Chem Factsheet

January 2003 Number 43

Rate Equations, Orders & Constants

To succeed with this topic you need to:

- Know and understand the AS material on kinetics -
  - collision theory
  - activation energy
  - Maxwell-Boltzman graph
  - Factors affecting rates of reaction
  - Catalysts and energy profiles covered in Factsheet No. 10 (Kinetics I)

After working through the Factsheet you will be able to:

- understand the parts making up the rate equation (or expression);
- be able to find the orders for a particular chemical reaction from the data given for it;
- be able to perform calculations based on the rate equation;
- be able to work out the units for the rate constant, *k*.

Rate expressions (equations)

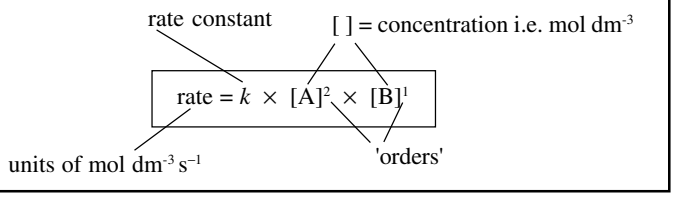
The **balanced chemical equation** (the stoichiometric equation) can tell you **nothing** about the rate expression.

The rate expression can only be worked out from the **data** provided by reaction rate **experiments.**

Let us consider a reaction of substances A, B and C where the equation is

$$A + B + 2C \rightarrow 2D + E$$

The **rate expression** (or equation) works out to be



In words:
The reaction is 2nd order with respect to A and 1st order with respect to B.
Overall, the reaction is 3rd order (2 + 1)

Note the following points about this example:
(1) We would mormally write [B], not $[B]^1$. The 1 is put in to make it clear
(2) C does not appear in the rate expression – it is '0 order' and **if shown** would look like this $[C]^0$
(3) the expression would normally be shown as

rate = $k[A]^2[B]$

with the '×' symbol removed.

Finding the orders from experimental data

This following worked example is typical of what will be expected of you in an examination question.

The reaction: $2C + D + 2E \rightarrow 3F + 2G$
products the following data

experiment number	concentrations / mol dm^{-3} [C]	[D]	[E]	initial rate / mol dm^{-3}s^{-1}
1	0.5	1.0	1.0	2
2	0.5	2.0	1.0	8
3	1.0	2.0	1.0	16
4	1.0	2.0	2.0	16

(a) What are the orders with respect to C, D and E?
(b) Write the rate equation for this reaction.

Hint the process involves looking at the experiments for C ,D and E and selecting two where **only one** of C, D or E changes - compare changes in concentration with the effect on the rate.

Working Out	Answer
For C compare experiments 2 and 3 because only C changes.	Rate ∝ [C] (NB. ∝ is the proportional sign)
When [C] **doubles**, the rate **doubles** i.e.**directly proportional** so is **first order**.	rate = k[C] (NB. the rate constant, k enables the '=' sign to be put in).
For D compare experiments 1 and 2.	rate ∝ $[D]^2$
when [D] **doubles**, the rate goes up **4 times** i.e. $4 = 2^2$, so 2nd order	rate = $k[D]^2$
For E compare experiments 3 and 4	rate ∝ $[E]^0$
when [E] **doubles**, the rate is **unchanged** i.e. **no effect** so is **zero order**	rate = $k[E]^0$
Combine the answers in (a)	(b) rate = $k[C][D]^2$ **or** rate = $k[C][D]^2[E]^0$

Summary

0 order - changing the concentration has no effect on the rate

1st order - directly proportional relationship e.g. half concentration and half rate, triple concentration and triple the rate.

2nd order - 'squared factor' involved e.g. triple concentration and rate increases 9×, double concentration and rate increases 4×.

Exam Hint - *The initial rate data is a common place for questions to catch out candidates by using 'powers of 10' (standard form). Look at this data:*

rate
2×10^{-3}
8×10^{-3}
3.2×10^{-2}
6.4×10^{-2}

Comparing these is a problem!

