REACTION RATES

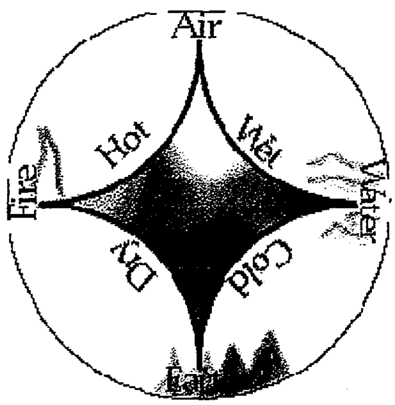
- Chemical reactions proceed at different rates depending on the chemicals involved and the environmental conditions. Some reactions are very fast (Caesium and Water) while others may take a considerable time (Rusting of Iron).
- Measuring the rate of a chemical reaction will involve one of two methodologies:
  - Measure the rate of disappearance of reactants.

    Eg: You may be able to measure the rate at which measured amounts of magnesium ribbon dissolve in acid.
  - Measure the rate of formation of products.

    Eg: You may be able to measure the rate of evolution of hydrogen gas in a reaction between magnesium and acid. This may involve measuring the inflation rate of a balloon or a syringe that is connected to the reaction vessel.
- There are many factors that influence the rate of a reaction:

NATURE OF REACTANTS

- Some elements and compounds are particularly unstable and will react vigorously in order to lower their chemical potential energy.
- In the case of metals their reactivity can be traced to the energy needed to remove electrons from their valence shells (***IONISATION ENERGY***) as metals always **lose electrons** (Oxidation) in reaction. Depending on the number of protons in the nucleus of the atom and the radius of orbit of the outer electrons, different metals will have different levels of attraction for these valence electrons. Differences in attraction for the valence electrons lead to different ionisation energies. Metals that react very easily have innately lower ionisation energies (Caesium, Potassium and Sodium) while others react far more slowly as their ionisation energies are higher (Copper, Gold and Silver).
- In the case of non-metals their reactivity is governed by their tendency to **gain electrons** (Reduction) in reaction. This is known as their ***REDUCTION POTENTIAL***. Different non-metals have different reduction potentials and so will react at different rates as a consequence.



COLLISION THEORY

- A chemical reaction can only occur if chemicals come in contact or COLLIDE with each other. There are many considerations that govern how often and how effectively chemicals come in contact and whether or not they react. The theory that governs reaction rate is called the COLLISION THEORY for this reason. Whenever you discuss reaction rates you should always relate the governing factors to this theory.

PHASE

- Whether materials are in the ***SOLID, LIQUID, GAS*** or ***AQUEOUS*** phase will have a big impact on the rate at which they react. In part this may be due to the extra energy that particles have in their particular phase. The melting and boiling points of different substances depend on the forces of cohesion that exist in the material. It goes without saying that a material in the liquid or gas phase is at a higher temperature than the same material in the solid phase. The effect of temperature on reaction rate will be discussed in the next section but all reactions occur at higher rates if the temperature is higher.

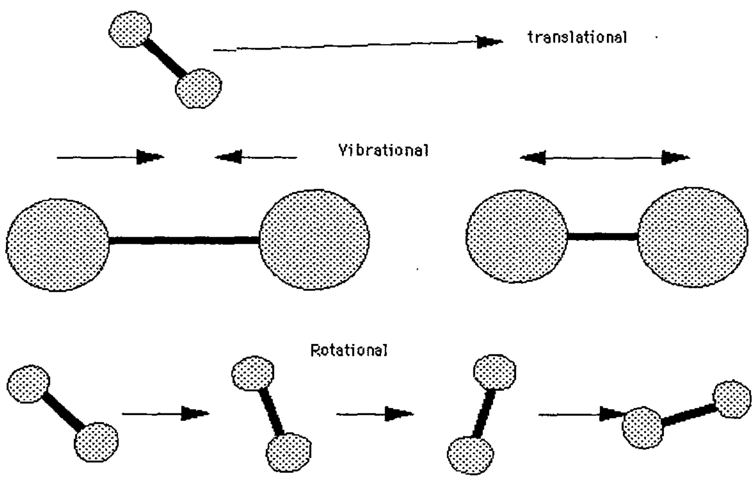
- The main reason that phase effects reaction rate is that it affects the ***MOBILITY*** of particles. In the liquid, gaseous and aqueous phases particles may move far more freely. If particles can move freely they are more able to encounter and **collide** with each other. The ***ACCESS*** of reactants for each other is a major influence on rate. Many reactions may be increased in rate by simply *STIRRING* chemicals together which increases access and enhances collision frequencies.

