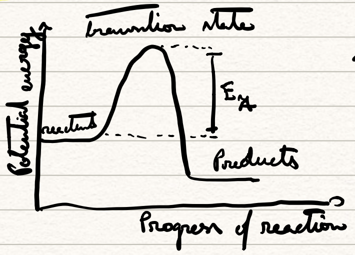
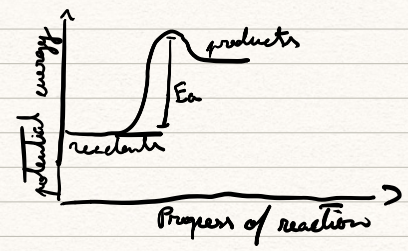
- Essential ideas
  - The greater the probability that molecules collide with sufficient energy and proper orientation, the higher the rate of reaction.
- 6.1 Collision theory and rates of reaction
  - Chemical kinetics regard
    - How quickly a reaction will take place
    - The condition required for a specific reaction rate
    - Propose a reaction mechanism
  - Collision theory
    - Simple collision theory states that before a reaction can occur, the following requirements must be met.
      - The reactants (ions, atoms, or molecules) must physically collide and come into direct contact with each other.
      - For many reacting molecules, steric factors are involved: The molecules must collide in the correct relative positions so their reactive atoms or functional groups are aligned.
        - The molecules must be oriented properly so that they can react.
        - Known as collision geometry
    - Low concentration will mean that there will be few collisions while at higher concentrations there will be more collisions that occur.
    - If molecules have sufficient energy to overcome the activation energy barrier must collide with the correct orientation for the reaction to occur. The correct orientation would be the molecules should hit where the molecule is held together (middle molecule).
      - Activation energy is given by E_A.
        - Definition of E_A: The activation energy is the energy required to overcome repulsion, to start rearranging the bonds to produce the product molecules.
    - Activation energy is the minimum amount of kinetic energy that colliding particles must posses for a collision to result in a reaction.
    - Activation energy varies with different chemical reactions. They control how the rates of reaction and how a reaction responds to a change in temp. (change in E_{KE}).
      - Fast reactions are associated with low values for their energy barriers (E_a) while slow reactions are associated with high energy barriers (high E_A).
      - If E_A isn't achieved, or the geometry isn't correct, then the reaction won't occur.
    - Graphs
      -

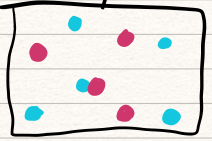


← Exothermic energy profile

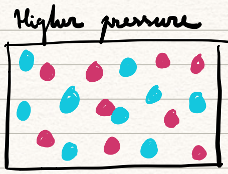


← Endothermic energy profile

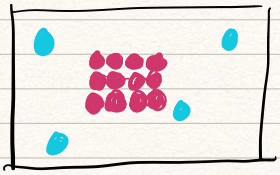
- Factors affecting the rate of reaction
  - Essentially, any change in conditions that would increase the collision frequency would result in a higher rate of reaction.
    - these changes would result in the particles of the reaction colliding with each other more often as an increase in # of particles or an increase in the kinetic energy would result in an increase in the rate of reaction.
- Concentration
  - The number of particles present in a particular volume of solution.
    - Expressed in $mol\,dm^{-3}$
  - Its generally found that increasing the concentration of the reactants will increase the rate of reaction.
    - The increase in the rate of reaction is due to the fact that increasing the concentration will mean that there will be an increase in the number of collisions between the reactants, increasing the amount of successful collisions.
    - In most cases, doubling the concentration will double the rate of reaction.
  - You'll always have the highest rate of reaction at the very start of the reaction, as there are the most amount of reactants at the start.
    - As the reaction continues, the rate of reaction will decrease as the concentration of the reactants will decrease.
- Pressure
  - When one or more of the reactants are gases an increase in pressure can lead to an increase in rate of reaction.
    - The increase in pressure means that the particles are forced closer together, which increases the collision rate and increases the rate of reaction.
  - Since liquids and solids undergo little change in volume when the pressure is increased, the rates of reaction aren't really affected by pressure.
  - Diagram
    - Both reactants are gases.
      - lower pressure



