

Lecture Contents

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Empirical chemical kinetics

22.1 Experimental techniques

(i) The first step in kinetic analysis of reactions are to establish the stoichiometry of the reaction and also identify any side reactions. Then, the basic data of chemical kinetics are the concentrations of reactants and products at different times after a reaction (normally, at constant T)

(a) Monitoring the progress of a reaction

(b) Application of the techniques



22.2 The rates of reactions

The reaction rates depend on the composition and the temperature.

(a) The definition of rate

For a reaction : $A + 2B \rightarrow 3C + D$

where, $[J]$: the molar concentration of J : $[J]$

$d[R] / dt$: the rate of consumption (the reactants) for (-) slope

$d[P] / dt$: the rate of formation (the products) for (+) slope

$$\frac{d[D]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt}$$

Define the unique **rate of reaction**, $U = \frac{d\xi}{Vdt}$ the rate change of the extent of reaction (ξ)

Since $v_J \xi = n_J - n_{J,0}$ (the change in ξ is related to the change in the amount of each substance by $v_J d\xi = dn_J$),

$$U = \frac{1}{v_J} \frac{dn_J}{Vdt} \quad \text{where } v_J : (-) \text{ for reactants and } (+) \text{ for products}$$

$$U = \frac{1}{v_J} \frac{d[J]}{dt} \quad [\text{mol/L}\cdot\text{s}] \text{ for a homogeneous reaction}$$

$$U = \frac{1}{v_J} \frac{d\sigma_J}{dt} \quad \begin{array}{l} \text{Surface density of J} \\ [\text{mol/m}^2\cdot\text{s}] \text{ for a heterogeneous reaction} \end{array}$$

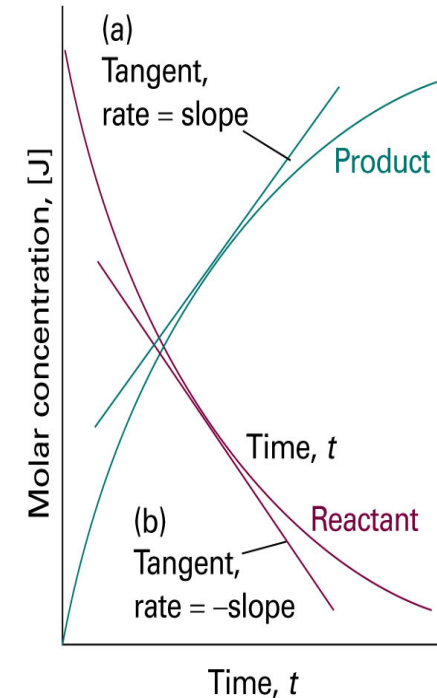


Fig. 22.3 The definition of (instantaneous) rate as the slope of the tangent drawn to the curve showing the variation of concentration with time. For negative slopes, the sign is changed when reporting the rate, so all reaction rates are positive.



22.2 The rates of reactions

(b) Rate laws and rate constants

Most probable assumption : Reaction rate $\nu \propto$ Concentrations of the reactants

$\nu = k[A][B]$ where k is the rate constant which is independent of concentration but depends on T

The rate law of the reaction : Experimentally determined equation of this kind

$$\nu = f([A],[B],K)$$

For a homogeneous gas-phase reaction ($p_i = RT[A]$), more convenient using partial pressure

$$\nu = f(p_A, p_B, K)$$

The rate law of the reaction is determined experimentally (cannot be inferred from the chemical equation)

Why? For instance, $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$ $\nu = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]}$ Very complicated!!!



22.2 The rates of reactions

(c) Reaction order

For many reactions,

$$v = k[A]^a[B]^b \quad \text{where } a, b : \text{ the orders of a reaction}$$

Overall reaction order = $a + b + \dots$

$$v = k[A][B] : \text{ 1st order in A, 1st in B but 2nd order overall}$$

$$\text{For other many gas-phase reactions, } v = k[A]^{1/2}[B]$$

: 1/2 order in A, 1st-order in B and 3/2 order overall

For some reactions, zero-order rate law

: independent of the concentration of the reactant (only heterogeneous reactions)

$$v = k \text{ for a catalytic decomposition of } \text{PH}_3 \text{ on hot tungsten at high } P$$