- Reactions in the solid phase are generally very slow unless a great deal of energy is supplied or the solids are finely divided and shaken together to promote access.

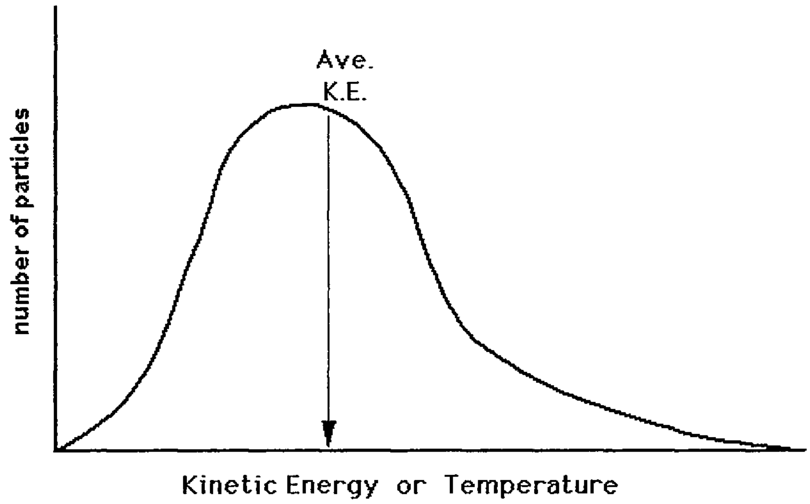
  Eg: The reaction between solid lead nitrate and solid potassium iodide is very slow, particularly if the solids are layered one on top of the other in a test tube. Reaction rate increases if the mixture is shaken vigorously. If however, the solids are dissolved in water and then mixed the reaction is almost instant.

TEMPERATURE

- The temperature of a material is a measurement of the kinetic energy of its particles. Kinetic energy or movement energy may manifest itself as ***TRANSLATIONAL*** (movement from point a to b), ***VIBRATIONAL*** (movement back and forth) or ***ROTATIONAL*** (end over end revolution).



- The temperature of a material measures the *AVERAGE KINETIC ENERGY* of its particles motion. Because particles constantly collide with each other, whether or not they are particles of different chemicals that react, their energies are constantly re-distributed. This means that not all the particles at a particular temperature are moving as energetically. Some will be moving faster and others slower. Which particles move faster and which move slower changes dynamically with each collision that re-distributes energy but does not increase it. At any one temperature there will be a kinetic energy distribution that may be represented by a ***KINETIC ENERGY DISTRIBUTION CURVE***.



- Irrespective of the type of kinetic energy, the more movement energy reacting particles have the more likely they are to collide with a reasonable *COLLISION FREQUENCY (f)* and the more likely they are to react.

- It is not only the fact that particles **collide** that governs reaction rate but the energy of their collisions is vital. Particles that are moving slowly may collide but simply bounce of each other and remain unchanged in any way other than to have perhaps re-distributed their energies. A collision that is not forceful enough is referred to as ***UNSUCCESFUL*** and does not result in reaction

- All reactions require that a certain minimum total energy value is reached from the combined TOTAL of the colliding particles in order that the collision is successful and results in chemical change. This minimum energy requirement is known as the *ACTIVATION ENERGY*.

- Increases in temperature will always increase the rate of a reaction as they allow for **greater collision frequencies** but much MORE IMPORTANTLY will result in a **greater proportion of collisions that are successful and overcome the activation energy barrier**.

