

II RATE LAW (equation) • Rate and concentration

For a rx:



the rate is,

$$= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Rates are often proportional to concn of 1 or 2 reactants with each reactant raised to a small integral power.

$$\text{eg. Rate} = V = k[A]^x[B]^y$$

Note "x" and "y" are not related to "a" and "b".

2 points

1. Order

The reaction is then x order w.r.t. A , and y order w.r.t. B

The overall order, n , is the sum of the various orders

$$n = x + y + \dots$$

determined
exptlly.

Examples

<u>Rx.</u>	<u>Rate law</u>	<u>Order</u>
$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$	$V = k[\text{N}_2\text{O}_5]$	1
$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$	$V = k[\text{NO}_2]^2$	2
$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	$V = k[\text{H}_2][\text{I}_2]$	2
$\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$	$V \approx k[\text{CH}_3\text{CHO}]^{3/2}$	$\approx 3/2$
$\text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{enzyme}]{\text{liver}} \text{CH}_3\text{CHO}$	$V = \text{constant}$	0

Note

a) Never possible to deduce the order by inspection of stoichiometric equn.

b) Order is determined exptlly

c) Orders may be non-integral (not common) - or even negative (-11-)

Even pseudo-order; one component, e.g. solvent in large excess (constant concn.)

d) Rx. rate may be different at beginning compared to end of rx.

e) Zero order - indep. of concn.

f) 3rd order - rare.

2. Rate constant

- the proportionality const. k is the rate constant

Units vary with order

1st order (time⁻¹) e.g. s⁻¹

2nd order M⁻¹s⁻¹

(172)

To determine the rate law

$$\text{Rate} = V = k[A]^x[B]^y[C]^z \dots \text{etc}$$

we need to do a series of expts.

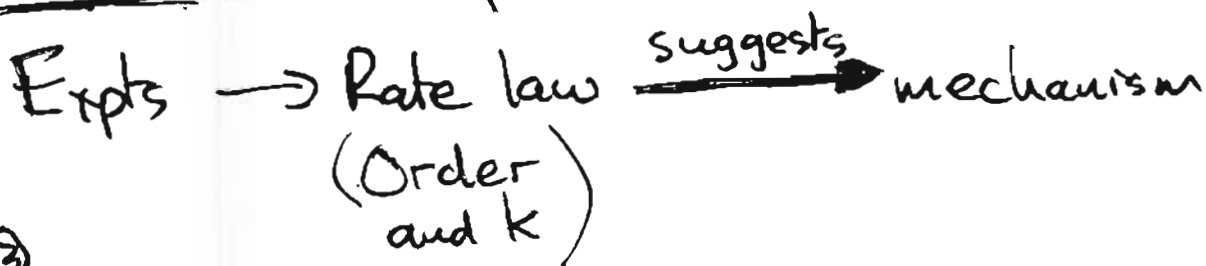
e.g. take data in the early stages of a rx; the method of initial rates, and determine values for x, y, z and k .

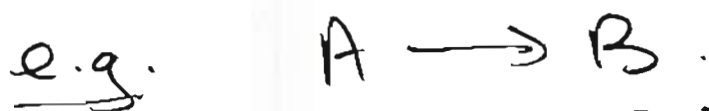
e.g. Rate = $k[A]^x[B]^y[C]^z$

↑ ↗ →
initial concns

Usually done by varying the concn of one species at a time.

