

3.2 More than one species involved

In the previous section we assumed that only one reactant specie A is involved in the reaction. This is of course too restrictive; in reality we much more often encounter reactions involving more than one species. This implies that the data analysis will be more complicated. For example, how can we determine the orders n and m when the rate law is given by

$$\text{Rate} = k[A]^n[B]^m \quad (35)$$

which means that the differential equation now contains two unknown time-dependent variables $[A]_t$ and $[B]_t$? Two representative strategies to work around this problem are the **isolation method** and the **initial rate method**.

3.2.1 Isolation Method

Suppose that we have prepared a large excess of one of the reactants, say A, compared to B. That is, the initial concentrations are such that $[A]_0 \gg [B]_0$. In this case, we may consider that $[A]$ will stay large in the course of the reaction so that its concentration change may be neglected approximately.

$$[A]_t \simeq [A]_0 \quad (= \text{constant})$$

Then the rate law will be approximated as

$$\text{Rate} \simeq k[A]_0^n[B]^m \equiv k'[B]^m$$

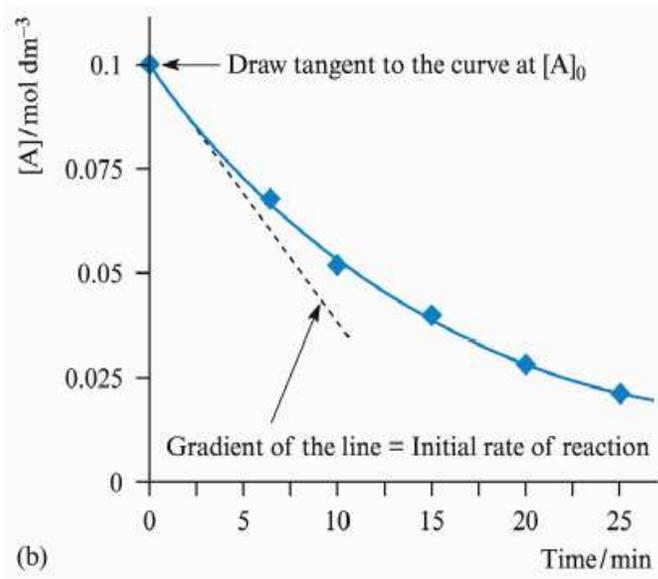
where k' is defined by $k' = k[A]_0^n$. In this way, the unknown variable $[A]$ has been (approximately) eliminated from the rate law. Now we can apply the methods in the previous section in order to determine the order m and the new rate constant k' .

In the next set of experiments, we prepare a large excess of B compared to A, and repeat similar procedure to determine the order n . Finally, from n and k' we determine the original rate constant k .

In this way, the contributions from each of the reactant species can be **isolated** one by one.

3.2.2 Initial Rate Method

Another method to avoid the complication coming from the involvement of multiple species is to consider only the **initial rates** (rates at $t = 0$).

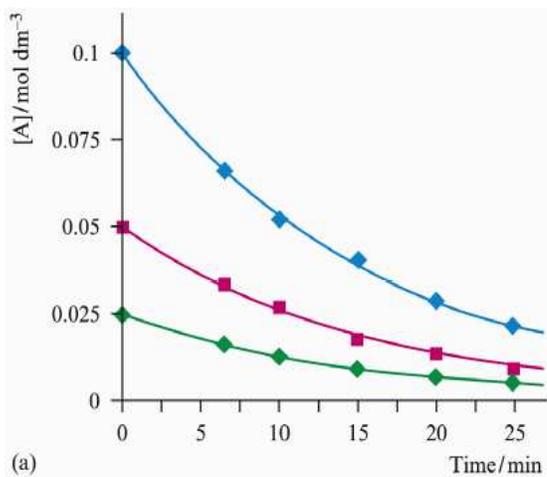


The essential point is that the concentrations of all the reactant species are precisely known at $t = 0$ as we have prepared them.

$$(\text{Initial Rate}) = k[A]_0^n[B]_0^m$$

Therefore, we do not have to be concerned with the complicated changes of the concentrations of the multiple species that will occur in $t > 0$.

For example, to determine the order n , we measure the initial rate of the decay of $[A]$, that is, $-d[A]/dt$ at $t = 0$. We repeat this for different initial concentrations $[A]_0$ as shown in the diagram below. It is important to keep $[B]_0$ to the same value in this series of experiments. (Otherwise we will mess up the analysis!)



Example: The following data have been obtained for a reaction $A + B \rightarrow P$.

$[A]_0$ / mol dm ⁻³	$[B]_0$ / mol dm ⁻³	Initial Rate / mol dm ⁻³ s ⁻¹
0.2	0.2	5×10^{-5}
0.4	0.2	1×10^{-4}
0.2	0.6	1.5×10^{-4}

Find the orders with respect to A and B and the rate constant k .

As illustrated by this Example, the analysis is easy when the orders are immediately found to be simple integers. For otherwise and more general cases, the following procedure is useful.

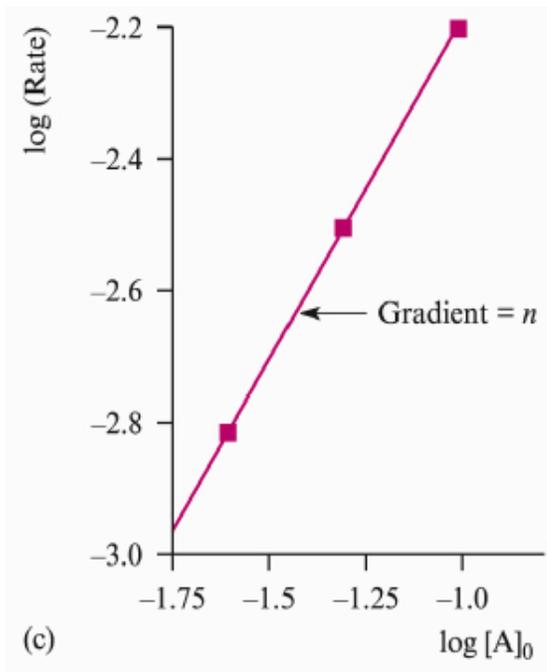
By taking the logarithms of both sides of

$$(\text{Initial Rate}) = k[A]_0^n[B]_0^m$$

we obtain**

$$\log(\text{Initial Rate}) = \log k + n \log[A]_0 + m \log[B]_0$$

Therefore, the rate constant k and order n can be determined from a plot of $\log(\text{Initial Rate})$ against $\log[A]_0$. Note that $[B]_0$ should be kept to the same value in this analysis. By exchanging A and B, we can determine the order m from another set of experiments.



** Remember that $\log XY = \log X + \log Y$ and $\log X^n = n \log X$. Here the base can be anything, so we can use either \log_{10} or \ln depending on our particular conveniences.