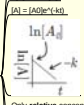
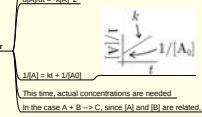
Kinetics

- **Getting data**
  - How to get concentration vs. time measurements
  - **Light absorbance**
    - Molecules absorb light at characteristic frequencies
    - We often use UV (1000 - 200 nm)
    - Need certain groups present
    - $I = I_0 e^{-\varepsilon c l}$ Beer's law
      - I0 is the **intensity** of the **light in**
      - I is the **intensity** of **light out**
      - l is the **path length**
      - c is the **concentration**
      - e is the **extinction coefficient**
        - Depends on species absorbing
        - And wavelength of light
    - $\ln(I_0 / I) = \varepsilon c l$ Can be written as
      - ln(I0 / I) = A (**absorbance)**
      - This is what's usually read out of the meters
    - Calibrate against a range of known concs, unless first-order, in which case relative is enough
    - Very useful
      - Non-invasive
      - Rapid
      - Can easily be automated
      - But rather broad, so can overlap
  - **Conductivity**
    - Resistance of a solution depends on the presence of ions therein
    - **Conductance (= 1/Resistance)** is **directly proportional** to the **concentration of ions**
    - If a reaction changes the number of charge species **OR** the identity of the charged species, this can be monitored
    - Only really good for first order - relation between conductance and concentration is rather involved
    - Easy and non-invasive with modern devices
  - **Gas pressure**
    - nV = p/RT
    - At constant temperature, pressure is directly proportional to concentration
    - We want the **partial pressures** (which sum tot he total pressure), and this can be done using dissociation constants
      - Each partial pressure follows the ideal gas law
  - **Electrochemistry**
    - EMF of a cell depends on the concentration of the species in the cell
    - By choosing appropriate electrodes, we can monitor a wide range of ions
    - Use the NERNST equation
  - **Chemical methods**
    - Can be titrations or the like
      - Take an alliquot
      - Quench [cool, take out a chemical]
    - Can use a GC w/ or w/out a mass spec
      - GC column separates chemicals, can look @ peaks to find concentrations
      - Mass spec can be used to identify them
  - **Fast reactions**
    - Continuous flow
      - Need to be mixed, and measured quickly
      - Reagents are mixed by two tubes coming together and continue flowing
      - Distance down tube is proportional to time since mixing
      - Reaction can then be monitored at leisure
      - Usually monitored by spectrophotometry
      - Need lots of reagents, though
    - *Afterglow*
      - To monitor concentration of O
      - Reacts with NO to form NO2*
      - Rapidly emits a green photon, which can be detected using a photomultiplier
      - NO2 reacts back with O to form NO again
    - Stopped flow
      - Like continuous flow
      - Only happens a certain amount of time, then end plunger hits end
      - Then measure (in real time - quickly!) at a point where mixing is complete
      - Need little reagent
      - Slightly faster time resolution than continuous flow
    - Flash photolysis
      - Intense flash of light used to create reagents (e.g.: radicals)
      - No problem of mixing, caus' created *in-situ*
      - However, rapid detection needed
- **Reaction rate theories**
  - What happens in a reaction
    - Molecules A and B are far apart
      - Largely independent of each other
      - Held together in a certain way by electrons in MOs
    - They approach
      - Start interacting with one another
      - MOs being to interact (usually HOMO + LUMO)
      - As a result, bonds begin to be made and broken - new MOs are made
    - The end
      - Products begin to get their identity and move apart
      - Molecules are now discrete again
  - Potential energy surfaces
    - In theory, using MO theory, can calculate PE of molecule or any arbitrary arrangement of nuclei and electrons
    - This will depend on the precise arrangement of all the species
    - A **potential energy surface** gives the **energy** of the system as a function of **all the atoms in the system**
      - The **stable molecules** (products or reagents) exist as **local minima** on the surface
    - This will be a function of a very large number of distances and angles - it'll be **multidimensional**
    - We can imagine a reagent as species "moving" along that surface
  - Reactions
    - To go from one minimum to another, energy must be **put in**
    - The one involving the least expenditure of energy is favoured
      - This is because the extra amount of energy that needs to be put in is the difference in energy between the reagents and the transition state
      - Only a small fraction of molecules will have that energy, given by the **Boltzmann distribution**
      - As this is an **exponential function of energy** , increasing the energy by even a small amount reduces greatly the number of molecules available with that energy
      - Therefore, nothing but the lowest energy pathway happens
    - The **highest** point in that pathway is called the **transition state**
      - Molecules exist in **potential energy minima**
      - If they're slightly distorted, there's a restoring force
      - For transition states, there is no restoring forces, so it collapses back to reagents or to products
    - The minimum energy pathway is called the **reaction coordinate**
      - It consists of a range of motions
      - Plotting the reaction coordinate against the energy gives the **reaction profile**
  - Collision theory
    - Assumptions
      - Molecules come together by making collisions
      - Particles much smaller than distance between them
      - Elastic and random collisions
    - Average speeds and relative speeds between particles is
      - $\bar{c} = \sqrt{\frac{8kT}{\pi m}}$
      - $\bar{c}_{rel} = \sqrt{\frac{8kT}{\pi \frac{m_1 + m_2}{m_1 m_2}}}$
    - From that, we can work out rate of collision
      - Proportional to the sum of the **collision section** , the two concentrations and the relative velocity above
      - Collision section given by PI * (ra + rb)^2
      - $Z = c_A c_B \sigma^2 \sqrt{\frac{8k_B T}{\pi \mu}}$
      - However, all collisions don't lead to a reaction - orientation is important
      - This is a big weakness of the theory
    - Considering the proportion of molecules that have an energy Ea, and assuming that all collisions involving these give a product, we can work out an expression for rate
      - $r = \frac{1}{N_A} Z e^{-E_A / kT}$
    - By comparing with the rate equation, this gives us a value for k
    - **Comparing with the Arrhenius equation**
      - Gives us a value for the pre-exponential factor
      - Collision rate per unit concentration of reagents
      - Proportional to T^(1/2), but very small compared to the temperature-dependence of the exponential
    - **Comparing with experiment**
      - We can find r using properties of viscosity and effusion
      - It turns out that the collision theory values of A are usually **overestimates**
      - This is understandable - we have assumed that all collisions will lead to a reaction
      - The **steric factor** is defined as *p = Aexperimental / Acollision theory*
      - Most of the time, it's much smaller than 1, but sometimes larger - the molecules interact over greater distances than would be expected
- **Rate laws**
  - **Introduction**
    - There **rate** of a reaction is dC/dt
    - Slope of the graph of concentration against time
    - Common to express concentrations in **molecules** per unit volume
    - The rate equation can be defined in terms of any reagent or product as
      - $r = \frac{1}{v_A} \frac{d[A]}{dt}$
      - va is the stoichiometric coefficient of chemical A
      - Given a **positive sign** for **products**, **negative** for **reagent**
  - Rates depend on the concentration of species
    - The relation can often be expressed as a **rate law**
    - Some simple rate laws are of the form r = k [A]a[B]b...
      - the a, b, c... are the **orders** of the reaction with respect to each of the reagents
    - A **first order rate law** is one in which the concentration is raised to the power of 1
      - Same with **second**, etc...
      - The **units** of the rate constant give a clue as to the order of the rate equation
    - Important because
      - Can be used to predict rate given concentrations
      - Can tell us something about the mechanism
      - Separate concentration dependence from underlying effects (rate constant)
  - Temperature affects things
    - Rate constants vary with temperature
    - Usually, increases with temperature
      - 2NO + O2 --> 2 NO2 is an exception
    - Experimentally, rate constant is found to vary according to the **Arrhenius equation**
      - $k(T) = A e^{-E_A / RT}$
      - Ea is is **activation energy**
      - A is called the **pre-exponential factor**
        - Usually independent (or very weakly dependent) on T
      - Can be identified as the **maximum possible rate constant**
        - When RT >> Ea
    - We can manipulate the equation into a linear form
      - $\ln k = \ln A - \frac{E_A}{R} \frac{1}{T}$
    - Even processes that aren't exactly Arrhenius-like might look it because limits in the accuracy of measurements
  - The **equilibrium constant** is the ratio of the rate constants of the forwards and reverse reactions (rf / rr)
    - The **rate** of the forward and backwards reactions will be the same, but not the **rate constants**
    - This is because rate also depends on the concentration of reactants
  - **Experimental determinations**
    - Look at data, suggest rate law and see if it's consistent
    - **First order**
      - r = k[A]
      - d[A]/dt = -k[A]
      - [A] = [A0]e^(-kt)
      - 