Remember the process is:





$$\text{Rate} = k[A]^x$$

Value of x
(Rx. order) Consider effect on rate
when [A] is
doubled (1M \rightarrow 2M)

- | | |
|---------------|------------------------------------------------------------------------------|
| 0 | $[1]^0 \rightarrow [2]^0 = 1$, no effect on rate |
| $\frac{1}{2}$ | $[1]^{\frac{1}{2}} \rightarrow [2]^{\frac{1}{2}} = 1.41$, rate inc. by 1.41 |
| 1 | $[1]^1 \rightarrow [2]^1 = 2$, —"—— 2 |
| 2 | $[1]^2 \rightarrow [2]^2 = 4$, —"—— 4 |

A real (well, almost!) example



$$\text{Rate} = k[A]^x[B]^y$$

Data on next page

EXPT. #	Initial Rate $\text{mol L}^{-1} \text{h}^{-1}$	Initial [A]	Initial concn [B] mol L^{-1}
1	0.5×10^{-2}	0.50	0.20
2	0.5×10^{-2}	0.75	0.20
3	0.5×10^{-2}	1.00	0.20
4	1×10^{-2}	0.50	0.40
5	1.5×10^{-2}	0.50	0.60

a) In first 3 expts. [B] is const.
and [A] changes.
— no change in rate

i.e. rate indep. of [A] ; zero order in [A]

b) In expts, 1, 4, 5 [A] kept const.
and [B] changes

Change of rate directly \propto change in [B]

\therefore first order in [B]

\therefore Rate = $k[A]^0[B]^1 = k[B]^1$

i.e. overall 1st order in [B]

Can get k from the data

$$k = \frac{\text{rate}}{[B]} = \frac{1.50 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1}}{0.6 \text{ mol L}^{-1}}$$

$$= \underline{\underline{2.5 \times 10^{-2} \text{ h}^{-1}}}$$

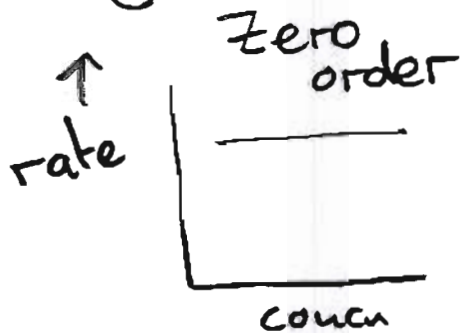
↑↑ This example was first order, $V = k[B]$

In other rxns, the rate could be indep. of concn.

e.g. $\text{rate} = k[\text{reactant}]^0 = k$
Zero order.

or e.g. $\text{rate} = k[B]^2$
 or $\text{rate} = k[A][B]$ } 2nd order Class I
 Class II

Typical rate/concn plots would be:



Rate = k_0



Rate = $k_1 []$



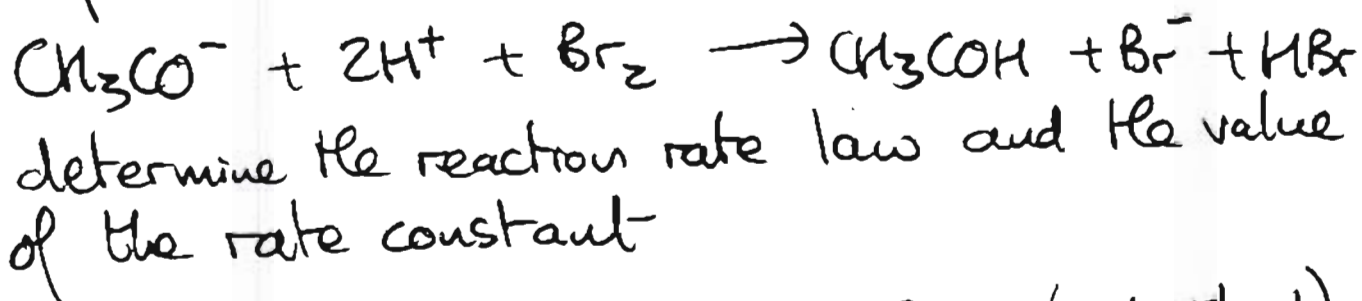
Rate = $k_2 []^2$

Units of k M s^{-1} ← or any old time s^{-1}

$\text{M}^{-1} \text{s}^{-1}$

(176)

Q. Given the following initial rate data for the rx.



	<u>$[\text{CH}_3\text{CO}^-]$</u>	<u>$[\text{Br}_2]$</u>	<u>$[\text{H}^+]$</u>	<u>Rate ($\text{mol L}^{-1}\text{s}^{-1}$)</u>
Expt. 1.	1.00	1.00	1.00	4.0×10^{-3}
2.	2.00	1.00	1.00	8.0×10^{-3}
3.	2.00	2.00	1.00	8.0×10^{-3}
4.	1.00	2.00	2.00	8.0×10^{-3}

Answer.

