

Aula 3 de Março 2023

Cinética Química

Velocidades de reação

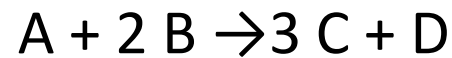
Leis cinéticas

Métodos de determinação de leis cinéticas

The rates of reactions

Reaction rates depend on the composition and the temperature of the reaction mixture.

(a) The definition of rate



The instantaneous rate of consumption of one of the reactants at a given time is $-d[R]/dt$, where R is A or B. This rate is a positive quantity.

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

The undesirability of having different rates to describe the same reaction is avoided by using the extent of reaction, ξ .

$$\xi = \frac{n_J - n_{J,0}}{\nu_J}$$

ν_J is the stoichiometric number of species J

$$\xi = \frac{1}{V} \frac{d\xi}{dt}$$

unique rate of reaction, ν , as the rate of change of the extent of reaction

Problem:

Predict how the total pressure varies during the gas-phase decomposition



in a constant-volume container.

Method: The total pressure (at constant volume and temperature and assuming perfect gas behaviour) is proportional to the number of gas-phase molecules. Therefore, because each mole of N_2O_5 gives rise to 5–2 mol of gas molecules, we can expect the pressure to rise to 5–2 times its initial value. To confirm this conclusion, express the progress of the reaction in terms of the fraction, α , of N_2O_5 molecules that have reacted.

Answer Let the initial pressure be p_0 and the initial amount of N_2O_5 molecules present be n . When a fraction α of the N_2O_5 molecules has decomposed, the amounts of the components in the reaction mixture are:

	N_2O_5	NO_2	O_2	Total
Amount:	$n(1 - \alpha)$	$2\alpha n$	$\frac{1}{2}\alpha n$	$n(1 + \frac{3}{2}\alpha)$

When $\alpha = 0$ the pressure is p_0 , so at any stage the total pressure is

$$p = (1 + \frac{3}{2}\alpha)p_0$$

When the reaction is complete, the pressure will have risen to $\frac{5}{2}$ times its initial value.

(b) Rate laws and rate constants

$$v = k [A]^a [B]^b \dots$$

The rate of reaction is often found to be proportional to the concentrations of the reactants raised to a power.

The coefficient k is called the rate constant for the reaction.

The power to which the concentration of a species (a product or a reactant) is raised in a rate law of this kind is the order of the reaction with respect to that species.



The rate law is complicated:

$$v = \frac{k[\text{H}_2][\text{Br}_2]^{3/2}}{[\text{Br}_2] + k'[\text{HBr}]}$$

$$v = k [A]^a [B]^b \dots$$

The power to which the concentration of a species (a product or a reactant) is raised in a rate law of this kind is the order of the reaction with respect to that species.

A reaction need not have an integral order, and many gas-phase reactions do not. For example, a reaction having the rate law

$$v = k[A]^{1/2}[B]$$

is half-order in A, first-order in B, and three-halves-order overall. Some reactions obey a zero-order rate law, and therefore have a rate that is independent of the concentration of the reactant (so long as some is present).

(d) The determination of the rate law

The determination of a rate law is simplified by the **isolation method** in which the concentrations of all the reactants except one are in large excess. If B is in large excess, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law might be $v = k [A] [B]$, we can approximate $[B]$ by $[B]_0$, its initial value, and write

$$v = k' [A] \quad k' = k[B]_0$$

The true rate law has been forced into first-order form by assuming that the concentration of B is constant, it is called a **pseudo first-order rate law**.

The dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn (by having all the other substances present in large excess), and so constructing a picture of the overall rate law.

The recombination of iodine atoms in the gas phase in the presence of argon was investigated and the order of the reaction was determined by the method of initial rates. The initial rates of reaction of $2 \text{I(g)} + \text{Ar(g)} \rightarrow \text{I}_2\text{(g)} + \text{Ar(g)}$ were as follows:

$[\text{I}]_0 / (10^{-5} \text{ mol dm}^{-3})$	1.0	2.0	4.0	6.0
$v_0 / (\text{mol dm}^{-3} \text{ s}^{-1})$	(a) 8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b) 4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c) 8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

The Ar concentrations are (a) 1.0 mmol dm^{-3} , (b) 5.0 mmol dm^{-3} , and (c) $10.0 \text{ mmol dm}^{-3}$. Determine the orders of reaction with respect to the I and Ar atom concentrations and the rate constant.