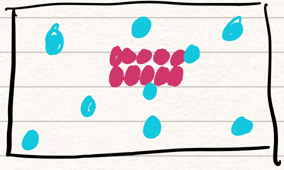
Higher pressure



    - One reactant is a solid
      - lower pressure



Higher pressure



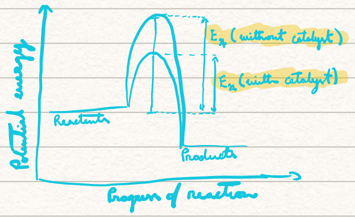
- Temperature
  - Increasing temp will mean that the particles in the substance will travel a greater distance in a given time meaning that they'll be involved in more collisions meaning that they'll increase the rate of reaction.
  - More importantly though, an increase in the temp will mean that more particles in the reaction mixture will have the required activation energy for a reaction to occur.
    - Frequently, an increase in 10°C will double the initial rate of reaction.

- Holds 'generally true' for reactions with an E_a of $\simeq 50\ kJ\,mol^{-1}$.

- Particle Size
  - When one of the reactants is a solid, the reaction takes place on the surface of the solid.
    - If the solid is broken up into smaller chunks, then the rate of reaction will increase as more particles from the solid will be able to react with the second reaction mixture.
    - This effect is similar to that of increasing concentration as it means that there will be more reactant particles that will collide and increase the rate of reaction.
- Light
  - Some reactions are greatly increased by exposure to sunlight. This is because the visible or UV light energy breaks bonds in the reactant molecules.
    - E.g Silver nitrate, nitric acid, & hydrogen peroxide are all photosensitive and undergo partial decomposition (forming radicals, often in form of reactive atoms) in presence of sunlight.
- Table
  -

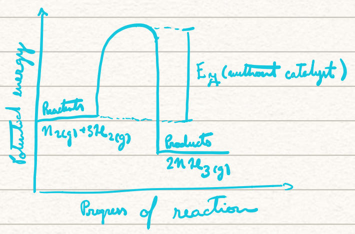
Factor	Reactions affected	Change made in conditions	Usual effect on initial rate of reaction
Temp	All	Increase (Increase by 10k)	Increase (Approx. doubles)
Concentration	All	Increase (doubling concentration)	Increase (unless zero order) (Usually exactly doubles (if first order))
Light	Generally those involving reactions of mixtures of gases, including the halogens (p.17)	Reactions in sunlight or UV light	Very large increase
Particle size	Reactions involving solids and liquids, solids and gases or mixtures of gases	Powdering solid, increasing surface area.	Very large increase

- Catalyst
  - Definition: A catalyst is a substance that can increase the rate of reaction by providing an alternative pathway that doesn't require as much energy as the non-catalysed pathway. They remain chemically altered during the reaction.
  - They're frequently transition metals or their compounds.
  - They provide an alternative pathway that doesn't require as much energy.
  - There are two types of catalysts, homogeneous and heterogeneous.
  - Increase rate of reaction of both forward and backward reaction, meaning that the equilibrium position isn't altered.
    - This is known the principle of microscopic reversibility.
    - It doesn't increase the yield of products, it only decreases the amount of time for a reaction to go to completion or reach equilibrium (rate of their production is increased).
  - Catalyst Graph
    -



- Biological catalysts are known as Enzymes, they consist of proteins, often associated with metal ions.
- A substance that decreases the rate of reaction is called an Inhibitor.
- CF_2Cl_2 is a highly stable compound that will go up into the stratosphere intact but when the UV radiation from the sun it will release a radical Chlorine atom: $CF_2Cl_2 \longrightarrow \cdot CF_2Cl + Cl\cdot$ (Chlorine free radical).
  - The highly reactive chlorine atoms will catalyse the breakdown of O_3 to diatomic oxygen molecules:
    - $Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$

