9

Reaction kinetics

9.4 Elementary reactions

- An elementary reaction is a single step reaction involving one or two molecules or atoms.
- For a general reaction $aA + bB \rightarrow pP + qQ$

$$\text{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{p}\frac{d[P]}{dt} = \frac{1}{q}\frac{d[Q]}{dt}$$

- The rate equation for an elementary reaction can be written directly from the chemical equation for the reaction.
- A rate equation in which the rate of consumption of a reactant, or the rate of formation of a product, is written as a differential is called a differential rate equation.
- An integrated rate equation gives the concentration of a reactant as a function of time.
- The half life of a reactant is the time taken for its concentration to fall to half its initial value.
- Table 9.2 summarizes the equations for the first order, second order, and pseudo-first order elementary reactions that you have met in Section 9.4.

Table 9.2 A summary of equations for elementary reactions

Type of reaction	Order of reaction	Differential rate equation	Integrated rate equation	Half life, $t_{1/2}$
$A \rightarrow$ products	First order	$-\dfrac{d[A]}{dt} = k[A]$	$\ln[A]_t = \ln[A]_0 - kt$	$\dfrac{\ln 2}{k}$
$A + A \rightarrow$ products	Second order	$-\dfrac{d[A]}{dt} = 2k[A]^2$	$\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + 2kt$	$\dfrac{1}{2k[A]_0}$
$A + B \rightarrow$ products where $[A] \ll [B]$	Pseudo-first order	$-\dfrac{d[A]}{dt} = k'[A]$ where $k' = k[B]_0$	$\ln[A]_t = \ln[A]_0 - k't$ $= \ln[A]_0 - kt[B]_0$	$\dfrac{\ln 2}{k'} = \dfrac{\ln 2}{k[B]_0}$

? For practice questions on the topics in Sections 9.1–9.4, see questions 2, 3, 6, 8–13, and 15–17 at the end of this chapter (pp.444–445).

9.5 Complex reactions: experimental methods

- A complex reaction takes place by a series of elementary reactions.
- The overall rate equation of a complex reaction cannot be predicted from the stoichiometric equation. It *must* be determined experimentally.
- For the complex reaction, $aA + bB \rightarrow$ products:

$$\text{rate of reaction} = k[A]^m[B]^n$$

where k is the overall rate constant, and m and n are the orders with respect to A and B, respectively. The overall order of the reaction is $m + n$.

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- The rate of a reaction can also depend on the concentration of a substance that does not appear as a reactant in the chemical equation, such as a catalyst.

- Orders of complex reactions often have values of 0, 1, or 2, but sometimes can take higher, or fractional, values.

- For reactions involving more than one reactant, the effect of the concentration of each reactant on the rate of reaction is studied using the isolation technique for each reactant in turn.

- Experimental methods for investigating the kinetics of complex reactions include: drawing tangents to a concentration–time curve; the initial rate method; using integrated rate equations; using half lives.

- Integrated rate equations provide the most accurate and reliable method for determining reaction orders and rate constants. Table 9.3 summarizes the characteristics for reaction orders 0, 1, and 2.

Table 9.3 Using integrated rate equations to study complex reactions

	Order		
	0	**1**	**2**
Rate equation	Rate $= k'$	Rate $= k'[A]$	Rate $= k'[A]^2$
Integrated rate equation	$[A]_t = [A]_0 - k't$	$\ln[A]_t = \ln[A]_0 - k't$	$\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + 2k't$ *
Plot of $[A]$ vs. t	**Straight line**	Curve	Curve
Plot of $\ln[A]$ vs. t	Curve	**Straight line**	Curve
Plot of $\dfrac{1}{[A]}$ vs. t	Curve	Curve	**Straight line**
Half life, $t_{1/2}$	Not constant	**Constant**	Not constant

* The multiplication factor before k' depends on the stoichiometry of the reaction.

? For practice questions on these topics, see questions 5, 7, 14, 18 and 28 at the end of this chapter (pp.444–446).

