Chapter 6: Kinetics – fast facts

6.1 Collision theory and rates of reaction

> The greater the probability that molecules will collide with sufficient energy and proper orientation, the higher the rate of reaction.

- Rate of reaction = decrease in concentration of reactants or increase in concentration of products per unit time
- Units of rate of reaction = $mol\ dm^{-3}\ s^{-1}$.
- Concentration changes in a reaction can be followed indirectly by measuring changes in mass, volume, or absorbance.
- Rate of reaction at time t = gradient of tangent to curve of [R] or [P] vs time, at time t.
- Absolute temperature is a measure of average kinetic energy.
- Activation energy, E_a, is the minimum KE particles must have in order to react.
- Collision theory: collisions between reactant particles will lead to reaction when:
    - i   the particles have KE > E_a *and*
    - ii   the particles have the correct collision geometry.
- The Maxwell–Boltzmann distribution shows the number of particles in a sample with a particular value of kinetic energy. The area under the curve represents the number of particles. It can be used to illustrate the effects of different factors on the rate of reaction.
- The effects of temperature, concentration, pressure, particle size, and catalysts on the rate of reaction can all be interpreted in terms of the collision theory.
- Catalysts speed up reactions by providing an alternate reaction route with a lower activation energy, but are not themselves chemically changed by the reaction. Catalysed reactions form a transition state of lower energy than the uncatalysed reaction.
- Enzymes are biological catalysts.

16.1   Rate expression and reaction mechanism

- Rate expressions can only be determined empirically and these limit possible reaction mechanisms. In particular cases, such as a linear chain of elementary reactions, no equilibria, and only one significant activation barrier, the rate equation is equivalent to the slowest step of the reaction.
- For a reaction with reactants A and B:

    rate = $k\ [A]^m\ [B]^n$
    where k = rate constant
    m and n are the orders of reaction with respect to A and B respectively
    $m + n$ = overall order of reaction.
- The value of k, the rate constant, depends on the particular reaction and on the temperature.
- The units of k depend on the order of the reaction.
- Constant half-life $\Rightarrow$ first-order reaction.
- Many reactions proceed in a series of small steps known as elementary steps.
- Molecularity = the number of reactant particles taking part in an elementary step.

- The rate-determining step = the slowest step in the reaction. It is the step with the highest activation energy.
- The order of the reaction is determined by the molecularity of the rate-determining step.
- Rate equations can *only* be derived from empirical data. The order of reaction with respect to a particular reactant can be determined by following the change in rate of reaction as the concentration of that reactant is changed.
- Concentration–time and rate–concentration graphs can be used to represent zero-, first-, and second-order reactions.
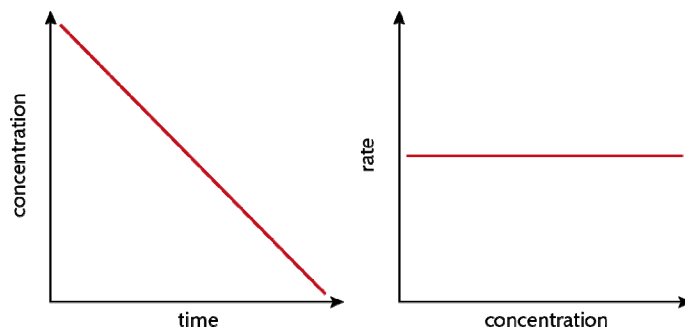
- A proposed mechanism for a reaction must be consistent with:
  - i   the overall reaction's stoichiometry
  - ii   kinetic data derived from experiment

16.2   Activation energy

The activation energy of a reaction can be determined from the effect of temperature on reaction rate.

- The Arrhenius equation (given in section 1 of the IB data booklet) shows the temperature dependence of the rate constant.
- The Arrhenius plot, ln k versus $1/T$, can be used to calculate the activation energy E_a. The gradient of the line in the Arrhenius plot = $-E_a/R$
- The Arrhenius equation shows that increasing the temperature increases the value of the rate constant k. But the extent of this increase depends on the value of E_a for the reaction. Reactions with higher values for E_a have a higher temperature dependency of k than reactions with lower values for E_a.

Get it straight

- All substances at the same temperature have the same average kinetic energy.
- The rate equation *cannot* be predicted from the overall stoichiometry of the reaction.
- The units of the rate constant k vary – they depend on the order of the reaction.
- Activation energy is not temperature dependent.