- $ClO\cdot + O \longrightarrow Cl\cdot + O_2$
- Its estimated that one chlorine free radical can eliminate about 1 million ozone molecules.
    - $O_3 + O \longrightarrow 2O_2$
- Question #3 (p. 206)
  - Energy profile of the bond haber process (ammonia)
    -



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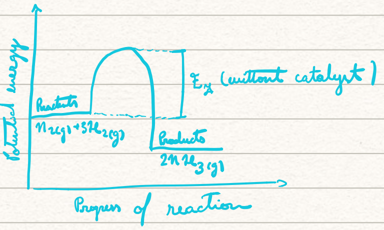
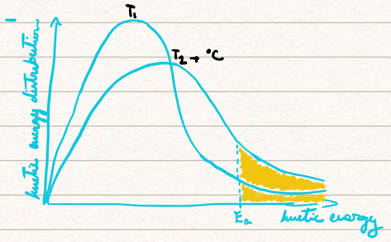
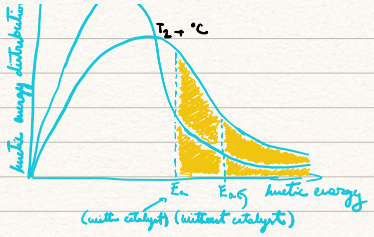


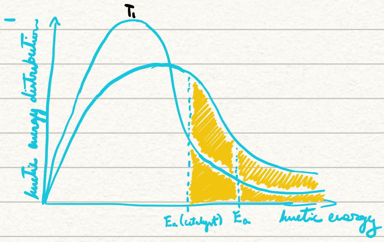
  - How are you supposed to answer the second question and third on p. 206? send e-mail!!!
- Maxwell-Boltzmann distribution
  - kinetic energies of gas molecules in ideal gas are distributed over a range known as a Maxwell-Boltzmann distribution.
    - these also occur in solutions & liquids.
  - The boltzmann-maxwell distribution is a representation of the amount of energy that different particles have in the mixture, not all particles have the same amount of energy.
  - Maxwell-Boltzmann distribution curve:



  - the total area under the Maxwell-Boltzmann distribution is directly proportional to the total number of of molecules, and the area under any portion of the curve is directly proportional to the number of molecules with kinetic energies in that range.
  - When the temperature increases a few changes occur:
    - the peak becomes lower, and shifts to the right as particles will gain kinetic energy as temp increases.
    - the curve flattens so that the total area under it and, therefore, the total number of molecules remains constant.
    - The area to the right of the E_a increases, meaning that the rate of reaction increases as the frequency of collisions in the volume increases.
      - In reality this is the amount of collisions don't really increase by that much. For example, if the temp increases by 10°C, the # of collisions only increases by 2%, but the rate of reaction will increase by 100% because a large amount of particles will have gained kinetic energy, meaning more particles will have more or the equal amount of energy for a successful collision to occur.
- Maxwell-Boltzmann distribution with catalyst.
  -