: PH_3 decomposes at a constant rate (independent of time : a steady state process)

If a rate law is not of the form $v = k[A]^a[B]^b \dots$

No overall order and no even definite orders with respect to each participant

ex)
$$v = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]}$$
 1st order in H_2 , an indefinite order with respect to both Br_2 and HBr
no overall order



22.2 The rates of reactions

(d) The determination of the rate laws

The isolation method : The concentration of all the reactants except one are in large excess

If B is in large excess, it can be assumed to remain constant during reaction

Ex) For $v = k[A][B]$, $v = k'[A]$ $k' = k[B]_0$ ($\because [B] \approx [B]_0$) : **pseudo first-order rate law**

Then, the dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn \rightarrow constructing the overall rate law

The method of initial rates

Often used in conjunction with the isolation method

- Measurement of the reaction rate at the beginning of the reaction
for several different concentration of reactants

ex) the rate law for a reaction with A is $v = k[A]^a$ with the initial rate of $v_0 = k[A]_0^a$

Then, $\log v_0 = \log k + a \log[A]_0$



22.2 The rates of reactions

For many initial concentrations, plot the curves of $\log v_0$ vs $\log[A]_0$

And determine its slope = the constant a

ex) $2\text{I}(\text{g}) + \text{Ar}(\text{g}) \rightarrow \text{I}_2(\text{g}) + \text{Ar}(\text{g}) : v_0 = k[\text{I}]_0^2[\text{Ar}]_0$ (see Fig. 22.4)

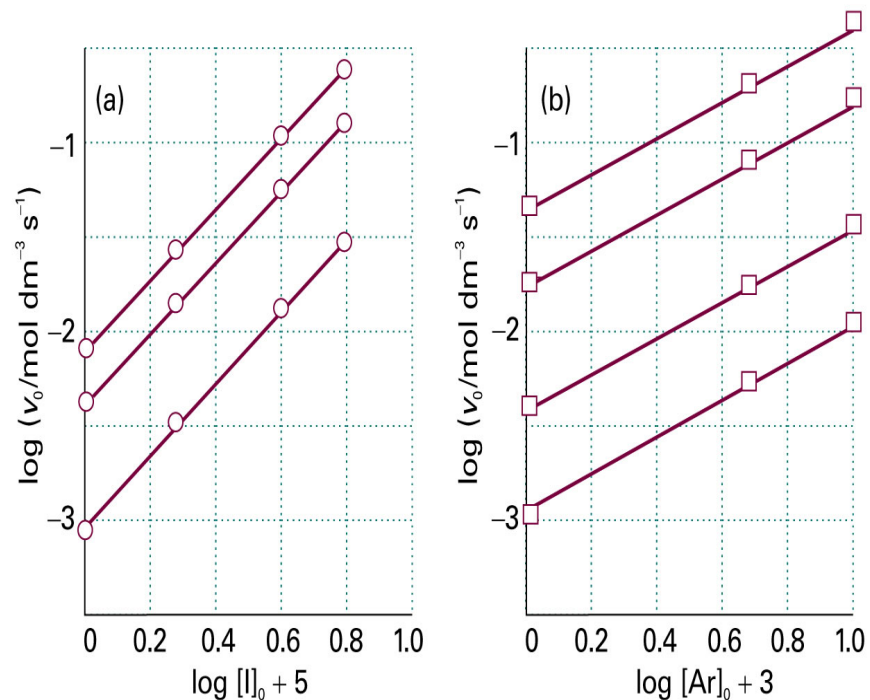


Fig. 22.4 The plot of $\log v_0$ against (a) $\log [\text{I}]_0$ for a given $[\text{Ar}]_0$, and (b) $\log [\text{Ar}]_0$ for a given $[\text{I}]_0$.



