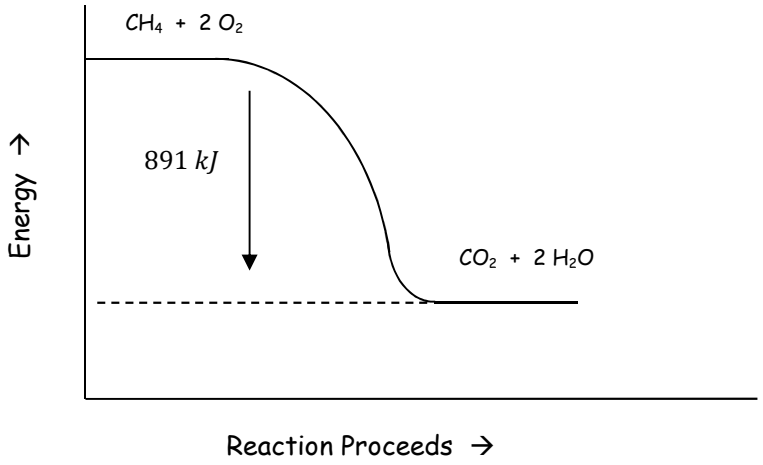
Unit 1 - Reaction Kinetics

- Reaction kinetics is chemistry speak for looking at the factors that affect the **speed or rate** that a chemical reaction occurs at.
- Recall from Chemistry 11 that most reactions are exothermic or reactions that give off heat. The diagram from last year looked like this



- With exothermic reactions the products end up at a lower energy state. This leads to the idea that the reaction should spontaneously occur, as all reactions are driven by the idea of more stable products.
- However, the reaction $2\ N_{2\,(g)} + 5\ O_{2\,(g)} + 2\ H_2O_{\,(l)} \rightarrow 4\ HNO_{3\,(l)} + 121\ KJ$ **<u>is exothermic</u>**. If this reaction occurred spontaneously, then the gases of air would be combining automatically and creating nitric acid, and thus killing all life on earth!
- There must be some type of <u>barrier</u> that is stopping (or extremely slowing this reaction). The following unit is looking into the rates of reactions, ways to measure this rate, and what this barrier is or in other words what factors control the rate of reactions.

<u>Part 1 – Definition</u>

- Reaction kinetics is the rate of a reaction and what causes this rate or speed.
- Another way of stating this is through math

$reaction\ rate$

Ex. – If $16\ g$ of HCl are usd up after $12\ min$ in a certain reaction, then what is the average reaction rate?

Ex. 2 – If a reaction between $CaCO_3$ and HCl produces $245\ mL$ of $CO_{2\,(g)}$ in $17\ s$, what is the average reaction rate?

Methods of Measuring Reaction Rates

- When copper is mixed with nitric acid the following reaction occurs:

$$Cu_{(s)} + 4\ HNO_{3\,(aq)} \rightarrow Cu(NO_3)_{2\,(aq)} + 2\ H_2O_{(l)} + 2\ NO_{2\,(g)} + \text{heat}$$

red-brown colourless blue brown

- The rate of this reaction can be found by measuring any one of at least four different properties

a.) Colour change – using a device called a spectrophotometer one can measure the intensity of a coloured chemical, such as the blue $Cu(NO_3)_2$. A spectrophotometer emits light through your chemical sample. The amount of light absorbed by the sample is directly proportional to the amount of that chemical. As this chemical is produced the intensity will increase along with the absorption of that light. By making a graph of **colour intensity versus time** allows the slope to be found.

$$Rate = \frac{\Delta\ colour\ intensity}{\Delta\ time}$$

b.) Temperature change –

$$Rate = \frac{\Delta\ temperature}{\Delta\ time}$$

c.) Pressure change – since the reaction is producing NO_2, a gas, the reaction can be carried out in a sealed container with a pressure gauge. A graph of pressure versus time will again allow the slope to solve for rate.

d.) Mass change – Since copper is the only metal present in the reaction, we can measure the rate at which the copper is used up. Here's how:

1.) Set up several containers with the same concentration of an acid.
2.) Weigh the copper so the mass is known.
3.) Drop the copper into the first acid and time the reaction for $30\ s$.
4.) Stop the reaction and rinse the acid off of the copper with water. Weigh the copper now.
5.) Repeat steps 2-4 for three more containers of the acid but increase the time by $30\ s$ each trial.

6.) Subtract the final mass from after the acid bath, from the mass before the acid bath, to solve for the amount that reacted.

7.) Plot the change in masses of the copper for each trial versus the time it reacted. The slope is the reaction rate.

Factors Affecting Reaction Rates

1. Temperature –

2. Concentration –

3. Pressure –

Note – the volume of a system is inversely proportional to the pressure applied to the system. In other words, when pressure increases, the volume decreases, and vice versa.