Rate law: $\text{Rate} = k[\text{CH}_3\text{CO}^-][\text{H}^+]$

$$k = \frac{4.0 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}}{(1.0 \text{ mol L}^{-1})(1.0 \text{ mol L}^{-1})} = 4.0 \times 10^{-3} \text{ L mol}^{-1}\text{s}^{-1}$$

or (check!) from any other sets of data.

III DEPENDENCE OF CONCEN on TIME

This serves a couple of purposes.

a) By examining how the concn changes with time during a single expt., we can determine the rate law [Note: the initial rate law method (earlier) needs several expts].

b) We can determine how long a rx. must proceed to give a particular concn. Or, -- we can determine what the concns are after a period of time.

Zero order rx's

Rate is independent of concn.

Corresponds to the rate law

$$-\frac{d[A]}{dt} = k_0 \left\{ \begin{array}{l} \leftarrow \text{zero order rx.} \\ \leftarrow \text{units of } M s^{-1} \end{array} \right.$$

← This is the differential form of the rate law.

Separate the variables, $[A]$ and t , and integrate each side between the limits $[A]_2, [A]_1$, and t_2, t_1 .

$$-\int_{[A]_1}^{[A]_2} d[A] = k_0 \int_{t_1}^{t_2} dt$$

$$\therefore [A]_1 - [A]_2 = k_0 (t_2 - t_1)$$

If $[A]_0 = \text{concn}$ at $t = 0$

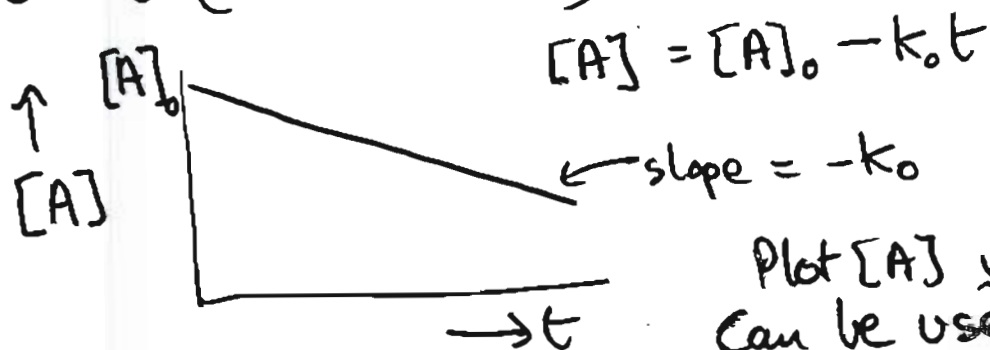
then, $[A]_0 - [A] = k_0 t$

or $[A] = [A]_0 - k_0 t$

↑ concn. at a later time

Integrated form of rate law

This is the equn for a straight line, slope k_0 (rate const.).



