Physical Chemistry – crib sheet
Rates of reaction & reaction rate

What is a reaction rate?

The rate of any reaction is the speed of change for the reactants : $R = \frac{\Delta[\,]}{t}$ (t = time in seconds, [ ] is the concentration in mol dm^{-3}).

Units for the reaction rate

The units are simple to find.

1. Write the units for concentration on the top
2. Write the units for time on the bottom

$$R = \frac{mol\,dm^{-3}}{s}$$

This can be re-written as mol dm^{-3}/s or more correctly, mol dm^{-3} s^{-1} (-1 means it was on the bottom here).

ALWAYS REMEMBER TO INCLUDE THE UNITS AFTER A CALCULATION!

This method of determining units will be used later.

Example

The concentration of I_2 in a reaction changes from 0.9 mol dm^{-3} to 0.25 mol dm^{-3}. The reaction lasts for 26 seconds. What is the rate?

The change in concentration is 0.9 – 0.25 = 0.65, time is 26 seconds.

$$R = \frac{0.65}{26} = 0.0250\,mol\,dm^{-3}\,s^{-1}$$

The concentration of phenol in a reaction increases from 0.24 mol dm^{-3} to 0.27 mol dm^{-3} in 2 minutes 22 seconds. What is the rate for the reaction?

The change is 0.27 – 0.24 = 0.03 mol dm^{-3}. The time needs to be converted to seconds. There are 60 seconds in a minute, so there are 2 x 60 seconds in 2 minutes = 120 seconds. The time is 2 minutes 22 seconds, therefore add the remaining 22 seconds = 120 + 22 = 142 seconds in total.

$$R = \frac{0.03}{142} = 2.1127\times10^{-4}\,mol\,dm^{-3}\,s^{-1}$$

It is important to remember to convert the time to seconds.

Rate of reaction

The rate of a reaction is a combination of different factors, such as reactant concentrations, the speed of reaction (*rate constant*) and how different reactants affect the rate (*the order*).

Orders of reactions

The order of a reaction is *how fast one reactant changes compared to the other reactants*. Normally, these go between 0 and 3 and can be both whole and decimals. It is unusual to find an individual reactant order greater than 3.

The order for a reactant is written like this : $[x]^y$ where *x* is the compound being looked at and *y* is the order.

The overall order for a reaction is different to the order of the reactant. It is all of the reactant orders added together. This can be a number far larger than 3. Do not get confused between them.

Initial rates of reaction.

The rate of a reaction will vary over time; the longer a reaction goes on, the less reactant there is so the slower a reaction becomes. For this reason, chemists only measure the initial reaction rate – the speed of the reaction at the beginning (roughly the first 10 to 15% of a reaction, depending on the reaction)

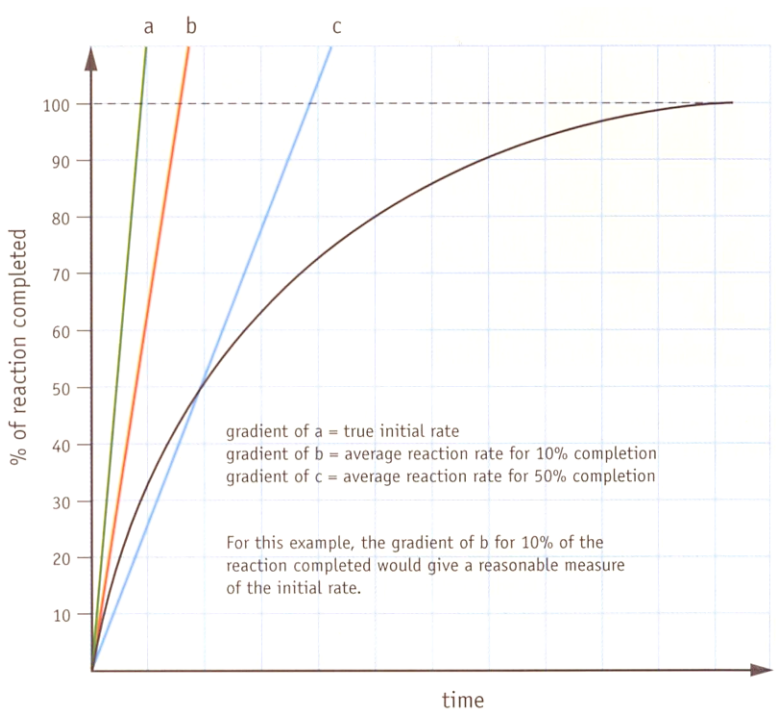


Illustration 1: Initial reactions rates. Taken from Chemistry in Context 5th Ed., Hill & Holman

In illustration 1 (*left*), a reaction is observed.

Line “a” would be if the rate of the reaction was constant

Line “b” is what would happen if the rate remained the same after a 10% completion of the reaction

Line “c” is the same, but for 50% completion.