A note on good practice The units of k come automatically from the calculation, and are always such as to convert the product of concentrations to a rate in concentration/time (for example, $\text{mol dm}^{-3} \text{ s}^{-1}$).

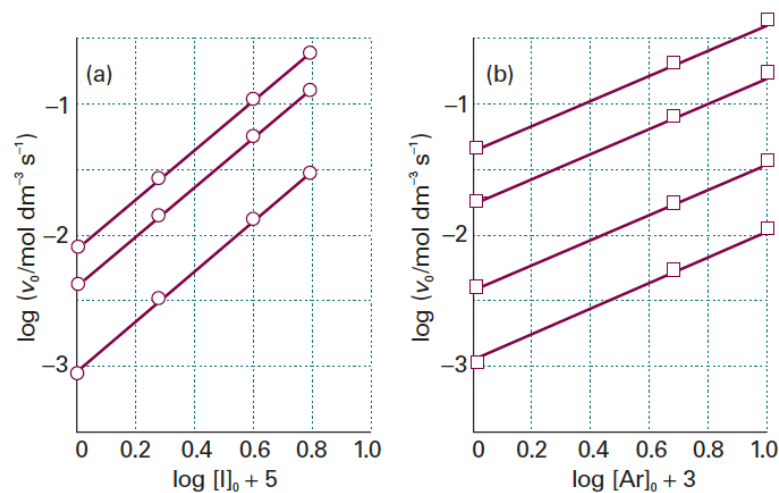
Method Plot the logarithm of the initial rate, $\log v_0$, against $\log [I]_0$ for a given concentration of Ar, and, separately, against $\log [Ar]_0$ for a given concentration of I. The slopes of the two lines are the orders of reaction with respect to I and Ar, respectively. The intercepts with the vertical axis give $\log k$.

Answer The plots are shown in Fig. 22.4. The slopes are 2 and 1, respectively, so the (initial) rate law is

$$v_0 = k[I]_0^2[Ar]_0$$

This rate law signifies that the reaction is second-order in [I], first-order in [Ar], and third-order overall. The intercept corresponds to $k = 9 \times 10^9 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$.

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



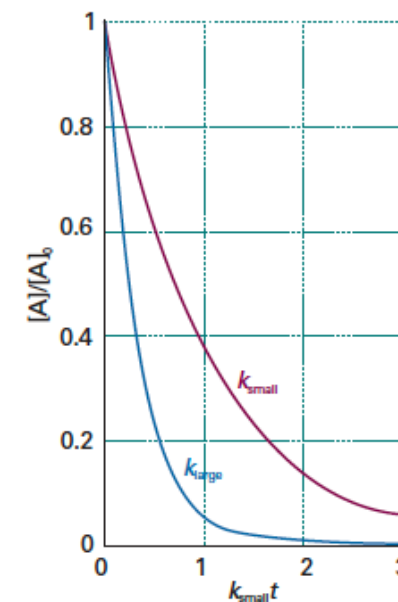
Integrated rate laws

(a) First-order reactions

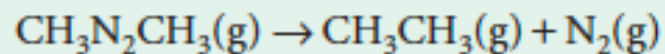
$$\frac{d[A]}{dt} = -k[A]$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \quad [A] = [A]_0 e^{-kt}$$

$[A]_0$ is the initial concentration of A (at $t = 0$).



The variation in the partial pressure of azomethane with time was followed at 600 K, with the results given below. Confirm that the decomposition



is first-order in azomethane, and find the rate constant at 600 K.

t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

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

Method As indicated in the text, to confirm that a reaction is first-order, plot $\ln([A]/[A]_0)$ against time and expect a straight line. Because the partial pressure of a gas is proportional to its concentration, an equivalent procedure is to plot $\ln(p/p_0)$ against t . If a straight line is obtained, its slope can be identified with $-k$.