Plot $[A]$ vs t .
Can be used to check for zero order

First order rxns

Corresponds to the rate law

$$-\frac{d[A]}{dt} = k_1 [A] \quad \leftarrow \text{differential rate law}$$

↑
units
(time⁻¹)

get the
integrated
rate law

Separate the variables

$$-\frac{d[A]}{[A]} = k_1 dt$$

Integrate

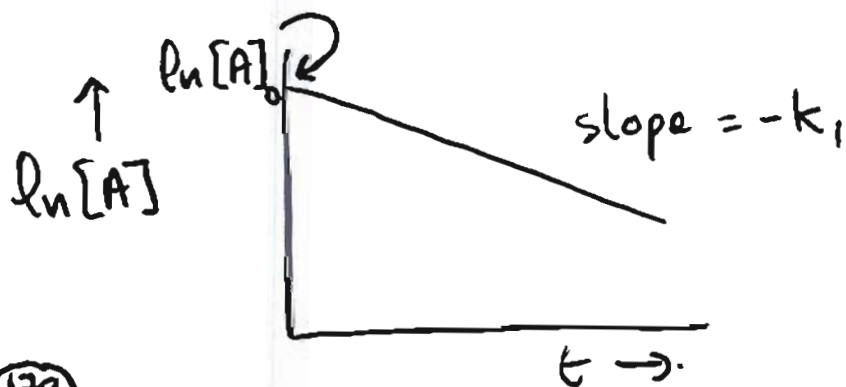
$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k_1 \int_0^t dt$$

$$-\ln[A] + \ln[A]_0 = k_1 t$$

$$\ln \frac{[A]_0}{[A]} = k_1 t$$

or $\ln [A] = \ln [A]_0 - k_1 t$

Integrated
rate law

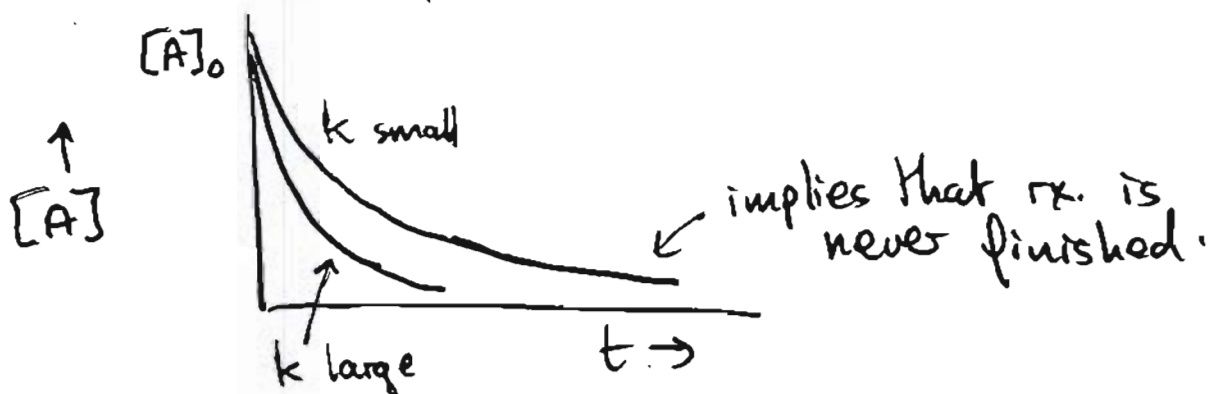


Plot provides
a test for
1st order.
If a straight line
 \rightarrow 1st order.

In exponential form the first order expression is

$$[A] = [A]_0 e^{-k_1 t}$$

i.e. concn. of A decreases exponentially



Half-life for 1st order rx

- time taken for half of the reactant to disappear.

We have $\ln\left(\frac{[A]}{[A]_0}\right) = -k_1 t$

Substitute $[A] = \frac{[A]_0}{2}$

$$\ln \frac{[A]_0}{2} = -k_1 t_{1/2}$$

$$\therefore \ln \frac{1}{2} = -k_1 t_{1/2}$$

$$\therefore \boxed{t_{1/2} = \frac{0.693}{k_1}}$$

↑
half-life

Radioactive decay is 1st order (can use to date relics, see Sec. 21.4) 8. Ed.

20.4 9. Ed.

← recip. relationship between k and $t_{1/2}$.

← $t_{1/2}$ indep. of concn. for 1st order rx.