15.   KINETIC METHODS OF ANALYSIS

15.1 Introduction

This chapter contains a section for the general terms and definitions of kinetic methods as used in analytical chemistry. It will be extended later with sections specifically on catalytic and enzymatic methods.

15.2 General terms and definitions

Activated complex

Those assemblies of atoms which correspond to an arbitrary small region near the col of a potential-energy surface. It can also be defined as being related to a small region close to the position of maximum standard Gibbs energy along the reaction path. The state of the activated complex can be called the *transition state*.

Activation, activator

A substance, other than the catalyst or one of the substrates, that increases the rate of a catalysed reaction without itself being consumed; the process is called *activation*. An activator of an enzyme-catalysed reaction may be called an *enzyme activator*, if it acts by binding to the enzyme.

Autocatalysis, autocatalyst

If a reaction is catalysed by one of its products, the product is known as an *autocatalyst* and the process is known as *autocatalysis*.

Catalysis

The phenomenon in which the addition of another material, called a *catalyst*, augments the rate of a chemical reaction without itself being consumed.

Catalyst

A catalyst is a substance that increases the rate of the reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called *catalysis*. This definition is equivalent to the statement that the catalyst does not enter into the overall

reaction; it is both a reactant and a product of the reaction. Catalysis can be subdivided into *homogeneous catalysis*, in which only one phase is involved, and *heterogeneous catalysis*, in which the reaction takes place at an interface between phases.

Catalytic method

A kinetic method which utilizes a catalysed reaction for analysis.

Catalymetric titration

A titration process, which involves the catalyst, where the end-point is detected by the sudden increase or decrease of the rate of a reaction.

Chain reaction

A reaction in which one or more reactive *reaction intermediates* (frequently radicals) are continuously regenerated, usually through a repetitive cycle of elementary steps (the propagation steps).

Composite (complex, stepwise) reaction

A chemical reaction for which the expression of the rate of disappearance of a reactant (or rate of appearance of a product) involves rate constants of more than a single elementary reaction. Examples are *opposing reactions* (where rate constants of two opposed chemical reactions are involved), *parallel reactions* (for which the rate of disappearance of any product is governed by the rate constants relating to several simultaneous reactions to form different respective products from a single set of reactants) and *stepwise reactions*.

Consecutive reaction

Reactions occurring in a sequence, such as

$$A \rightarrow X \rightarrow Y \rightarrow Z$$
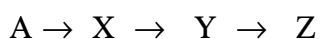
are known as consecutive reactions, and the overall process is said to occur by *consecutive steps*.

Continuous addition method

A mode of measurement in a kinetic method of analysis, in which the response curve is

obtained by continuously adding the reagent at a constant rate to the sample solution.

Differential reaction rate method

A mode of measurement in kinetic methods of analysis, in which a multicomponent determination is based on the different rates at which two or more species interact with a common reagent.

Elementary reaction

A reaction in which no reaction intermediates have been detected, or need to be postulated in order to describe the chemical reaction on a molecular scale. Until evidence to the contrary is discovered, an elementary reaction is assumed to occur in a single step and to pass through a single transition state.

Energy of activation

An operationally defined quantity expressing the dependence of a rate constant on temperature according to

$$E_a = RT^2(\partial \ln k/\partial T)_p$$

as derived from the *Arrhenius equation*,

$$k = A \exp[-E_a/(RT)]$$

where A is termed the *pre-exponential factor*.

Enthalpy of activation

The standard enthalpy difference between the transition state and the ground state of the reactants at the same temperature and pressure. It is related to the temperature coefficient of the rate constant according to the equation:

$$\Delta^{\ddagger}H = RT^2(\ln k/T)_p - RT = E_a - RT = -R(\ln(k/T)/(1/T))_p$$

where E_a is the energy of activation, provided that the rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g. mol dm^{-3}, measured at fixed temperature and pressure).

Entropy of activation

The standard entropy difference between the transition state and the ground state of the reactants, at the same temperature and pressure. It is related to the Gibbs energy of activation and enthalpy of activation through the equations

$$\Delta^{\ddagger}S = (\Delta^{\ddagger}H - \Delta^{\ddagger}G)/T = \Delta^{\ddagger}H - R\ln(k_B/h) + R\ln(k/T)$$

provided that the rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g. mol dm^{-3}, measured at fixed temperature and pressure). Here k_B is the Boltzmann constant, h is the Planck constant and R is the gas constant.

Enzyme

A protein that acts as a catalyst.

Extent of a reaction

ξ is defined by

$$d\xi = v_B^{-1}dn_B$$

where n_B is the amount and v_B the stoichiometric number of the substance B. When a reaction has time-independent stoichiometry (i.e. the stoichiometric equation is obeyed throughout the course of the reaction), it is possible to define ξ by

$$\xi = (n_i - n_{i,0})/v_i$$

where $n_{i,0}$ is the initial amount of the substance i and n_i is the amount at any time. v_i is the stoichiometric number for the substance i.

Fixed concentration method

A mode of measurement in a kinetic method of analysis, in which the period of time, required to bring about the same predetermined change in he concentration of a reactant or product, is measured. The use of the term "variable time method" is not recommended.

Fixed time method

A mode of measurement in a kinetic method of analysis, in which the change of a parameter, related to the concentration of a reactant or product, is measured over a

predetermined time interval.

Gibbs (free) energy of activation

The standard Gibbs energy difference between the transition state of a reaction (either an elementary reaction or a stepwise reaction) and the ground state of the reactants. It is calculated from the experimental rate constant k via the convential form of the absolute rate equation:

$$\Delta^{\ddagger}G = RT(\ln k_B/h - \ln k/T)$$

where k_B is the Boltzmann constant, h is the Planck constant and R is the gas constant.