Now do this conversion to 10^{-3} for all figures:

rate	
2×10^{-3}	
8×10^{-3}	x 4 comparison
$3.2 \times 10^{-2} = 32 \times 10^{-1} \times 10^{-2} = 32 \times 10^{-3}$	x 4 are
$6.4 \times 10^{-2} = 64 \times 10^{-1} \times 10^{-2} = 64 \times 10^{-3}$	x 2 now possible

(check conversions on your calculator if you are unsure)

Finding the units of *k*

To do this you need to

(1) remember the units of : [ ] = mol dm^{-3}
rate = mol dm^{-3} s^{-1}

(2) be able to rearrange the rate equation

(3) Know how to combine powers

Powers
- Anything without a number by it is to the power 1.
- Multiply ⇒ add powers.
- Dividing ⇒ subtract powers.
- Powers on the bottom change sign when you bring them to the top.
- If you are finding a "power of a power" you multiply.
  e.g. $(\text{mol dm}^{-3})^3 = \text{mol}^{1\times3}\text{dm}^{-3\times3}$
  $= \text{mol}^3\text{dm}^{-9}$
- You can only simplify powers of the same thing
  e.g. $\text{mol}^2 \times \text{mol} = \text{mol}^3$, but mol dm^{-3} can't be simplified.

Example 1 rate = *k*[A][B]

$$k = \frac{\text{rate}}{[A][B]} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \frac{\cancel{\text{mol dm}^{-3}}\text{s}^{-1}}{\cancel{\text{mol dm}^{-3}}\text{mol dm}^{-3}}$$

$$= \frac{\text{s}^{-1}}{\text{mol dm}^{-3}} = \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$$

Example 2 rate = *k*[C]²[D]

$$k = \frac{\text{rate}}{[C]^2[D]} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{(\text{mol dm}^{-3})^3} = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^3\text{ dm}^{-9}}$$

$$= \text{mol dm}^{-3}\text{ s}^{-1}\text{ mol}^{-3}\text{ dm}^9 = \text{mol}^{-2}\text{dm}^{-6}\text{s}^{-1}$$

Finding the value of *k*

This is a relatively straightforward procedure:
1. choose the values for any one of the experiments in the data table
2. substitute these values for [ ] and rate into the rate expression
3. rearrange the equation and calculate *k*.

You will find examples of this calculation in the questions at the end of this Factsheet.

Questions

1. For the reaction between A, B and C the following results were obtained:

experiment	concentration / mol dm^{-3}			initial rate / mol $dm^{-3}s^{-1}$
	[A]	[B]	[C]	
1	1	1	1	2.0×10^{-4}
2	2	1	1	4.0×10^{-4}
3	1	2	1	2.0×10^{-4}
4	2	1	2	1.6×10^{-3}

(a) What are the orders with respect to A, B and C?
(b) What is the rate expression for this reaction?
(c) Calculate the value for *k*. What are its units?

2. For the reaction between C and D the following results were obtained:

experiment	concentration / mol dm^{-3}		rate / mol $dm^{-3}s^{-1}$
	[C]	[D]	
1	0.01	0.1	2.5×10^{-4}
2	0.01	0.2	2.5×10^{-4}
3	0.02	0.3	5.0×10^{-4}

(a) Write the rate expression for this reaction.
(b) Calculate the value for *k* and give its units.

3. The following results were obtained for the reaction between E, F and G:

experiment	concentration / mol dm^{-3}			initial rate / mol $dm^{-3}s^{-1}$
	[E]	[F]	[G]	
1	1	1	0.5	7.0×10^{-3}
2	1	2	0.5	1.4×10^{-2}
3	2	2	0.5	1.4×10^{-2}
4	2	2	1.5	4.2×10^{-2}

(a) Write the rate expression for this reaction.
(b) Calculate the value for *k* and state its units.

Answers

1. (a) rate = $k[A]^1$ rate = $k[B]^0$ rate = $k[C]^2$
(b) rate = k $[A][C]^2$
(c) $k = \frac{\text{rate}}{[A][C]^2}$
use experiment 1:
$= \frac{2.0 \times 10^4}{1 \times 1^2}$
$= 2.0 \times 10^{-4}$

Units: $= \frac{\cancel{\text{mol dm}^{-3}}\text{ s}^{-1}}{\cancel{\text{mol dm}^{-3}}\ (\text{mol dm}^{-3})^2}$
$= \text{mol}^{-2}\text{ dm}^6\text{ s}^{-1}$

2. (a) rate = $k[C]$
(b) $k = \frac{2.5 \times 10^{-4}}{0.01}$
$= 2.5 \times 10^{-2}\text{s}^{-1}$

3. (a) rate = $k[F][G]$
(b) $k = 1.4 \times 10^{-2}$ $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$

Acknowledgements:
This Factsheet was researched and written by Sam Goodman
Curriculum Press, Unit 305B, The Big Peg, 120 Vyse Street, Birmingham, B18 6NF