Answer We draw up the following table:

t/s	0	1000	2000	3000	4000
$\ln(p/p_0)$	1	-0.360	-0.720	-1.082	-1.441

Figure 22.6 shows the plot of $\ln(p/p_0)$ against t . The plot is straight, confirming a first-order reaction, and its slope is -3.6×10^{-4} . Therefore, $k = 3.6 \times 10^{-4} \text{ s}^{-1}$.

A note on good practice Because the horizontal and vertical axes of graphs are labelled with pure numbers, the slope of a graph is always dimensionless. For a graph of the form $y = b + mx$ we can write

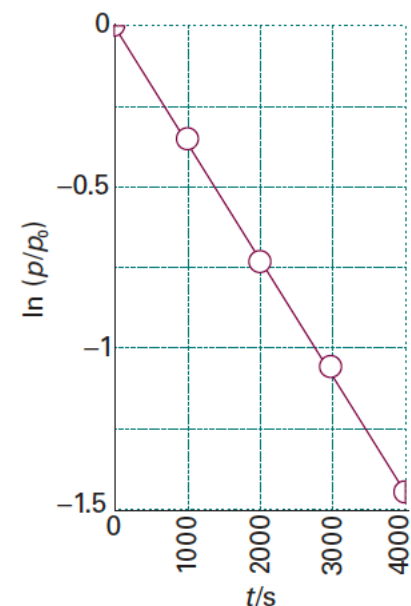
$$y = b + (m \text{ units})(x/\text{units})$$

where ‘units’ are the units of x , and identify the (dimensionless) slope with ‘ m units’. Then

$$m = \text{slope}/\text{units}$$

In the present case, because the graph shown here is a plot of $\ln(p/p_0)$ against t/s (with ‘units’ = s) and k is the negative value of the slope of $\ln(p/p_0)$ against t itself,

$$k = -\text{slope}/s$$



The determination of the rate constant of a first-order reaction: a straight line is obtained when $\ln [A]$ (or, as here, $\ln p$) is plotted against t ; the slope gives k .

(b) Half-lives and time constants

The **half-life**, $t_{1/2}$, of a substance, the time taken for the concentration of a reactant to fall to half its initial value.

The time for $[A]$ to decrease from $[A]_0$ to $\frac{1}{2} [A]_0$ in a first-order reaction is given by

$$kt_{1/2} = -\ln \left(\frac{\frac{1}{2}[A]_0}{[A]_0} \right) = -\ln \frac{1}{2} = \ln 2 \qquad t_{1/2} = \frac{\ln 2}{k} \qquad (\ln 2 = 0.693)$$

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

Time constant, τ (tau), is the time required for the concentration of a reactant to fall to $1/e$ of its initial value.

$$k\tau = -\ln \left(\frac{[A]_0/e}{[A]_0} \right) = -\ln \frac{1}{e} = 1$$

The **time constant** of a first-order reaction is the reciprocal of the rate constant:

$$\tau = \frac{1}{k}$$

(c) Second-order reactions

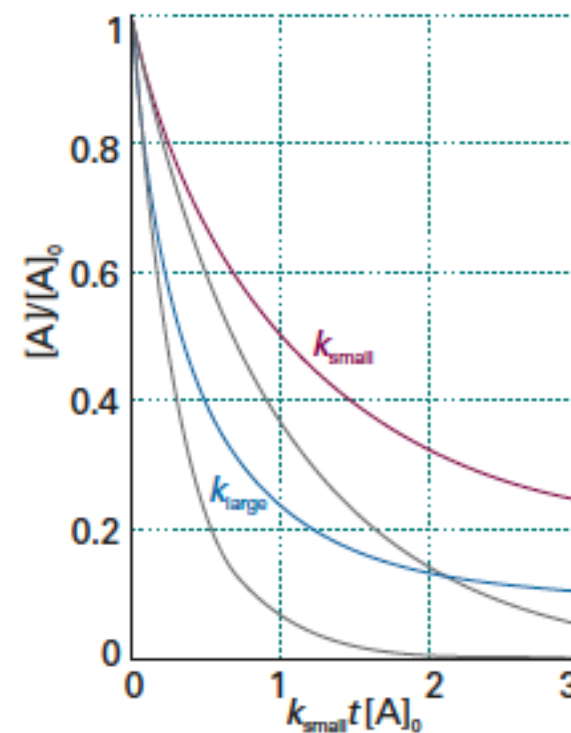
$$\frac{d[A]}{dt} = -k[A]^2$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \quad [A] = \frac{[A]_0}{1 + kt[A]_0}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

For an n^{th} -order reaction of the form $A \rightarrow \text{products}$, the half-life is related to the rate constant and the initial concentration of A by

$$t_{1/2} = \frac{1}{k[A]^{n-1}}$$



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, $k_{\text{large}} = 3k_{\text{small}}$.