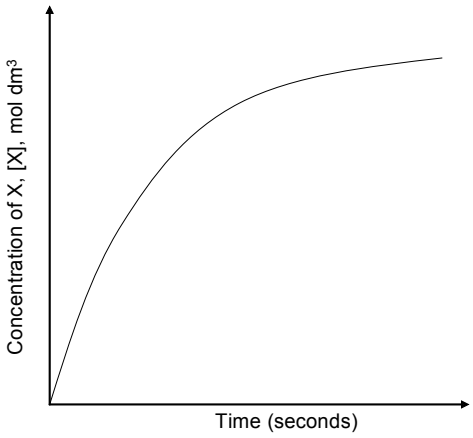
The black line is the true rate. Notice the change is much less as time increases.

At 10%, the lines for a, b and c and the black line are close enough together to take this as a good value for the initial rate.

Rate order graphs

As previously discussed, the order of a reactant has a value of (typically) between 0 and 3. For here, only orders 0, 1 and 2 need be considered.

In an experiment, it is usual to measure a concentration change over a period of time and construct a graph from the data (*a concentration – time graph, right*).

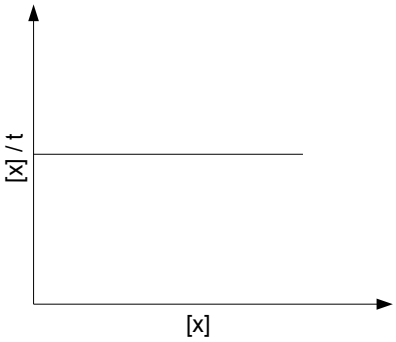


While this graph is useful, it does not give the order of a reactant directly.

To find the order from a concentration – time graph, gradients of the curve need to be taken by drawing tangents to the line (a tangent is a line which just touches the curve at a single point). A gradient is the change in y (here it is a concentration) over change in x (time).

These values are then replotted versus the concentration ($\frac{\Delta[\ ]}{t}$ on the *y* axis, concentration on the *x*) – this is the rate graph for the reactant.

<u>Zero order, $[x]^0$</u>

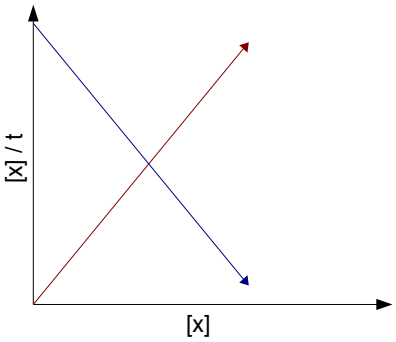


The graph for 0 order (left) shows that it doesn't matter how much the concentration changes, the rate never does.

A zero order reactant is usually in great excess (lots of it) so over the length of a reaction, the concentration of it hardly changes.

An example is the reaction between dilute acid and dilute base. Both the acid and base are diluted in water. For example, a 0.1 mol dm^{-3} solution of sodium hydroxide is 4g of the solid dissolved in roughly 996 cm^3 of water; the water is in great excess. Over the length of the reaction, this excess will not change, so is considered to be 0 order with respect to the other components.

<u>1st order, $[x]^1$</u>

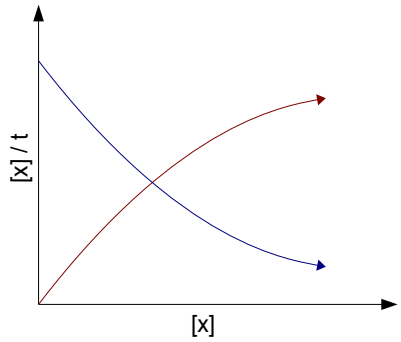


The graph for 1st order (left) shows that as the concentration increases, the rate increase by the same amount – it is proportional (symbol α) ([] α rate).

A rate can both increase and decrease. If the rate of formation of a compound is being watched, the line increases (red). If the rate of a reactant being used up in a reaction is being observed, the line decreases (blue)

2nd order $[x]^2$

It is not uncommon to be confused between a concentration versus time graph and a second order graph as they look the same. The difference though are the axes. A rate graph is always [] / t (y axis) and [] (x axis).



A second order reaction shows that the rate of change for the rate is not the same as the one for the concentration – for every change in concentration, the rate increases by the square ([] α rate^2).

If the concentration doubles (x 2), the rate increases by $2^2 = 4$. If the concentration triples (x 3), the rate increases by $3^2 = 9$ and so on.

The rate constant, k.

The rate constant is the speed of the chemical change. It is a number which is different for different reactions.

The rate equation

The rate equation is not the same as a reaction rate. They unfortunately have similar names though.

$$\text{Rate} = k\,[a]^x\,[b]^y\,[c]^z$$

where [a], [b] and [c] are the reactants. There doesn't have to be 3 reactants, there can be any number of them.

Finding the units for k.

