Kinetics Summary

Reaction rates:

Defined as rate = $\dfrac{d[A]}{dt}$

Differential rate laws:

- often just referred to as the 'rate law'
- gives the relationship of the rate to the concentration
- use initial rate method to determine

$$rate = k[A]^n$$

where k = rate constant (be careful with units)
   n = order of the reaction with respect to A

- The order of the overall reaction is the sum of the order with respect to each reactant
- *Order does not follow stoichiometry as at this point you do not know the mechanism.*

Integrated rate laws:

- gives relationship between concentration and time.

1st order:

$$\ln[A] = -kt + \ln[A]_0$$
Plot this as a straight line with slope = -k

$$t_{1/2} = \frac{\ln 2}{k}$$

2nd order:

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

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

If you're asked to determine the rate law but aren't told whether it is first or second order, you have to plot both and see which gives a straight line.

If you have a reaction with more than 1 reactant, the integrated rate law is complicated. You can simplify it to a pseudo-first-order by running the reaction so only one reactant changes its concentration significantly.

eg. $A + B + C \rightarrow$ products
       rate $= k[A][B]^2[C]$

if $[A]_0 = 1 \times 10^{-3}$ M
       $[B]_0 = 1$ M
       $[C]_0 = 1$ M
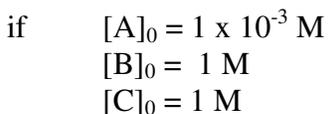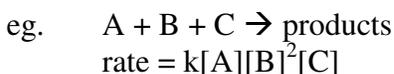
Only [A] will change significantly so we can assume $[B] = [B]_0$ and $[C] = [C]_0$, so the rate law can be written as:
$$Rate = k^{'}[A]$$
Where $k^{'} = k[B][C]$ (as [B] and [C] are constants)

A plot of ln[A] vs t will give you a straight line with a slope of $-k^{'}$, and as $[B]_0$ and $[C]_0$ are known, k can be calculated.

Reaction Mechanisms:

Most reactions don't occur as written, rather as a series of elementary steps. You are (or definitely should be!) familiar with this from organic.

If you break a reaction down to its elementary steps, you can find the overall rate law from the rate determining step (a reaction can't go faster than that step, so it controls the rate), which can be determined from its molecularity.

Molecularity: how many species must collide for the reaction to occur.

$A \rightarrow$ products	unimolecular	1st order
$A + B \rightarrow$ products	bimolecular	2nd order
etc		

➡ As you are now dealing with elementary steps, the stoichiometry can be used to determine the rate… but *only for elementary steps!*

Two things must be true:
1. Elementary steps must add together to give the overall reaction
2. The rate determined from the mechanism must agree with the overall rate law.

➡ Overall rate law must not have intermediates in it!

You can make a steady state approximation for the intermediates, but you should always note that you have made that assumption.

Arrhenius equation:

Collision model of kinetics:
- species must collide for a reaction to occur
  - o require specific orientation
  - o sufficient energy (E_a)

From this we can represent k as:

$$k = Ae^{\frac{-E_a}{RT}}$$

where A is a "frequency factor" and takes the orientation and frequency of collisions into account.

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Catalysis:

-lowers the activation energy, thus speeding up the reaction.