(d) Another type of second-order reactions

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

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

$$\int_0^x \frac{dx}{([A]_0 - x)([B]_0 - x)} = k \int_0^t dt$$

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

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

To use the method of partial fractions to evaluate an integral of the form

$\int \frac{1}{(a-x)(b-x)} dx$, where a and b are constants, we write

$$\frac{1}{(a-x)(b-x)} = \frac{1}{b-a} \left(\frac{1}{a-x} - \frac{1}{b-x} \right)$$

and integrate the expression on the right. It follows that

$$\begin{aligned} \int \frac{dx}{(a-x)(b-x)} &= \frac{1}{b-a} \left[\int \frac{dx}{a-x} - \int \frac{dx}{b-x} \right] \\ &= \frac{1}{b-a} \left(\ln \frac{1}{a-x} - \ln \frac{1}{b-x} \right) + \text{constant} \end{aligned}$$

Explicação

$$\frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{a}{[A]_0 - x} + \frac{b}{[B]_0 - x} \quad (1)$$

$$\Rightarrow \frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{a([B]_0 - x) + b([A]_0 - x)}{([A]_0 - x)([B]_0 - x)} \quad (2)$$

$$\Rightarrow \frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{a[B]_0 - ax + b[A]_0 - bx}{([A]_0 - x)([B]_0 - x)} \quad (3)$$

Para que as duas frações sejam iguais, os numeradores terão de ser iguais. Logo:

$$1 = a[B]_0 - ax + b[A]_0 - bx \quad \Rightarrow 1 = (-a-b)x + a[B]_0 + b[A]_0$$

$$\Rightarrow 0x + 1 = (-a-b)x + a[B]_0 + b[A]_0$$

Temos assim 2 equações a 2 incógnitas

$$\begin{cases} 0 = -a-b \\ 1 = a[B]_0 + b[A]_0 \end{cases} \Leftrightarrow \begin{cases} b = -a \\ 1 = a[B]_0 - a[A]_0 \end{cases} \Rightarrow \begin{cases} b = -\frac{1}{[B]_0 - [A]_0} \\ a = \frac{1}{[B]_0 - [A]_0} \end{cases}$$

Logo substituindo em (1)

$$\frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{\frac{1}{[B]_0 - [A]_0}}{[A]_0 - x} + \frac{-\frac{1}{[B]_0 - [A]_0}}{[B]_0 - x} \quad (4)$$

$$\Rightarrow \frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{1}{[B]_0 - [A]_0} \left(\frac{1}{[A]_0 - x} - \frac{1}{[B]_0 - x} \right)$$

c. q. d.

Explicação

$$\int_0^x \frac{1}{([A]_0 - x)([B]_0 - x)} dx = \int_0^x \frac{1}{[B]_0 - [A]_0} \left(\frac{1}{[A]_0 - x} - \frac{1}{[B]_0 - x} \right) dx$$

Logo:

$$\int_0^x \frac{1}{([A]_0 - x)([B]_0 - x)} dx = \int_0^t u dt \Leftrightarrow \int_0^x \frac{1}{[B]_0 - [A]_0} \left(\frac{1}{[A]_0 - x} - \frac{1}{[B]_0 - x} \right) dx = \int_0^t u dt$$

$$\frac{1}{[B]_0 - [A]_0} \int_0^x \left(\frac{1}{[A]_0 - x} - \frac{1}{[B]_0 - x} \right) dx = \int_0^t u dt \Leftrightarrow$$

$$\Leftrightarrow \frac{1}{[B]_0 - [A]_0} \left(\int_0^x \frac{1}{[A]_0 - x} dx - \int_0^x \frac{1}{[B]_0 - x} dx \right) = u \int_0^t dt \Leftrightarrow$$