      - Only **relative** concentrations are necessary for first order reactions
        - In other words, the rate-per-conc is the same at any time
      - Sometimes want to find the rate of change of reagents in terms of products, or vice-versa
        - In which case, express one in terms of the other
        - By noting that A --> 2B means that [A] = [A0] - 1/2[B]
    - **Second order**
      - r = k[A]^2
      - d[A]/dt = -k[A]^2
      - 

      - 1/[A] = kt + 1/[A0]
      - This time, actual concentrations are needed
      - In the case A + B --> C, since [A] and [B] are related, can solve
    - **Isolation method**
      - We make measurements with one reagent in great excess (more than 50 times that of the other)
      - The concentration of this reagent is then effectively constant
      - The reaction is then **pseudo-first-order** and we get a **pseudo-first-order rate constant**
        - Can find the *real* rate constant using a plot
      - Problems
        - Large excess might make reaction inconveniently fast
        - Could alter mechanism of a complex reaction
    - **Differential method**
      - If we have something of the form r = k [A]^n
      - Can plot ln(r) against ln[A]
      - However
        - Much harder to measure rates
        - Has to be done as slope of conc. vs. time
    - **Half-life**
      - Time taken for concentration of specified reagent to fall to half of its value
      - For a first order, t(1/2) = k / ln(2)
      - Independent of concentration - wherever we take it, it'll take the same time to halve
      - Better to find k using the graphing method, but this can be useful
      - For a second order reaction, t(1/2) = 1/k * 1/[A0]
      - Can measure the **extent** of the reaction by **how many half-lives** have passed since it's started
    - **Comparing rates**
      - For first order reactions, the half-life/rate constant gives a good indication of how fast the reaction is
      - For other rates laws, concentration has to be taken into account

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