- Just as increases in temperature will increase reaction rate the reverse is true of cooling. If we lower the temperature, particles will move more slowly and will collide **less often** and with **insufficient energy to overcome the activation energy barrier**. In society there are many chemical reactions that we would choose to occur at slow rates. These would include environmental corrosion of materials or even food spoilage.

CONCENTRATION

- The concentration of a chemical reactant has a very important bearing on collision frequencies and hence reaction rate.
- Concentration is a measure of the density of particle arrangement with respect to volume. If a chemical is dissolved it refers to the quantity, measured in moles or mass, of the ***SOLUTE*** per unit volume of ***SOLVENT***, in most cases water. If the chemical is in the gas phase it again refers to the relative quantity of gas when compared with the volume of the container. The pressure that the gas exerts in this container, as the particles **collide** with the walls, is a measure of this concentration or particle density.
- NB: Pure liquids and solids do not have concentrations as they are not dissolved or free enough to spread throughout their container. These phases have fixed volume.
- The **greater the concentration** of reactants the greater will be the reaction rate. This is simply because the particles, if mobile, will **collide more frequently** and this leads to an increased probability of some **successful collisions** occurring.

  Eg 1:. 6M HCl will react far faster with magnesium than will 0.1M.

  Eg 2: A glowing splint will glow faintly when burning in air but will burst into flames when added to pure oxygen!

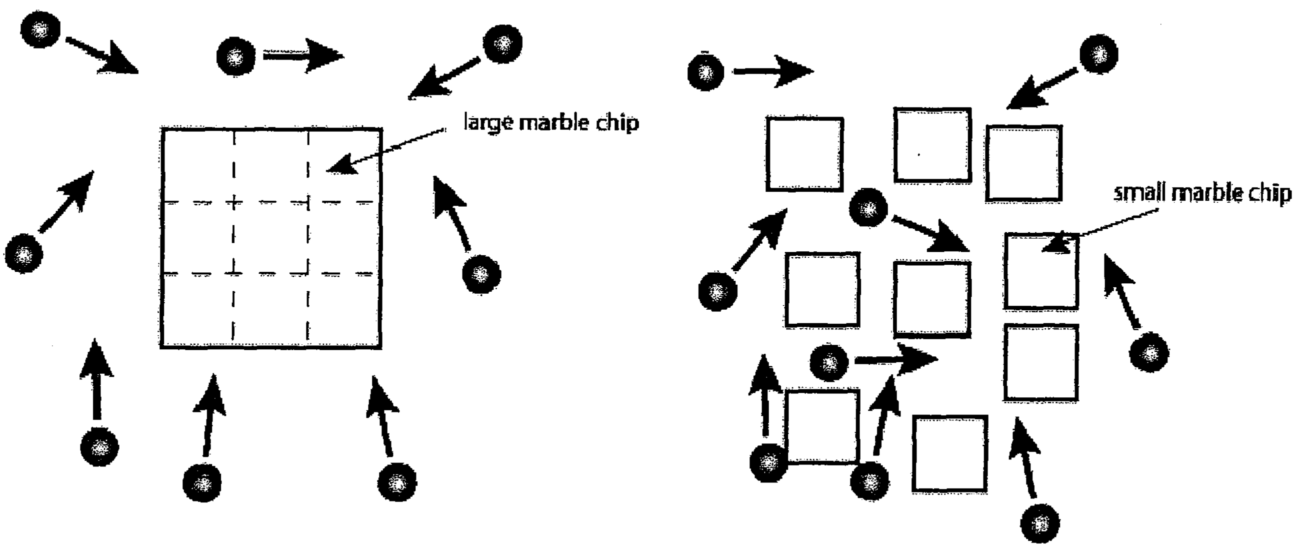
  Eg3: A steak will cook far faster in a hot frying pan.

SPECIAL CASE:

- Solids do not have a concentration but collision frequency can be increased by finely dividing solids into powders or filings in which their surface area is greatly increased. Very high ***SURFACE AREA*** allows other reactants very effective access to the solid allowing them to **collide** with it much more effectively.