The units for k depends on the number of reactants and their individual orders. If the rate equation is re-arranged to give k, it becomes

$$k = \frac{Rate}{[a]^x[b]^y[c]^z}$$

if x = 2, y = 1 and z = 1 and the units for each and put in (Rate = mol dm^{-3} s^{-1}, concentration = mol dm^{-3}), then it looks like this

$$k = \frac{mol\,dm^{-3}\,s^{-1}}{(mol\,dm^{-3})^2 \times mol\,dm^{-3} \times mol\,dm^{-3}}$$

$$k = \frac{mol\,dm^{-3}\,s^{-1}}{mol^2\,dm^6 \times mol\,dm^{-3} \times mol\,dm^{-3}}$$

One of the mol dm^{-3} on the bottom will cancel out the mol dm^{-3} on the top leaving

$$k = \frac{s^{-1}}{mol^2\, dm^6 \times mol\, dm^{-3}}$$

$$k = \frac{s^{-1}}{mol^3\, dm^{-9}}$$

k is therefore $mol^{-3}\ dm^9\ s^{-1}$

Again, different reactions and differing number of reactants will change the units for k. It is important that this calculation is carried out for **each** reaction.

Finding the order for a reaction from a data table

Data tables normally come in one of two types : complete and incomplete

Experiment	[c]	Rate
1	0.1	1 x 10^{-3}
2	0.3	3 x 10^{-3}
3	0.6	6 x 10^{-3}

Complete

Experiment	[c]	Rate
1	0.1	1 x 10^{-3}
2	0.2	
3		4 x 10^{-3}

Incomplete

Some tables will have multiple reactants on them, they are all handled in the same way.

Using the complete table

To find the order for [c], look first for two concentrations where they have doubled or if that is not available, tripled (gone up by 3)

If experiments 2 and 3 are taken (concentration has gone up by doubling), the order can be found by comparing the rates. The concentration has gone up by multiplying by x2 – the rate has gone up by the same (3 x 10^{-3} x 2 = 6 x 10^{-3}).

Another way of saying it has doubled is to divide the rate from experiment 3 by the rate from experiment 2 (6 x 10^{-3} / 3 x 10^{-3} = 2) then compare the division answer to the amount the concentration has gone up by.

If the concentration and rate go up by the same amount, it is 1st order.

If experiments 1 and 2 are taken (concentration has gone up by x3), then if the rate from experiment 2 is divided by the rate from experiment 1 (3 x 10^{-3} / 1 x 10^{-3} = 3) and compared, they are the same, so are first order.

It makes no difference which experiments are used as long as the same procedure is used.

For concentrations which don't change by “easy” numbers

Unfortunately, experiments don't always have simple numbers, so the increase (or decrease) is not always clear (below)

Experiment	[c]	Rate
1	0.1331	1.17×10^{-3}
2	0.2903	2.33×10^{-3}
3	0.4107	4.68×10^{-3}

Again though, the increase can be found by dividing the concentration from 2 by the concentration from 1 (0.2903 / 0.1331 = 2.1811) – roughly the concentration has doubled between experiments 1 and 2, but what about the rate?

Divide the rate from experiment 2 by the rate from experiment 1 (2.33×10^{-3} / 1.17×10^{-3} = 1.9915). The rate has roughly doubled.

As the concentration and rates have gone up by roughly the same amount (x 2), the order for [c] is 1.

For tables with multiple reactants.

This can be treated in the same way as for a table with a single reactant with an exception. When comparing concentrations of the first reactant, the other reactant concentrations **must** stay the same

Experiment	[A]	[B]	Rate ($\times 10^{-3}$)
1	0.1	0.2	3
2	0.2	0.2	6
3	0.3	0.1	2
4	0.3	0.2	8

In the example above, to find the order of [A], only the experiments where [B] remains unchanged can be used. The same apply for finding the order of [B] – only those experiments where [A] remains unchanged can be used.

Special numbers

In the above example, between experiment 1 and 2, the concentration of [A] is doubled (0.2 / 0.1 = 2) and the rate is (6 / 3) 2. As the numbers are the same, it is 1st order.

Between experiment 3 and 4, the concentration of [B] is doubled (0.2 / 0.1 = 2) and the rate is (8 / 2) 4.

4 is a special number – it is more accurately called a square number ($2^2 = 4$). There is a series of these numbers – 9 (3^2), 16 (4^2), 25 (5^2), 36 (6^2), 49 (7^2) and so on. When these numbers are seen, the reaction is 2nd order.

Finding the rate constant

If the table on the page before this is used, the rate constant can be found by substituting in the values of any of the experiments into the rate equation. The constant will be the same for all of the experiments.

Take experiment 4. [A] = 0.3, [B] = 0.2 and the rate is 8×10^{-3}. B is second order, A is first order

$$8 \times 10^{-3} = k\,[0.3]^1\,[0.2]^2$$

$$k = \frac{8 \times 10^{-3}}{0.3 \times 0.2^2}$$

$$k = \frac{8 \times 10^{-3}}{0.3 \times 0.04}$$

$$k = 0.6667$$