$$\Leftrightarrow \frac{1}{[B]_0 - [A]_0} \left(- \left[\ln([A]_0 - x) \right]_0^x + \left[\ln([B]_0 - x) \right]_0^x \right) = u t \Leftrightarrow$$

$$\Leftrightarrow \frac{1}{[B]_0 - [A]_0} \left(-\ln([A]_0 - x) + \ln([A]_0) + \ln([B]_0 - x) - \ln([B]_0) \right) = u t$$

$$\Leftrightarrow \frac{1}{[B]_0 - [A]_0} \left(\ln \frac{([B]_0 - x)}{[B]_0} - \ln \frac{([A]_0 - x)}{[A]_0} \right) = u t \Leftrightarrow$$

$$\Leftrightarrow \frac{1}{[B]_0 - [A]_0} \cdot \ln \frac{([B]_0 - x)/[B]_0}{([A]_0 - x)/[A]_0} = u t \Leftrightarrow$$

como $[B] = [B]_0 - x$ e $[A] = [A]_0 - x$ tem-se:

$$\frac{1}{[B]_0 - [A]_0} \cdot \ln \left(\frac{[B]/[B]_0}{[A]/[A]_0} \right) = u t$$

c. q. d.

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	$A \rightarrow P$	$v = k[A]^2$ $kt = \frac{x}{[A]_0([A]_0 - x)}$	$1/k[A]_0$
	$A + B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2 B \rightarrow P$	$v = k[A][B]$ $kt = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ with autocatalysis	$v = k[A][P]$ $kt = \frac{1}{[A]_0 + [P]_0} \ln \frac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	

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

Mecanismo duma reação

– sucessão de passos reacionais elementares

Conceitos importantes:

- ordem = molecularidade num passo elementar
- passo mais **lento** controla a velocidade
- estado estacionário de produto(s) intermediários

Reactions approaching equilibrium

(a) First-order reactions close to equilibrium



The concentration of A is reduced by the forward reaction (at a rate $k[A]$) but it is increased by the reverse reaction (at a rate $k'[B]$). The net rate of change is

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

If the initial concentration of A is $[A]_0$, and no B is present initially, then at all times $[A] + [B] = [A]_0 \Leftrightarrow [B] = [A]_0 - [A]$

Therefore,

$$\frac{d[A]}{dt} = -k[A] + k'([A]_0 - [A]) = -(k + k')[A] + k'[A]_0$$

The solution of this first-order differential equation (as may be checked by differentiation) is

$$[A] = \frac{k' + ke^{-(k+k')t}}{k' + k} [A]_0$$

As $t \rightarrow \infty$, the concentrations reach their equilibrium values

$$[A]_{\text{eq}} = \frac{k' [A]_0}{k + k'} \quad [B]_{\text{eq}} = [A]_0 - [A]_{\infty} = \frac{k [A]_0}{k + k'}$$

The equilibrium constant of the reaction is

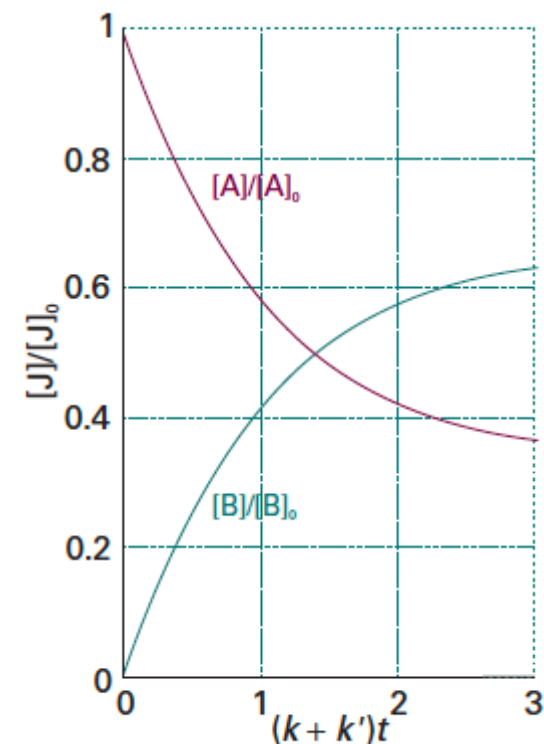
$$K = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k}{k'}$$

(This expression is only approximate because thermodynamic equilibrium constants are expressed in terms of activities, not concentrations.)