- Questions (p.208)
  - Q.6



    - b) The activation energy of a reaction is the minimum energy required for a succesful reaction to occur. If particles don't have the required energy, then the reaction wont occur.
  - Q.7
    - The reason that at higher pressure for gases will have a higher rate of reaction because the molecules are forced closer together therefore the number of collisions will increase.
    - The reason that concentration increases the rate of reaction is because more reactant particles will collide with one another meaning that more collisions will occur per second meaning that the percentage chance of a succesful collision will increase.
    - A larger solid will have a lower rate of reaction because the reactants can only react with the particles on the surface rather than all of them in the solid, dividing the solid up into smaller chunks will mean that more particles will be freed to react with the second reactant meaning that more reactant particles are free to react increasing the rate of reaction.
      - This is a similar effect that is seen when increasing the concentration of a reactant.
    - The reason that the temp will lead to an increase in rate of reaction is because the particles in the reaction will gain more kinetic energy, meaning that more succesful collision will occur as more particles will have the required E_a for a succesful collisions.
  - Q.8
    - B
    - 298K, 323K, 273K, 449K
- Reaction Rates
  - Neutralisation and precipitation are very fast reactions. While other reactions such as enzymatic browning of fruits, and rusting are slow.
  - The rate of a chemical reaction is a measure of "speed" of the reactions: those reactions that are complete in a relatively short space of time are said to have higher rates.
    - The rate refers to the change in the amount (for liquids and solids) or concentration (for gas solutions) of a reactant or product in unit time (t).
  - Rate of reaction refers to the change in concentrations or amount of a reactant or product with time, t:
    - $\text{rate} = \frac{\text{change in concentration}}{\text{change in time}}$ or $\text{rate} = \frac{(\text{concentration at time } t_2 - \text{concentration at time } t_1)}{(\text{time } t_2 - \text{time } t_1)}$
  - To find the rate of reaction, using the concentration of the reactants and products, this is done with the calculus formula below.
    - $\text{rate} = -\frac{d[A]}{dt}$ (units = mol dm^{-3} s^{-1}).
      - The formula states that the rate of reaction can be found using the concentration of the reactants and dividing it by the time that the reaction lasted.
      - It's negative because the reactant is decreasing.
    - Worked example:
      - 0.04 mol of substance in 2.5 dm³ in 20 seconds.
        - $n = cv$ $\quad$ $\text{rate} = \frac{[0.016]}{20}$
          $c = \frac{n}{v}$

$= \frac{0.04}{2.5}$ rate $= 0.0008$ mol dm^{-3} s^{-1} ✓

$c = 0.016$ mol dm^{-3} $= 8 \cdot 10^{-4}$ mol dm^{-3} s^{-1} ✓

- Questions
  - 22g of CO_2, 15 seconds, 4 dm^3.
    - $n = \frac{m}{rma}$ $c = \frac{n}{v}$ Rate of reaction $= \frac{[0.125]}{15}$

      $= \frac{22g}{44g\,mol^{-1}}$ $= \frac{0.5}{4}$ $= 0.00833$

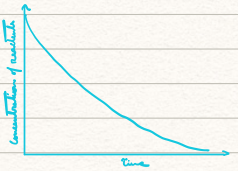
      $n = 0.5$ mol $c = 0.125$ mol dm^{-3} $= 8.33 \cdot 10^{-3}$ mol dm^{-3} s^{-1}
  - 0.06 mol dm^{-3} of Iodine after 30 seconds.
    - $r = \frac{0.006}{30}$ Why aren't we finding the rate to form Iodine atoms rather than finding the rate to form I_2?

      $= 0.002$

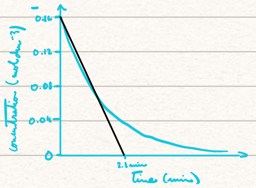
      $= 2 \cdot 10^{-3}$ mol dm^{-3} s^{-1}

- The rate of change in concentration of all reactants and products expressed in molecular units are related to each other via the cofficients in the balanced equation:
  - $\underset{\text{reactants}}{aA + bB} \longrightarrow \underset{\text{products}}{cC + dD}$

    ↓ Given formula
  - rate $= -\left(\frac{1}{a}\right)\left(\frac{d[A]}{dt}\right) = -\left(\frac{1}{b}\right)\left(\frac{d[B]}{dt}\right) = +\left(\frac{1}{c}\right)\left(\frac{\partial[C]}{\partial t}\right) = +\left(\frac{1}{d}\right)\left(\frac{\partial[D]}{\partial t}\right)$
- Again, the negative signs for a and b are negative because they are being used up meaning that they're going to lose particles compared to the products. While the positive signs of the products is because of the fact that their concentrations increase as the the reaction goes on.
- For the reaction $2H^+_{(aq)} + H_2O_{2(aq)} + 2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2H_2O_{(aq)}$ the average rate of apperance of water will be twice the average apperance of Iodine. Due to two water molecules are formed for every iodine molecule formed.
  - rate $= \left(\frac{1}{2}\right)\left(\frac{\partial[I_{2(aq)}]}{\partial t}\right) = \frac{\partial[H_2O_{(l)}]}{\partial t}$
- The rate of disappearance or consumption of $H_2O_{2(aq)}$ will be the same rate of apperance of iodine. The formula is shown below:
  - rate $= \frac{-\partial[H_2O_{2(aq)}]}{\partial t} = \frac{\partial[I_{2(aq)}]}{\partial t}$
    - This is because one molecule of iodine is formed for every hydrogen peroxide molecule consumed. The negative sign indicates a decrease in the peroxide concentration with time. Why aren't the $[H^+$ & $[I^-$ equal to the rate of apperance of Iodine? Is it because of the coefficients? (p. 211)
- The rate of reaction will decrease as the reaction goes on, due to the fact that there are less reactant particles, meaning less successful reactions. Shown in the graph:
  -