22.3 Integrated rate laws

(a) First-order reactions

The first-order rate law for the consumption of a reactant A,

$$\frac{d[A]}{dt} = -k[A] \rightarrow \ln\left(\frac{[A]}{[A]_0}\right) = -kt \quad [A] = [A]_0 e^{-kt} \quad \text{integrated rate law}$$

Justification 22.1

$$\frac{d[A]}{dt} = -k[A] \rightarrow \frac{d[A]}{[A]} = -k dt$$

Concentration of A = $[A]_0$ at $t = 0$ and $[A]$ at $t > 0$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt \rightarrow \ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

In the plot of $\ln([A]/[A]_0)$ vs t

a slope = $-k$ (see Table 22.1)

For $[A] = [A]_0 e^{-kt}$ (see Fig. 22.5)

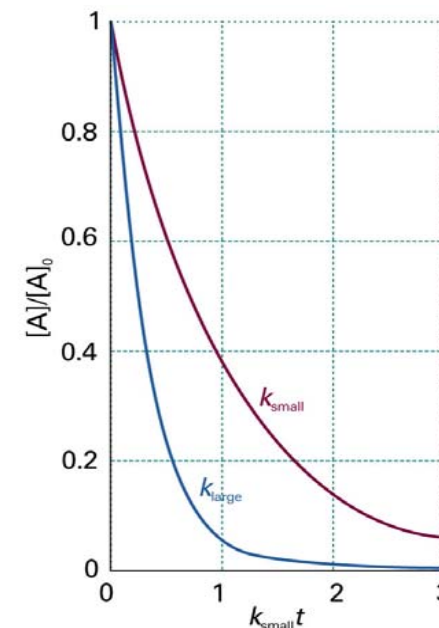


Fig. 22.5 The exponential decay of the reactant in a first-order reaction. The larger the rate constant, the more rapid the decay: here $k_{\text{large}} = 3k_{\text{small}}$.

Synoptic table 22.1* Kinetic data for first-order reactions

Reaction	Phase	$\theta/^\circ\text{C}$	k/s^{-1}	$t_{1/2}$
$2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$	g	25	3.38×10^{-5}	5.70 h
	$\text{Br}_2(\text{l})$	25	4.27×10^{-5}	4.51 h
$\text{C}_2\text{H}_6 \rightarrow 2 \text{CH}_3$	g	700	5.36×10^{-4}	21.6 min



22.3 Integrated rate laws

(b) Half-lives and time constants

Half-life ($t_{1/2}$) :

- The time taken for the concentration of a reactant A to fall to half of its initial value
- A useful indication of the rate of a first-order chemical reaction for a substance

$$kt_{1/2} = -\ln\left(\frac{1/2[A]_0}{[A]_0}\right) = -\ln\frac{1}{2} = \ln 2 \quad \therefore t_{1/2} = \frac{\ln 2}{k}$$

For a first-order reaction, the half-life of a reactant is **independent of its initial concentration**

Time constant (τ) : The time required for the concentration of a reactant to fall to 1/e of its initial value

$$\text{For a first-order reaction, } \tau = \frac{1}{k}$$

(c) Second-order reactions

The second-order rate law for the consumption of a reactant A,

$$\frac{d[A]}{dt} = -k[A]^2 \quad \longrightarrow \quad \frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad [A] = \frac{[A]_0}{1 + kt[A]_0}$$



22.3 Integrated rate laws

Justification 22.2

$$\frac{d[A]}{dt} = -k[A]^2 \quad \longrightarrow \quad \frac{d[A]}{[A]^2} = -kdt$$

Concentration of A = $[A]_0$ at $t = 0$ and $[A]$ at $t > 0$

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k \int_0^t dt \quad \therefore \frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

In the plot of $1/[A]$ vs t , a slope = k (see Table 22.2)
The concentration of A in 2nd order approaches zero more slowly than that of 1st order (see Fig. 22.7)

The half-life of species A for a second-order reaction,

$$t_{1/2} = \frac{1}{k[A]_0} \left(\ominus t = t_{1/2} \text{ for } [A] = 1/2[A]_0 \text{ and } [A] = \frac{[A]_0}{1 + kt[A]_0} \right)$$

$t_{1/2}$ of a second-order reaction varies with the initial concentration!!!