Indicator reaction

A reaction which follows the (slower) reaction of kinetic interest, so as to provide means of monitoring the formation of a reaction product (indicator substance). This reaction is referred to as the *indicator reaction*.

Induced reaction, inductor

A reaction, which occurs or is accelerated only, if another reaction is simultaneously occurring in the same system, is called an *induced reaction*. The substance, which causes an induced reaction, is termed *inductor*. The inductor, unlike the *catalyst*, is used up irreversibly during the process.

Induction period

A period of a time which elapses between the start of the reaction and the formation of a product.

Inhibition, inhibitor

A substance that diminishes the rate of a chemical reaction; the process is called *inhibition*. Inhibitors are sometime called negative catalysts, but since the action of an inhibitor is fundamentally different from that of a catalyst, this terminology is discouraged. In contrast to a catalyst, an inhibitor may be consumed during the course of a reaction.

In enzyme-catalysed reactions an inhibitor frequently acts by binding to the enzyme, in which case it may be called an *enzyme inhibitor*.

Initial rate method

A mode of measurement in a kinetic method of analysis, in which the initial reaction rate is determined (usually by the slope method) and utilized for the measurement of concentration.

Kinetic method of analysis

An analytical method in which the rate of a reaction or a related quantity is measured and utilized to determine concentrations.

Landolt reaction

A slow chemical reaction, in which the formation of a product is delayed by a suitable reagent added for the purpose.

Landolt reaction method

A special form of the fixed concentration method, utilizing Landolt reactions to measure concentrations.

Molecularity of a reaction

The number of molecular entities (atoms, radicals, ins, etc.) that are involved in the microscopic chemical event constituting an elementary reaction. (For reactions in solution this number is always taken to exclude molecular entities that form part of a medium and which are involved solely by virtue of their solvation of solutes.) A reaction with a molecularity of one is called *unimolecular*, one with the molecularity of two *bimolecular* and of three *termolecular*. The molecularity of a reaction is also the number of reactant particles present in the transition state. The term molecularity should not be applied to a composite reaction, even if there is a clearly identified rate-determining step.

Opposing reactions

Composite reactions, occurring in forward and reverse directions, like

$$A + B \rightleftharpoons Z$$

Order of reaction

If the rate of reaction (v) for any reaction can be expressed by an empirical differential rate equation (or *rate law*) which contains a factor of the form $k[A]^\alpha[B]^\beta$ (expressing in full the dependence of the rate of the reaction on the concentrations [A], [B]…) where α and β are constant exponents (independent of concentration and time) and k is a constants, then the reaction is said to be of order α with respect to A, of order β with respect to B…, and of (total or overall) order $n = (\alpha + \beta + …)$.

The exponents α, β… can be positive or negative integral or rational, non-integral numbers. They are the reaction orders with respect to A, B,… and are sometimes called *partial orders* of the reaction. The proportionality factor k is called the (n-th order) *rate coefficient*. Rate coefficients referring to elementary reactions are called *rate constants*.

Preexponential factor

See *Energy of activation*.

Quenching

Stopping the course of a chemical reaction by chemical or physical means.

Rate coefficient, rate constant

See *Order of reaction*.

Reaction time

The period of a time that elapses between the start of the reaction and the attainment of a given extent of a reaction.

Relaxation, relaxation time and related terms

If a system is disturbed from its state of equilibrium it *relaxes* to that state; the branch of kinetics concerned with this effect is known as *relaxation kinetics*. Techniques include *temperature jump* (T-jump) and *pressure jump*, in which temperature and pressure respectively are changed very rapidly and the relaxation studied. The relaxation time, τ, is defined as the time it takes for the extent of the reaction to change by 1-(1/e) of the total change during the relaxation process (e is the base of natural logarithms).

Signal-stat method

A mode of measurement in a kinetic method of analysis, in which the concentration of a substance is determined from the rate of addition of a reagent, as required to maintain a constant measured signal (e.g. pH).

Simultaneous comparison method

A mode of measurement in a kinetic method of analysis, in which reactions of unknown samples and standards are started and monitored simultaneously.

Simultaneous reactions

Composite reactions, in which processes like

$$A \rightarrow Y \quad \text{and} \quad B \rightarrow Z$$

occur in parallel, can be called *simultaneous* or *parallel reactions*. Sometimes there is competition involved, like in the scheme

$$A + B \rightarrow Y \quad \text{and} \quad A + C \rightarrow Z$$

where B and C compete with one another for A.

Slope method (tangent method)

A mode of measurement in a kinetic method of analysis, in which the slope of the response curve at a selected point is measured and related to concentration.

Steady state

A reactive reaction intermediate reaches a steady state in a reaction sequence when the processes leading to its formation and those resulting in its removal are nearly in balance, so that the rate of its change of concentration is negligible compared with the rate of change of concentration of other species involved.

To a good approximation

$$d[X]/dt = 0$$

where *X* is said to be in *steady state*. The use of this approximation to obtain an overall rate expression is known as the *steady state approximation* or steady state treatment.

Stopped flow method

A mode of measurement in kinetic methods of analysis, utilising a way of mixing sample and reagents to obtain the response curve for a fast reaction.

Substrate

A chemical species of particular interest, the reaction of which with some other chemical reagent is under observation (e.g., a compound that is transformed under the influence of a catalyst).

Transition state

See *Activated complex*.

Uncatalysed reaction

A reaction proceeding without the participation of the catalyst.

15.3 References

Relevant papers for section 15.2:

G.Svehla: Nomenclature of kinetic methods of analysis
PAC 65 (10) 2291-2298 (1993)

H.Müller: Catalytic methods of analysis: characterization, classification and methodology.
PAC 67 (4) 601-613 (1995)