Chapter 11

Kinetics

The first topic of year 11 is our first real foray into the world of how fast reactions happen. This expands on work done at GCSE by making quantitative use of data to work out equilibrium constants and activation energies and also to inform ideas about the mechanisms behind reactions.

11.1 Rate equations

The rate of a reaction is normally measured as the rate of change in concentration (or less commonly pressure) of one reactant. For instance, the rate of change of concentration of hydrochloric acid would be given the symbol r_{HCl}.

We are introduced to a generic rate equation for the reaction

$$x\mathrm{A} + y\mathrm{B} \longrightarrow \text{products} \tag{11.1}$$

as $r_{\mathrm{A}} = k[\mathrm{A}]^a[\mathrm{B}]^b[\mathrm{C}]^c$.

- r_{A} is normally expressed is units of mol $\mathrm{dm^{-3}s^{-1}}$.

- Note that substance C is not even a reactant in the chemical equation.

A denotes the concentration of species A and so on. The usual units for concentration are mol $\mathrm{dm^{-3}}$.

- a, b, and c are called the *order* of reaction with respect to A, B and C respectively. The sum of these individual orders is called the *overall order* of the reaction. The orders can only be determined experimentally - you are not expected to know them. We usually only deal with zero, first and second order reactions. Note that a, b and c are not x or y.

- k is called the *rate constant* and can be useful for comparing rates of the same reaction at different temperatures. The units of k depend on the overall order of the reaction.

11.2 Measuring rates

There are many ways of monitoring the rates of reactions. We can see variations in concentrations if we *quench and titrate* at particular times; *colorimetry* allows us to monitor the formation or disappearance of a coloured substance; *dilatometry* allows us to see how the volume of the reacting mixture varies over time; if the reaction involves ions then changes in *electrical conductivity* enable us to monitor the rate; if a *gaseous* substance is produced we can measure the volume of gas generated (you probably did this at GCSE).

Typical graphs

You should be able to recognise typical graphs for zero, first and second order reactions. These are sketched for you. There are two types - concentration against time and rate against concentration.

Zero order graphs will give a straight line. The concentration will vary linearly with time, and the rate will not change with concentration (as this is what zero order means).

First order reactions will have a rate which varies in direct proportion to concentration. The Concentration will fall with time, giving a constant half life. In questions you may be asked to measure successive half-lives, and in these cases you *must* measure successive half-lives, not just any group of half-lives you like.

Second order reactions will have a rate which depends strongly on concentration - the graph will be a curve. A graph of concentration against time will be a steep curve with increasing successive half-lives.

11.3 Mechanisms

Rate equations can tell us whether or not the slow part of a reaction mechanism involves 1 or 2 species. The slow part of a reaction is called the *rate determining step*. Even seemingly simple reactions may happen in many parts and so there are many possible mechanisms. Rate data can only tell us what is wrong, not what is right, in our study of mechanisms. If our mechanism contains two particles in the rate determining step, but our rate equation is first order, we can be pretty sure that we're wrong. You should be familiar with the S_N1 and S_N2 mechanisms for nucleophilic substitution as examples of using rate data to elucidate possible mechanisms. You should also be able to describe the change in substitution mechanism from primary halogenoalkanes to tertiary halogenoalkanes in terms of the relative stabilities of the intermediates formed.

11.4 Temperature

Temperature can have a profound effect on reaction rates. This effect is usually quantifiable and studying changes in rate as a function of temperature can enable us to work out activation energies and rate constants.

The reason for the strong dependence of rates on temperature can be seen if we consider the *collision theory* for kinetics. For reactions to happen the reactants must collide and they must have a certain energy, the *activation energy* E_{A}, when they collide. If we raise the temperature we increase the average kinetic energy of the particles in the mixture. This means that we increase the probability of particles colliding and the proportion of collisions which happen with energy greater than E_{A}. Magical maths leaves us gawping with astonishment at the *Arrhenius equation*:

$$\ln k = A - \frac{E_{\mathrm{A}}}{RT} \tag{11.2}$$

Equation 11.2 is a powerful tool for working out activation energies, if you can spot that it can be described as a straight line like $y = c + mx$

$$\ln k = A - \frac{E_{\mathrm{A}}}{R}(1/T) \tag{11.3}$$

in which ln k would be the y axis value and $(1/T)$ the x axis. The gradient of our straight line is $-\frac{E_{\mathrm{A}}}{R}$ in which $R = 8.31\mathrm{J\ K^{-1}\ mol^{-1}}$ is the gas constant. E_{A} is measured in J $\mathrm{mol^{-1}}$ and T is the absolute temperature - the temperature in kelvin[1]. Plotting a graph of ln k against $1/T$ (in kelvin) or ln rate against $1/T$ should give a straight line graph from which you can work out E_{A}. A in equation 11.2 is sometimes called a 'steric factor' and is supposed to describe the chance of the reacting molecules meeting at the correct orientation and so on. Really it's a mathematical fiddle to account for all the other things which could affect the chance of reaction.

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[1] **Absolute temperature** I don't know what the highest possible temperature is. Probably pretty high. I know however that the coldest (theoretically) possible temperature is 0 K. This is equal to -273.16 °C. This theoretical temperature is the point at which all molecular motion and disorder are zero. If you do physics you may have met Charles' law, which states that this is the temperature at which an ideal gas has no volume.

11.5 Catalysis

The idea of a catalyst will be familiar to you from descriptions of enzymes in biology and from some reactions you've met in chemistry. In this topic we briefly investigate different catalysts and see that some substances catalyse some reactions but not others. This is simply a restatement of the specificity of catalysts. You will know that biochemical reactions are catalysed by specific enzymes and the same is true in the wider chemical world. Finding a suitable catalyst for a process can be a multi-million dollar discovery, but is an enormously hit-and-miss affair. You should be aware of the meanings of *heterogeneous* and *homogeneous* catalysts and be able to give examples of each.

You should be able to regurgitate the accepted description of how catalysts speed up reactions (things which slow down reactions are normally called inhibitors). The catalyst provides an alternative route for the reaction which has a lower activation energy than the uncatalysed route. (This in turn means that a greater proportion of the collisions are successful at a given temperature and so the rate increases.) Catalysts are not *permanently* involved in reactions - they may change during the course of the reaction, but if they do they should be regenerated at some point. We have looked at a few examples of this.