Chemistry Notes: Kinetics

6.1.1: Define *Rate of Chemical Reaction*

The rate of a chemical reaction is a measure of how quickly the products are formed. This is usually measured in change in concentration over change in time (IB calls it $dm^{-3}s^{-1}$)

The measure of how fast the products are made is equal to the measure of how fast the reactants are consumed.

$$rate = \frac{\Delta[Products]}{\Delta t} = -(\frac{\Delta[Reactants]}{\Delta t})$$

For the reaction aA → bB, where a and b are coefficients, and A and B are the species involved, the rate of the chemical reaction is calculated as follows:

$$rate = \frac{1}{b} \times \frac{\Delta[B]}{\Delta t} = -(\frac{1}{a} \times \frac{\Delta[A]}{\Delta t})$$

The formula concerning the aA species is negative because the concentration of the reactant goes down as the concentration of the products goes up.

The rate of a reaction decreases with time because the concentration of the reactants lowers with time.

In comparisons of reaction rates, the slope of the line tangent to the reaction function is most accurate because:

- Concentrations of all reactants are known.

- Temperature of the system is known.

6.1.2 & 6.1.3: Describe Suitable Experimental Procedures for Measuring Reaction Rates/ Analyze Data From Rate Experiments

Reaction rates can be measured by observing any property that changes from the beginning to the end of the reaction. It is best if this property changes by a large amount and is directly proportional to the concentration of any given component of the reaction.

- Monitoring pH is generally not recommended because it will only change by 0.30 when the concentration of hydrogen doubles.

Remember that the reaction rate is inversely proportional to the time taken for the reaction to finish. Therefore, the longer it takes for the reaction to complete, the smaller the reaction rate.

If the purpose of an experiment were to observe the effect of a single variable, most commonly the concentration of a single species, on the rate, of the reaction, a simple graph of the property (which should be proportional to concentration) against time will do.

Constants:

- Temperature must be kept constant (another reason for preferring the initial rate of the reaction to the rate at time x is that the endothermic/exothermic effects of a given reaction will be minimized).

Titration

To measure reaction rates:

- Remove small samples from reaction mixture at different times and the titrate those samples to determine concentration at different times (the collected data points (time, concentration) can then be used to generate a reaction curve.

This method is only reasonable for slow reactions because the time taken to titrate each sample is significant compared to reactions that occur quickly. It is possible to mitigate these effects by "quenching" the reaction, or changing its conditions so as to stop it during the titration of the samples.

Quenching Methods:

- Rapidly cooling the mixture

- Adding an excess of a compound that rapidly reacts with one of the reactants.

Reactions commonly studied using this method:

$$H_2O_{2\,(aq)} + 2H^+_{(aq)} + 2I^-_{(aq)} \rightarrow 2H_2O_{(l)} + I_{2\,(aq)}$$

Collection/Measurement of an Evolved Gas

The gas produced by a given reaction is collected by a gas syringe or a graduated vessel over water. The volume of the gas collected at different times is recorded.

Another method is by measuring the change in gas pressure of a reaction taking place in a volume-constant container.

This method is suitable for reactions that evolve gas only.

Reactions commonly studied using this method:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+} + H_{2\,(g)}$$

$$Na_2CO_{3\,(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + CO_{2\,(g)} + H_2O_{(l)}$$

Measurement of the mass of the reaction mixture

The total mass of a given reaction mixture will only vary if a gas is evolved. To be effective the gas evolved has to have a high molar mass. The gas also cannot be significantly soluble in the solvent used to house the reaction. The method would be suitable for reactions that produce a significant amount of lost mass in the form of gaseous species such as carbon dioxide.

$$CaCO_{3\,(aq)} + 2H^{+}_{(aq)} \rightarrow Ca^{2+}_{(aq)} + H_2O_{(l)} + CO_{2\,(g)}$$

Light Absorption

If a reaction produces a precipitate, then the time taken for that precipitate to obscure a mark made on a piece of paper under the reaction vessel can be used to measure the reaction rate.

The depth of the liquid must be kept constant. Remember this is also inversely proportion, if the time taken doubles, then the reaction rate is halved.

$$S_2O^{2-}_{3\,(aq)} + 2H^{+}_{(aq)} \rightarrow H_2O_{(l)} + SO_{2\,(aq)} + S_{(s)}$$

The above reaction is typically studied using the light absorption method.

If the reaction involves a colored reactant or product, the intensity of the color can be used to monitor the concentration of that species. The simplest method is recording by eye, however two instruments can be used to make this method much more precise:

- Calorimeter: A filter of complementary color to that of the colored species is chosen. A blue solution is blue because it absorbs red light, thus it is not the intensity of transmitted blue light , but the intensity of transmitted red light that varies the concentration.

- Spectrophotometer: A wavelength near the absorption maximum is selected and the rate of reaction is determined by the change of intensity of this wavelength color that passes through.

The reaction between propanone and iodine is commonly studied using this method. The yellow brown iodine reactant is the only colored species, thus as the amount of iodine diminishes, less blue light is absorbed and the intensity of blue light passing through the solution increases.

Absorbance decreases with time, while the intensity increase with time.

Electrical Conductivity:

The presence of ions allows a solution to conduct electricity, so if there is a significant change in the concentration of ions present between the endpoints of the reaction, the change in electrical conductivity of the substance can be used to determine the rate of reaction.