9.6 Complex reactions: reaction mechanisms

- The series of elementary steps that make up a complex reaction is known as the mechanism of the reaction.

- A valid mechanism must correctly predict the experimentally determined rate equation and be consistent with all related kinetic experimental data and stereochemical observations. The sum of the elementary steps must give the overall equation for the reaction.

- Kinetic studies are the main source of evidence for the mechanism of many organic reactions.

- The rate equation for the slow rate-determining step is the rate equation for the overall reaction.

- For an equilibrium reaction where the forward and reverse reactions are elementary processes, the ratio of the rate constants for the forward and reverse reactions is equal to the equilibrium constant for the reaction.

$$\frac{k_1}{k_{-1}} = K_c$$

- The steady state approximation is used to simplify analysis of the kinetics of consecutive reactions involving a highly reactive intermediate, B. It is assumed that the concentration of B is very small, and that the rate of change of the concentration of B is zero.

? For practice questions on these topics, see questions 23–26, 29, and 30 at the end of this chapter (pp.445–446).

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9.7   Effect of temperature on the rate of a reaction

- The way the rate constant varies with temperature is described by the Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

- A plot of $\ln k$ against $1/T$ is a straight line with a gradient $-E_a/R$.

- The activation energy, E_a, is the energy barrier reactants must overcome in order to form products.

- The rate constant of a reaction increases with temperature because a greater fraction of reactant molecules has enough energy to pass over the energy barrier.

- An energy profile shows how the potential energy of the system changes as the reaction progresses.

? For practice questions on these topics, see questions 1, and 19–22 at the end of this chapter (p.443 and p.445).

9.8   Theories of reactions

- The molecularity of a reaction is the number of reactant molecules involved in forming the transition state.

- Collision theory is most useful for bimolecular reactions in the gas phase. It relates the A factor in the Arrhenius equation to the frequency of collisions taking place with the correct orientation for reaction.

- Transition state theory shows that the rate constant, k, depends on the Gibbs energy of activation, $\Delta^{\ddagger}G$. The A factor is related to $\Delta^{\ddagger}S$ and the activation energy, E_a, to $\Delta^{\ddagger}H$.

- Gibbs energy profiles are used extensively in organic chemistry and biochemistry to illustrate the mechanisms of reactions.

? For practice questions on these topics, see questions 4, 27, and 30 at the end of this chapter (pp.444–447).

9.9   Catalysis

- A catalyst increases the rate of a chemical reaction without being consumed in the reaction.

- Catalysts act by providing an alternative pathway for reaction in which the rate-determining step has a lower Gibbs energy of activation than the uncatalysed reaction.

- The Michaelis–Menten equation is used to analyse the kinetics of enzyme-catalysed reactions.

? For a practice question on these topics, see question 31 at the end of this chapter (p.447).

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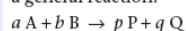UNIVERSITY PRESS

» Concept review

By the end of this chapter, you should be able to do the following.

- Understand what is meant by the rate of a reaction.

- Write a differential for the rate in terms of consumption of a reactant or formation of a product.

- Be aware of the different techniques used to monitor the progress of a reaction.

- Write the rate equation for an elementary reaction from the stoichiometric chemical equation and understand the meaning of the terms order and rate constant.

- Understand that the mechanism of a complex reaction involves a series of elementary reactions and that the rate equation must be determined experimentally.

- Describe and use a range of methods for investigating the kinetics of a reaction, including the isolation technique (when there is more than one reactant), drawing tangents to a plot of concentration against time, measuring initial rates, and using integrated rate equations and half lives.

- Explain how kinetic studies can be used as evidence for organic reaction mechanisms.

- Explain why some reactions show zero order kinetics.

- Explain the kinetics of a series of reactions using the idea of pre-equilibrium and the steady state approximation.

- Explain the effect of temperature on the rate of a reaction.

- Understand what is meant by the molecularity of an elementary reaction.

- Be familiar with the outlines of collision theory and transition state theory and their importance.