At equilibrium, the forward and reverse rates must be the same:

$$k[A]_{\text{eq}} = k'[B]_{\text{eq}}$$

if one of the rate constants can be measured, then the other may be obtained if the equilibrium constant is known



The approach of concentrations to their equilibrium values as predicted for a reaction $A \leftrightarrow B$ that is first order in each direction, and for which $k = 2k'$.

(b) Relaxation methods

When the temperature of a system at equilibrium is increased suddenly, the rate constants change from their earlier values to the new values k_a and k_b characteristic of that temperature, but the concentrations of A and B remain for an instant at their old equilibrium values. As the system is no longer at equilibrium, it readjusts to the new equilibrium concentrations:

$$k_a[A]_{eq} = k_b[B]_{eq} \quad (**)$$

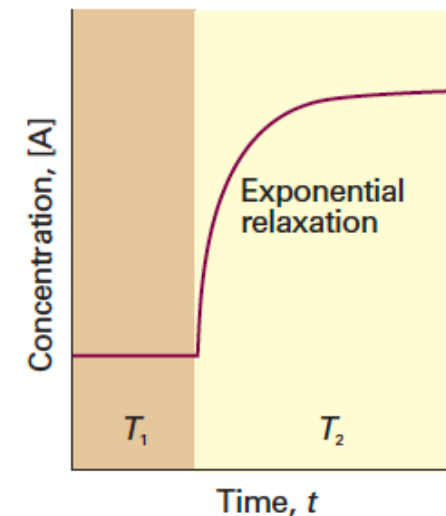
the deviation of [A] from its new equilibrium value is x , so:

$$[A] = x + [A]_{eq}$$

$$[B] = [B]_{eq} - x$$

$$\frac{d[A]}{dt} = -k_a[A] + k_b[B]$$

$$\begin{aligned} &= -k_a([A]_{eq} + x) + k_b([B]_{eq} - x) && \text{because of} \\ &= -(k_a + k_b)x && \text{eq. (**)} \end{aligned}$$



The relaxation to the new equilibrium composition when a reaction initially at equilibrium at a temperature T_1 is subjected to a sudden change of temperature, which takes it to T_2 .

Because $d[A]/dt = dx/dt$, this equation is a first-order differential equation with the solution:

$$x = x_0 e^{-t/\tau} \quad \frac{1}{\tau} = k_a + k_b$$

The equilibrium constant for the autoprotolysis of water, $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$, is $K_{\text{w}} = a(\text{H}^+)a(\text{OH}^-) = 1.008 \times 10^{-14}$ at 298 K. After a temperature-jump, the reaction returns to equilibrium with a relaxation time of 37 μs at 298 K and $\text{pH} \approx 7$. Given that the forward reaction is first-order and the reverse is second-order overall, calculate the rate constants for the forward and reverse reactions.

Method We need to derive an expression for the relaxation time, τ (the time constant for return to equilibrium), in terms of k_1 (forward, first-order reaction) and k_2 (reverse, second-order reaction). We can proceed as above, but it will be necessary to make the assumption that the deviation from equilibrium (x) is so small that terms in x^2 can be neglected. Relate k_1 and k_2 through the equilibrium constant, but be careful with units because K_{w} is dimensionless.

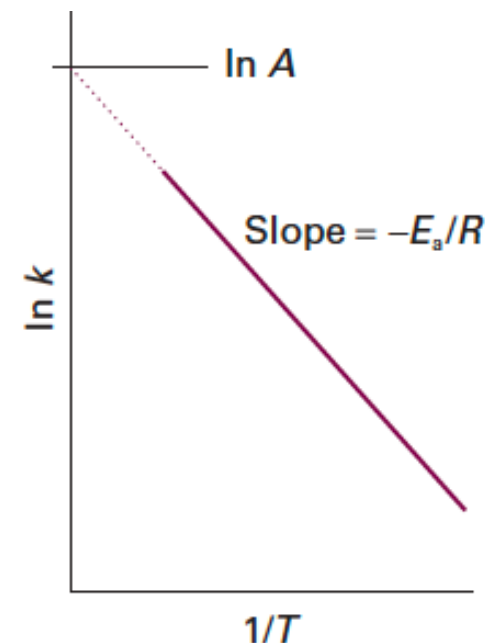
The temperature dependence of reaction rates

(a) The Arrhenius parameters

$$\ln k = \ln A - \frac{E_a}{RT}$$

A to the intercept of the line at $1/T = 0$ (at infinite temperature), is called the pre-exponential factor or the 'frequency factor'.

