fitting.

(b) Integral Method

The integral method uses the integrated form of the rate law. For an n -th order reaction:

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{-r_A} = t$$

For example:

- First-order reaction: $\ln \frac{C_{A0}}{C_A} = kt$
- Second-order reaction: $\frac{1}{C_A} - \frac{1}{C_{A0}} = kt$

Plotting these expressions allows the determination of k from the slope of the linear graph.

Regression and Model Fitting

When reactions are complex or involve multiple parameters, statistical methods such as nonlinear regression are applied. The experimental data are fitted to a proposed rate equation $r = kf(C, T)$, and the optimal parameters are obtained by minimizing the sum of squared residuals:

$$S = \sum_i (r_{exp,i} - r_{calc,i})^2$$

Error and Sensitivity Analysis

Accuracy in kinetic data depends on measurement precision, sampling frequency, and temperature control. The propagation of error should be considered, especially for derived quantities such as rate or activation energy. Sensitivity analysis evaluates how uncertainties in measured variables affect the estimated kinetic constants.

Data Representation and Visualization

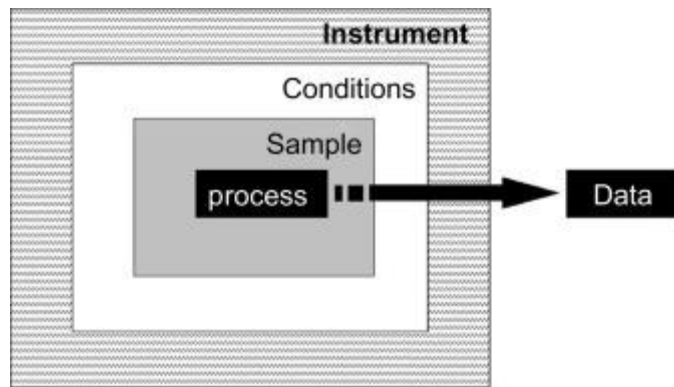
Graphical representation helps validate reaction models. Typical plots include:

- C_A vs. t : raw experimental data
 - $\ln C_A$ vs. t : test for first-order kinetics
 - $1/C_A$ vs. t : test for second-order kinetics
- Modern software (e.g., Origin, MATLAB) is used for data fitting and parameter optimization.

Table 1. Comparison of Methods for Kinetic Data Analysis

Method	Principle	Advantages	Limitations	Typical Use
Differential	Derivative of $C_A(t)$	Direct relation to rate	Sensitive to noise	Fast reactions
Integral	Integration of rate law	Noise resistant	Requires assumed rate law	Simple systems
Graphical	Linearization of data	Easy visualization	Limited precision	Initial analysis
Regression	Curve fitting of data	High accuracy	Computationally intensive	Complex kinetics

Figure 1. Example of Kinetic Data Analysis



Questions for Self-Control

1. What are the main differences between differential and integral methods of kinetic data analysis?
2. How can experimental errors influence the estimation of the rate constant?
3. What are the advantages of regression analysis over graphical methods?
4. How does the choice of reactor type affect the collection of kinetic data?
5. What parameters are essential to control during kinetic experiments?

Literature

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