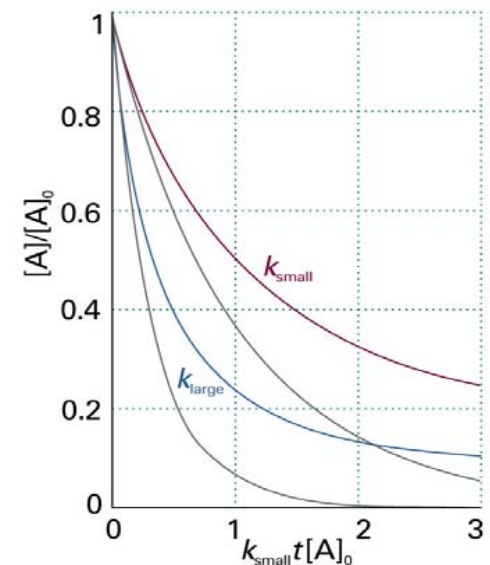


Fig. 22.7 The variation with time of the concentration of a reactant in a second-order reaction. The grey lines are the corresponding decays in a first-order reaction with the same initial rate. For this illustration, $k_{\text{large}} = 3k_{\text{small}}$.

Synoptic table 22.2* Kinetic data for second-order reactions

Reaction	Phase	$\theta/^\circ\text{C}$	$k/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$
$2 \text{NOBr} \rightarrow 2 \text{NO} + \text{Br}_2$	g	10	0.80
$2 \text{I} \rightarrow \text{I}_2$	g	23	7×10^9
$\text{CH}_3\text{Cl} + \text{CH}_3\text{O}^-$	$\text{CH}_3\text{OH}(\text{l})$	20	2.29×10^{-6}



22.3 Integrated rate laws

Another type of second-order reaction: for the first-order in each of two reactants A and B

$$\frac{d[A]}{dt} = -k[A][B]$$

However, this rate law cannot be determined if we do not know the relation between [A] and [B]

If the reaction is $A + B \rightarrow P$ (products), and the initial concentrations are $[A]_0$ and $[B]_0$, respectively

$$\text{At a time } t, \quad \ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = ([B]_0 - [A]_0)kt$$

Justification 22.3

$$[A] \rightarrow [A]_0 - x \quad \text{and} \quad [B] \rightarrow [B]_0 - x$$

$$\frac{d[A]}{dt} = -k[A][B] \rightarrow \frac{d[A]}{dt} = -k([A]_0 - x)([B]_0 - x)$$

Because $d[A]/dt = -dx/dt$,

$$\frac{dx}{dt} = k([A]_0 - x)([B]_0 - x)$$

The initial condition is that $x = 0$ when $t = 0$,



22.3 Integrated rate laws

$$\int_0^x \frac{dx}{([A]_0 - x)([B]_0 - x)} = k \int_0^t dt, \quad \int_0^x \frac{dx}{([A]_0 - x)([B]_0 - x)} = \frac{1}{[B]_0 - [A]_0} \left\{ \ln \left(\frac{[A]_0}{[A]_0 - x} \right) - \ln \left(\frac{[B]_0}{[B]_0 - x} \right) \right\}$$

By $[A] = [A]_0 - x$ and $[B] = [B]_0 - x$,

$$\therefore \ln \left(\frac{[B]/[B]_0}{[A]/[A]_0} \right) = ([B]_0 - [A]_0)kt$$

- **Similar calculations**
(See Table 22.3)

Table 22.3 Integrated rate laws

Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k$ $kt = x$ for $0 \leq x \leq [A]_0$	$[A]_0/2k$
1	$A \rightarrow P$	$v = k[A]$ $kt = \ln \frac{[A]_0}{[A]_0 - x}$	$(\ln 2)/k$
2	$A \rightarrow P$	$v = k[A]^2$ $kt = \frac{x}{[A]_0([A]_0 - x)}$	$1/k[A]_0$
	$A + B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ with autocatalysis	$v = k[A][P]$ $kt = \frac{1}{[A]_0 + [P]_0} \ln \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	$A + 2B \rightarrow P$	$v = k[A][B]^2$ $kt = \frac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0} + \frac{1}{(2[A]_0 - [B]_0)^2} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \geq 2$	$A \rightarrow P$	$v = k[A]^n$ $kt = \frac{1}{n-1} \left\{ \frac{1}{([A]_0 - x)^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$	$\frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$