- Draw and interpret Gibbs energy profiles for reactions.

- Explain how a catalyst speeds up a reaction and understand the difference between heterogeneous and homogeneous catalysis.

- Understand the Michaelis–Menten mechanism for an enzyme-catalysed reaction, and use a Lineweaver–Burk plot to analyse experimental data.

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⇄ Key equations

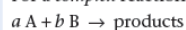|		
Definition of rate of reaction for a general reaction: $aA + bB \rightarrow pP + qQ$	Rate of reaction $= -\dfrac{1}{a}\dfrac{d[A]}{dt} = -\dfrac{1}{b}\dfrac{d[B]}{dt} = \dfrac{1}{p}\dfrac{d[P]}{dt} = \dfrac{1}{q}\dfrac{d[Q]}{dt}$	(9.4)
For an *elementary* reaction: $aA + bB \rightarrow$ products	Rate of reaction $= k[A]^a[B]^b$ where k is the rate constant, and the stoichiometric coefficients in the chemical equation, a and b, are the orders with respect to A and B, respectively. The overall order is $a + b$.	(9.5)
For a *complex* reaction: $aA + bB \rightarrow$ products	Rate of reaction $= k[A]^m[B]^n$ where k is the overall rate constant, and m and n are the orders with respect to A and B, respectively. The overall order is $m + n$.	(9.11)
Reaction mechanisms of complex reactions For a reversible *elementary* reaction:	$\dfrac{k_1}{k_{-1}} = K_c$	(9.14)
The steady state approximation for a reactive intermediate X:	$\dfrac{d[X]}{dt} =$ (rate of formation of X – rate of consumption of X) $= 0$	(9.15)
The Arrhenius equation	$k = Ae^{-\frac{E_a}{RT}}$	(9.24a)
	$\ln k = \ln A - \dfrac{E_a}{R}\left(\dfrac{1}{T}\right)$	(9.24b)
	$\ln k_2 - \ln k_1 = \ln\dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$	(9.25)
Michaelis–Menten equation	Rate of an enzyme-catalysed reaction $= \dfrac{k_2[E]_0[S]}{[S]+K_M}$ where $K_M = \dfrac{k_{-1}+k_2}{k_1}$	(9.31)

Table 9.2 A summary of equations for elementary reactions

Type of reaction	Order of reaction	Differential rate equation	Integrated rate equation	Half life, $t_{1/2}$
A → products	First order	$-\dfrac{d[A]}{dt} = k[A]$	$\ln[A]_t = \ln[A]_0 - kt$	$\dfrac{\ln 2}{k}$
A + A → products	Second order	$-\dfrac{d[A]}{dt} = 2k[A]^2$	$\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + 2kt$	$\dfrac{1}{2k[A]_0}$
A + B → products where [A] <<[B]	Pseudo-first order	$-\dfrac{d[A]}{dt} = k'[A]$ where $k' = k[B]_0$	$\ln[A]_t = \ln[A]_0 - k't$ $= \ln[A]_0 - kt[B]_0$	$\dfrac{\ln 2}{k'} = \dfrac{\ln 2}{k[B]_0}$

Table 9.3 Using integrated rate equations to study complex reactions **

	Order		
	0	**1**	**2**
Rate equation	Rate $= k'$	Rate $= k'[A]$	Rate $= k'[A]_2$
Integrated rate equation	$[A]_t = [A]_0 - k't$	$\ln[A]_t = \ln[A]_0 - k't$	$\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + 2k't$ *
Plot of [A] vs. t	**Straight line**	Curve	Curve
Plot of ln[A] vs. t	Curve	**Straight line**	Curve
Plot of $\dfrac{1}{[A]}$ vs. t	Curve	Curve	**Straight line**
Half life, $t_{1/2}$	Not constant	**Constant**	Not constant

* The multiplication factor before k' depends on the stoichiometry of the reaction.
** The order of a complex reaction may be higher than 2 or have a fractional value.

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