E_a which is obtained from the slope of the line ($-E_a/R$), is called the activation energy.



Determining the Arrhenius parameters

The rate of the second-order decomposition of acetaldehyde (ethanal, CH_3CHO) was measured over the temperature range 700–1000 K, and the rate constants are reported below. Find E_a and A .

T/K	700	730	760	790	810	840	910	1000
$k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	0.011	0.035	0.105	0.343	0.789	2.17	20.0	145

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

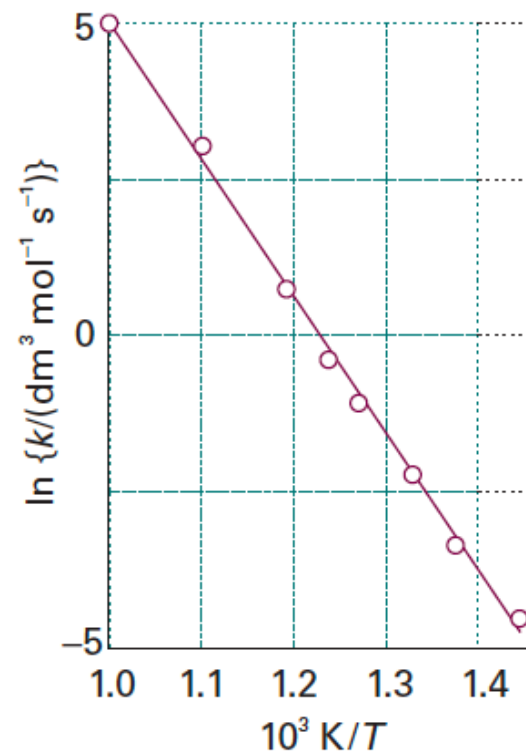
Answer We draw up the following table:

$(10^3 \text{ K})/T$	1.43	1.37	1.32	1.27	1.23	1.19	1.10	1.00
$\ln(k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	-4.51	-3.35	-2.25	-1.07	-0.24	0.77	3.00	4.98

Now plot $\ln k$ against $1/T$ (Fig. 22.11). The least-squares fit is to a line with slope -22.7 and intercept 27.7 . Therefore,

$$E_a = 22.7 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times 10^3 \text{ K} = 189 \text{ kJ mol}^{-1}$$

$$A = e^{27.7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 1.1 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$



The Arrhenius plot

(b) The interpretation of the parameters

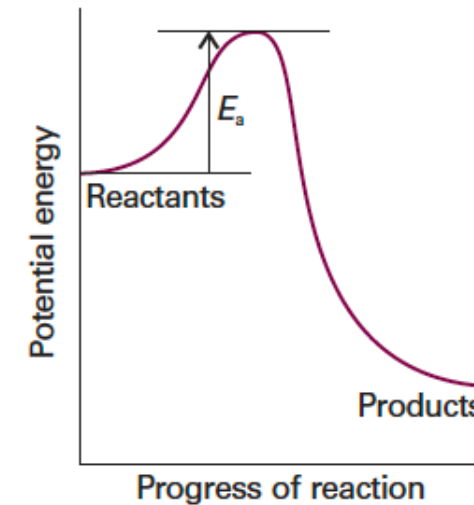
The Arrhenius parameters as purely empirical quantities that enable us to discuss the variation of rate constants with

$$k = Ae^{-E_a/RT}$$

The activation energy is the minimum kinetic energy that reactants must have in order to form products

In a gas-phase reaction there are numerous collisions each second, but only a tiny proportion are sufficiently energetic to lead to reaction.

The fraction of collisions with a kinetic energy in excess of an energy E_a is given by the Boltzmann distribution as $e^{-E_a/RT}$.



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.