22.5 The temperature dependence of reaction rates

$k \uparrow$ as $T \uparrow$ for most reactions

(a) The Arrhenius parameters

A plot of $\ln k$ as $1/T$: a straight line of slope (see Fig. 22.10)

$$\ln k = \ln A - \frac{E_a}{RT} \quad \text{: the Arrhenius equation}$$

- The Arrhenius parameters (see Table 22.4)
 - A : pre-exponential factor (frequency factor) & E_a : activation energy
- High $E_a \rightarrow$ the stronger temperature dependency of the rate constant
- $E_a = 0 \rightarrow$ no temperature dependency
- $E_a < 0 \rightarrow$ the rate \downarrow as $T \uparrow$ (the reaction has a complex mechanism)

The temperature dependence of some reactions
(not Arrhenius-like)

$$E_a = RT^2 \left(\frac{d \ln k}{dT} \right)$$

More general equation than $\ln k = \ln A - \frac{E_a}{RT}$

E_a can be obtained from the slope of $\ln k$ vs $1/T$

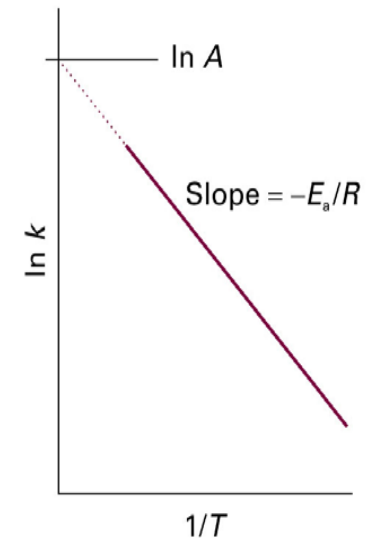


Fig. 22.10 A plot of $\ln k$ against $1/T$ is a straight line when the reaction follows the behaviour described by the Arrhenius equation (eqn 22.29). The slope gives $-E_a/R$ and the intercept at $1/T=0$ gives $\ln A$.

Synoptic table 22.4* Arrhenius parameters

	A/s^{-1}	$E_a/(kJ mol^{-1})$
(1) First-order reactions		
$CH_3NC \rightarrow CH_3CN$	3.98×10^{13}	160
$2 N_2O_5 \rightarrow 4 NO_2 + O_2$	4.94×10^{13}	103.4
(2) Second-order reactions		
$OH + H_2 \rightarrow H_2O + H$	8.0×10^{10}	42
$NaC_2H_3O + CH_3I$ in ethanol	2.42×10^{11}	81.6



22.5 The temperature dependence of reaction rates

(b) The interpretation of the parameters

$$\ln k = \ln A - \frac{E_a}{RT} \rightarrow k = Ae^{-E_a/RT}$$

- How the potential energy changes in the course of a chemical reaction that begins with a collision between A and B : the interpretation of E_a (see Fig. 22.12)
- The reaction coordinate : the collection of motions (changes in interatomic distances and bond angles)
- The region of the cluster of atoms in maximum E_a : called as “the activated complex”
- ∴ The activation energy is the minimum kinetic energy that reactants must have in order to form products.
- The fraction of collisions with a kinetic energy in excess of E_a
 $= e^{-E_a/RT}$ (by the Boltzmann distribution)
- The product of A with $e^{-E_a/RT} \rightarrow$ the rate of successful collisions

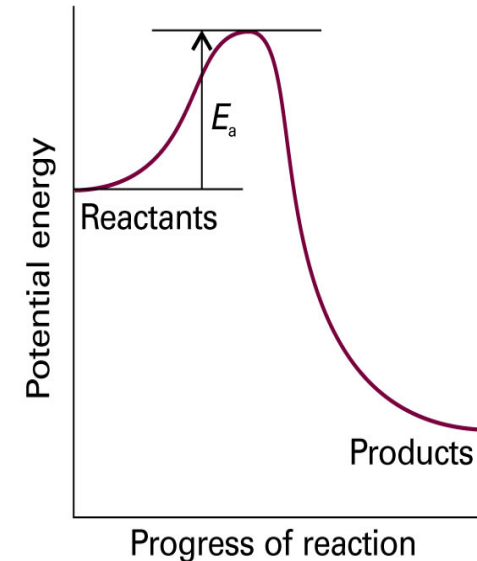


Fig. 22.12 A potential energy profile for an exothermic reaction. The height of the barrier between the reactants and products is the activation energy of the reaction.