4. Nature of Reactants – some reactions are inherently slow due to the strong bonds between the atoms needing to be broken (or many in number) or the electrons may be held very tightly. Other reactions are naturally slow because the bonds between the atoms are weak (or few in number) and easily broken or the electrons are not held tightly.
   - The "Nature of the Reactants" refers to the chemical properties of the chemicals involved in the reaction. As such, some reactions take a long time and can only be sped up or slowed down to a small degree by altering the reaction rate. Ex. -
   - Other reactions are naturally fast and can also only be sped up or slowed to a small degree by altering the reaction rate. Ex. –

5. The Ability of Reactants to Collide: Surface Area and Phase Considerations – as surface area **increases**, reaction rate **increases**. The more atoms of reactants that are exposed to collide with each other, the more likely they will collide and in greater amounts.

- Phase has an effect on surface area.

- **Homogeneous reaction** – a reaction in which the reactants are all in the same phase.

  Ex. –

- **Heterogeneous reaction** –

  Ex. –

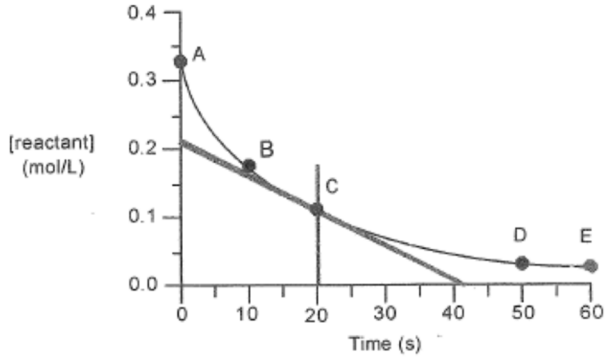
- Phases affect reaction rates based largely on the phase allowing movement of the atoms. Solids are slowest due to the reactants not moving freely. Fluids (liquids and gases) are fee to move around and move faster. As such, the reaction rate is faster. Aqueous ions are fastest due to the free movement in the solvent, the opposite charged ions attracting, and the close proximity of the ions.

Fastest ⟶ Slowest
Aqueous ions > Fluids > Solids

6. Catalysts and Inhibitors – a **catalyst** is a chemical that **increases** reaction rate, without being part of the reaction. An **inhibitor** is a chemical that **decreases** the reaction rate through combining with one of the reactants or a catalyst.

Experimental Measurement of Reaction Rates

- A typical concentration of reactants as time proceeds graph is shown below.



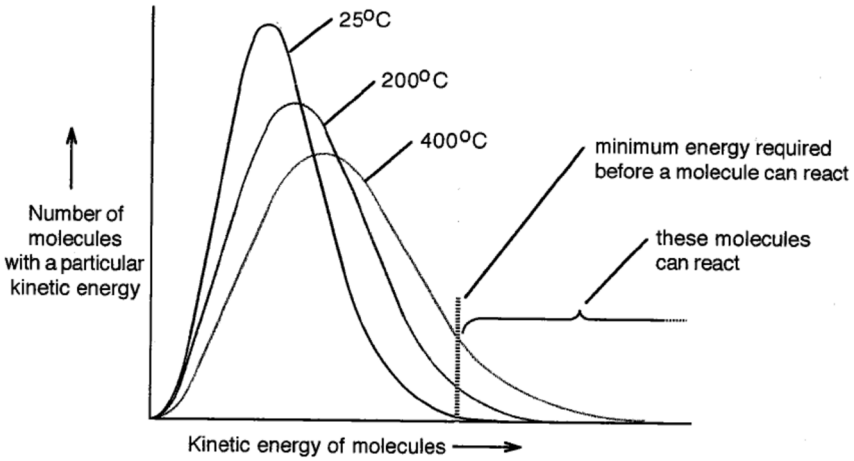
- There is a tangent line drawn at $20\ s$ (point C) allowing the slope at that time to be solved for. The slope is _____, so the slope must represent the reaction rate!
- The important part lesson of this graph is how it is showing how the reaction rate changes over time. In the first $10\ s$ the high [reactant] leads to a high rate (many collisions), however, as the reaction proceeds we can see that the reaction rate drops significantly, last $10\ s$, as the [reactants] decreases (less reactant to collide).

Collision Theory

- Also known as Kinetic Molecular Theory (KMT), collision theory says that molecules contain energy and thus are moving all around rapidly. They act like hard spheres and transfer energy whenever they collide with other molecules.
- KMT explains (at a molecular level) why reaction rates change when the conditions are altered. Below are two examples of how conditions could change:

  a.) _____ -

  b.) Temperature – increasing temperature gives the molecules more energy to move faster. This causes more and harder collisions resulting in a faster reaction rate.



- As we can see, heating increases the reaction rate by **increasing the number of molecules that have sufficient energy to react**, and not the number of collisions!