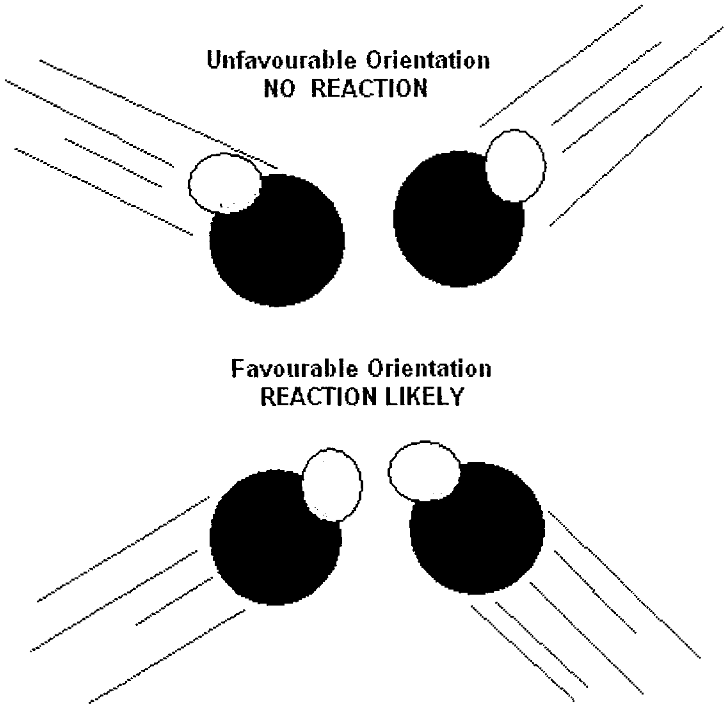
  Eg 1: The reaction of solid iron with air is very slow even when heat is applied. If the same reaction is tried using iron filings the filings will glow and sparkle as they react.

  Eg 2: Calcium carbonate in the form of marble chips will react quite well with 4M HCl but if the marble chips are ground using a mortar and pestle the mixture will effervesce and froth violently.



COLLISION GEOMETRY

In some reactions it is not only necessary that reactants collide with sufficient energy but that the collision occurs with a certain orientation of the **colliding** particles. All chemical species have certain geometry to their structure and if a collision occurs with a favourable orientation of reactants it may be more **successful** and lead to greater reaction rate.

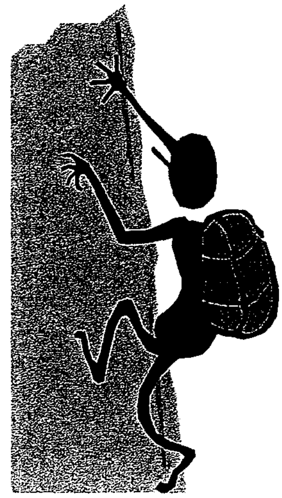


REACTION MECHANISM

- Many chemical reactions do not simply involve the collision of two reacting particles to achieve reaction. The stoichiometry or balancing of equations frequently requires three, four or even higher numbers of reacting particles to come together. The chances of **more than two** particles colliding at any one time with the minimum energy requirement and correct orientation are very small. Most reactions involve a number of collisions with the formation of *INTERMEDIATE* substance between one collision and the next.

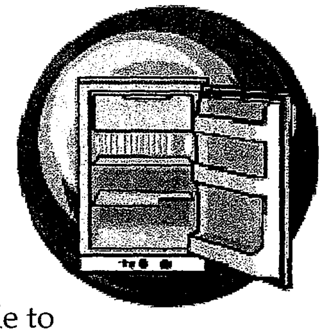
- The sequence of collisions and the intermediate stages involved in a reaction are known as the *REACTION MECHANISM*. Reactions that are simple two particle collisions will often occur far faster than those that require many stages, as long as access, mobility, orientation and energy issues are the same.

- In multi-stage reactions there is often one stage that is hardest to achieve and determines the progress of the reaction. This is known as the *RATE DETERMING STEP*.