This is usually found by measuring the electrical impedance between two electrodes that are immersed in the reaction solution. The hydrolysis of phosphorus trichloride is a good example of a reaction that would be measured using this method because all of its products are ions (thus the reaction ends with a high amount of electrical conductivity.

$$PCl_{3\,(aq)} + 3H_2O_{(l)} \rightarrow H_2PO_3^- + 4H^+_{(aq)} + 3Cl^-_{(aq)}$$

Clock Techniques

Some reaction rates can be measured by further reacting the reactions products with another substance. When all of the substance is consumed there will be an observable change in color. The time taken for this change to occur is inversely proportional to the rate of the original reaction.

The most common reaction measured using this technique is the reaction between hydrogen peroxide with iodine ions in the presence of a dilute acid.

$$H_2O_{2\,(aq)} + 2H^+_{(aq)} + 2I^-_{(aq)} \rightarrow 2H_2O_{(l)} + I_{2\,(aq)}$$

Thiosulfate ions are added to the system and react with aqueous iodine as such:

$2S_2O^{2-}_{3\,(aq)} + I_{2\,(aq)} \rightarrow S_4O^{2-}_{6\,(aq)} + 2I^-_{(aq)}$ (Blue colored iodine starch complex appears when all of the thiosulfate is consumed.)

6.2: Collision Theory

6.2.1 & 6.2.2: Describe Kinetic theory in terms of movement of particles whose average energy is proportional to temperature in kelvins

Collisions are vital for chemical change because they both provide the energy required for a particle to change and bring the reactants to contact.

As particles approach each other there is repulsion between the electron clouds of the particles. In order for a reaction to occur, the collision must have a sufficient kinetic energy to overcome the repulsion between these clouds. The minimum amount of energy required for a reaction is called the activation energy (E_a).

In order to react, two particles must:

- collide with each other
- be energetic enough to overcome the activation energy of the reaction
- collide in with correct orientation (reactive parts must come in contact). This is known as the steric factor and usually concerns reactions between large organic molecules.

Anything that increases the collision rate increases the reaction rate.

6.2.3 – 6.2.7: Predict and Explain, using collision theory, the qualitative effects of particles sizes, temperature, concentration, and pressure on the rate of a reaction.

Factors that influence collision rate:

- Concentration/Pressure
- Surface area

Factors that affect the proportion of particles with required E_a:

- Temperature
- Catalyst

The Effect of Concentration:

Increasing the concentration of reactants increases the collision rate wich in turn, increases the reaction rate. Thus, marble chips will react faster with concentrated hydrochloric acid that they would with dilute hydrochloric acid. For reacting gases, increasing pressure is the same as increasing concentration.

The Effect of Surface Area:

More surface area implies more effective collisions; therefore powdered solids will react with aqueous acids than lumps of solids because more hydrogen ions can come into contact with more of the solid at once in its powdered form.

Note that another way of saying this would be that smaller particles react faster than larger ones.

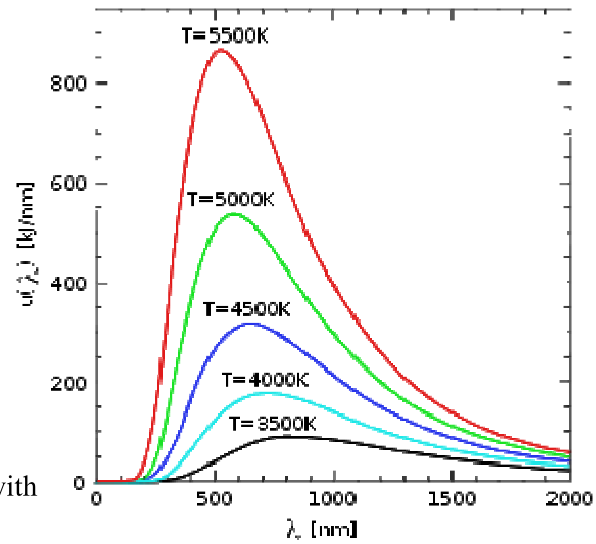
The Effect of Temperature:

Not all particles have the same kinetic energy so there is a distribution of kinetic energy (particle velocity), known as the Maxwell-Boltzmann distribution. The average kinetic energy is coincides with the mean speed of the particles, but not with the most probable speed.

The Maxwell-Boltzmann distribution is a plot of energy vs. probability of that energy:

As the distribution demonstrates, the particles with the highest velocity are actually the least probable ones. On the distribution, the activation energy is a vertical line that intersects each function at one point. If the reaction is catalyzed, this line will be closer to the y-axis, if the reaction is not catalyzed, this line will appear farther from the y-axis. The lower temperature reaction function will always have the higher peak, which implies that more particles have a lower velocity than not.

The area under the graph of the curves that is also to the right of the activation energy represent that fraction of all particles in the system that have an energy that is sufficient to for a reaction. Conversely, all the area under the curve that is to the left of this line represents the fraction of all particles that do not have a sufficient energy to react.



As the graph demonstrates, the reactions with a higher average kinetic energy have lower peaks.

Increasing temperature has a slight effect on collision rate, but its most significant influence is on the proportion of particles with effective kinetic energies to react.

<u>The Effect of Catalysts</u>

A catalyst increases the rate of reaction without being consumed by the reaction itself. Catalysts speed the reactions by providing an alternate reaction pathway with lower activation energy.

The effectiveness of a catalyst decreases with time because it becomes inactive due to impurities in the reaction mixture, side reactions, and unwanted surface coatings. Note that catalysts do not change the heat of reaction.

<u>The Effect of Light</u>

Some chemical reactions are brought about by exposure to light.

- Darkening of silver halides with exposure to sunlight.

- Reactions of alkanes with chlorine or bromine.

Light influences reactions because reactant particles absorb light yielding two possibilities:

- Excitation of reactants

- Breaking of a bond

Many chemicals are stored in brown-glass containers so that they do not become excited as a result of exposure to light.