****Rule of Thumb****

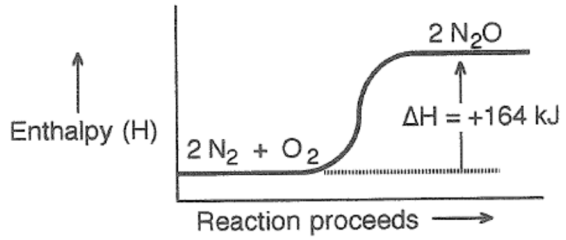
- For a reaction to occur **two** conditions need to be met. The molecules must both collide with **sufficient energy** and with **proper orientation**.
- When atoms combine to form a new bond, they give off energy and go to a lower, more stable level of energy. The energy required to break or form the bond is known as **bond energy**. The energy being discussed is the attractive/repulsive forces contained between the protons of the nucleus (repulsion), the protons and electrons (attraction), and the electrons to each other (repulsion).
- These forces exist in the form of _____ and _____:

a.) Potential energy – the energy that exists as a result of the object's position in space and in the chemical bonds, as well as the number and type of atoms in the molecules.

b.) _____ – the energy that exists due to the movement of the entire system or the individual molecules (or atoms) in the system.

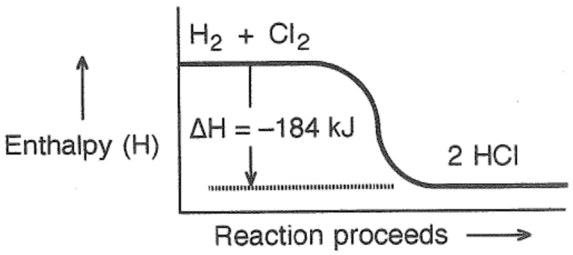
- In science we call all the energy contained in a reaction as the **ENTHALPY** (H). The change then in the energy of the system as a reaction occurs is the "change in enthalpy". This is simply $H_{prod} - H_{react} = \Delta \boldsymbol{H}$.

- An endothermic reaction requires energy from the surroundings to break the reactants bonds. As such it takes in energy from the surroundings. $H_{prod} > H_{react}$ $H_{prod} - H_{react} = +\Delta \boldsymbol{H}$



- An exothermic reaction releases excess energy to the surroundings from forming lower more stable bonds of the products. As such it takes in releases energy into the surroundings.

$H_{prod} < H_{react}$ $H_{prod} - H_{react} = -\Delta \boldsymbol{H}$



Heat **EN**ters the system in an **EN**dothermic reaction
Heat **EX**its the system in an **EX**othermic reaction

Activation Energy

- Activation energy is the energy required by the colliding molecules (atoms) to allow for a reaction to occur.
- If lesser amount of energy is absorbed, reactants don't have enough energy and fall back apart.
- If sufficient KE is transformed into PE then an **activated complex** is formed and the reaction proceeds to make the products. The activated complex is an arrangement of the atoms that are in the process of rearranging into the products.

Endothermic

$\Delta H = +$ as products are "higher" than reactants

1. Reactants have relatively low energy. Collisions are unsuccessful in producing a reaction.
2. Occasional random collision has sufficient energy to produce activated complex.
3. With enough energy, reaction proceeds to products.

Reaction Mechanisms

- A reaction mechanism is the actual **sequence of steps** which make an overall reaction.
- When there are less than 3 reactant molecules it is likely the reaction will happen in one step.

  - likely one step

- If there are 3 reactant molecules (or more) then it is unlikely all 3 (or more) reactants will collide at the same time with sufficient orientation and energy to cause a reaction. As such, then there will be a sequence of steps in producing the product.

  Ex. – making a shirt. A shirt is thought of as one thing. However, it's actually a collection of many fabric pieces and thread put together. One does not just dump the pieces into a bag and have a shirt fall out. A shirt is constructed in a certain order.

$4\ HBr_{(g)} + O_{2\,(g)} \rightarrow 2\ H_2O_{(g)} + 2\ Br_{2\,(g)}$ - unlikely one step

1. $HBr_{(g)} + O_{2\,(g)} \rightarrow HOOBr_{(g)}$ - slow (rate determining step)
2. $HOOBr_{(g)} + HBr_{(g)} \rightarrow 2\ HOBr_{(g)}$ - fast
3. $HOBr_{(g)} + HBr_{(g)} \rightarrow H_2O_{(g)} + Br_{2\,(g)}$ - fast

- Overall reaction is found by adding all the steps.

- Products of one step which become reactants in a subsequent step are known as **reaction intermediates**.
- What chemicals are reaction intermediates in the above reaction? _____

Catalysts and Inhibitors

- A catalyst is a substance that lowers the overall activation energy through providing an alternate mechanism.
- Catalysts are used up in the reaction and then regenerated later as a product.

- Inhibitors are a substance that combine with reactants to form a stable complex, stopping the reaction from occurring.
- Knowing reaction rates is very important in both:
    1. Commercially – money is saved in getting reactions to go quickly ("time is money").
    2. Biologically – sometimes we want slow reactions – drug use for infections (time release).