- Instantaneous rate of reaction is the rate of reaction at a specific point.
  - The instantaneous rate at any time is equal to the gradient of the graph at that time. The steeper the gradient, the faster the reaction.
  - When the graph is horizontal (gradient is zero) rate of reaction is zero.
  - Can be graphically determined from a graph of product or reactant concentration or amount against time.
  - Example Graph



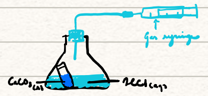
Instantaneous rate $= -\frac{\Delta y}{\Delta x} = -\frac{\partial[A]}{\partial t}$

$= \frac{0.16}{2.1}$

$= -0.076$ mol dm^{-3}

- To find the rate of reaction, you have to use a tangent to determine it. The way it works is that you have to have the tangent pass through the concentration points on the graph, and intersect it on the x-axis.

  - Average rate of reaction is the rate of reaction over the whole experiment / over specific time interval.
  - Reactants which show a direct relationship between concentration and rate are said to be first order.
- Measuring rates of reaction
  - The concentration of either the products or reactants is measured against time. At constant temp, pressure, volume, etc.
    - Suitable changes to indicate change in products / reactants are:
      - Color
      - Formation of percipitate
      - Change in mass, e.g gas in the product while solid in reactant meaning reaction will have loss in mass
      - Volume of gas produced
      - Time taken for a given mass of a product to appear.
      - pH
      - Temperature.
  - Reactions that produce gases
    - Reactions that produce a gas are investigated by collecting and measuring the volume of gas produced in a gas syringe.
      - Volume of a gas will increase as reaction goes on.
    - Diagram
      -



    - If the reaction is changed, for example such as increased temp, higher concentration, or powdered reactants, then the reaction will end quicker, but it won't have a higher final volume. The start and end will be the same for the same reactions at different concentrations / temp / etc.
    - On the other hand, another experiment can be done to find the change during a reaction by seeing the change in mass by having an open flask.
  - Reactions that produce a color change
    - If the reactant is colored, then to see a differnce you have to see the change in the mixture.
    - The colorimeter experiment shows the concentration depending on how the reactant / product shows color depending on presentation.
  - Reactions involving changes in ion concentration
    - If one of the reactants is $OH^-_{(aq)}$ or $H^+_{(aq)}$, then there will be a change in pH. This can be calculated with pH probes and meter.
    - If theres a change in number of ions during a reaction, then there'll be a change in conductivity measured with conductivity probe and meter.
      - Conductivity increases with increase in ions and vice versa.
  - Pressure and volume changes
    - Gas reactions are measured by using changes in volume (constant pressure) or change in pressure (constant volume).
      - This is used by seen the difference in moles from the reactant to product side. If theres no difference, then there will be no change in volume or pressure.
  - Withdrawal of samples and titration
    - Some reactions small samples of the reaction mixture can be removed and then analyzed by performing an acid-base titration with standard solution. Showing the concentration of reactants (with either OH^- or H^+ ions).
      - Write down acid titration
  - Rotation of the plane of polarized light
    - Some organic molecules e.g sugars & amino acids, rotate the plane of polarized light.
      - Change in concentration = change in rotation.