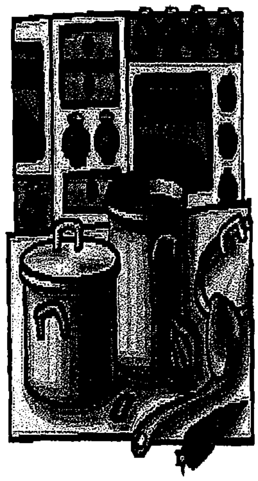


RATES IN AND AROUND THE HOME

▶ The rates of chemical reactions are frequently important in and around the home as is an ability to modify them:



- The chemistry of food spoilage must be modified if we are to store our food for any prolonged period of time. By refrigerating our food we are able to remove a lot of the energy from these spoilage reactions. By reducing energy we lower the rates of these reactions as there is not enough activation energy or energy of collision for them to occur very quickly. By deep freezing it is possible to store food for a very long period of time.

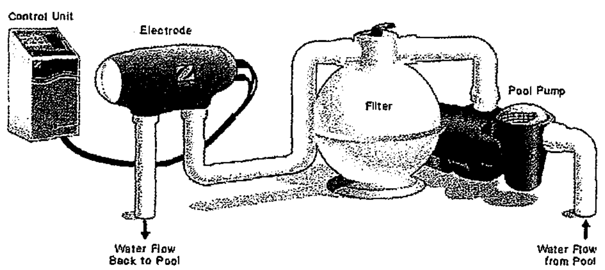


- Any cooking process involves both chemical and physical change to the food we are cooking. We modify the rates of these cooking processes by controlling the temperature or state of sub-division. If we want to cook a potato we may boil it in hot water as this will obviously give it far greater energy than trying to cook it in cold water. We may choose to cut it into smaller segments with a greater surface area (particle subdivision) if we wish to cook it even faster!

- When cooking a steak and causing the denaturation of the proteins we may use a high or low flame so as to cook the food more or less quickly.

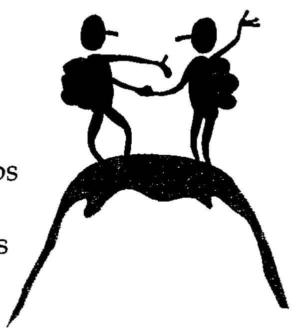
- The rate at which the materials used in the construction of our homes corrode also needs to be modified. We use paints to provide a barrier between oxygen and the metal of our gutters so that the collision frequency with atmospheric oxygen and moisture is minimal. The rate of corrosion is very slow as a result and the gutters do not need replacing at great cost.

- In our swimming pools it is necessary to produce chlorine so as to kill harmful bacteria. Many pools do this by electrolysis of aqueous salts. The rate of this chlorination is modified and controlled precisely by varying the current flow to the electrodes. We can modify the time for this electrolysis with a timer and the concentration of salt can be kept at measured levels through addition of bags of salt when water analysis indicates the need.



CATALYSTS

- The particular reaction mechanism that a reaction follows may be different if there are different substances introduced to the reaction environment. A material that influences the set of reaction steps in a way that increases the rate of a reaction is known as a *CATALYST*.



- Catalysts raise the rate of reaction by providing an ***ALTERNATIVE REACTION MECHANISM*** that has steps with lower activation energy. If the activation energy barrier is lowered then more collisions between reactants will be successful and lead to reaction.
- Catalysts may be many and varied. They may be solid surfaces where chemicals bind and are brought together to facilitate reaction or even ions in solution. The chemistry of life is governed by complex biological catalysts called ***ENZYMES***. Enzymes are complex protein molecules with very specific geometry that catalyse the reactions of life such as Respiration, Digestion or Photosynthesis. The specific geometry allows an enzyme to catalyse only a very specific reaction, they are said to be substrate specific.
- A unique feature of the role played by a catalyst is that it is REGENERATED at the end of the reaction mechanism. The catalyst takes part in the reaction and forms intermediate compounds but when the chemicals have finished reacting is left unchanged by its intervention. This means that the catalyst is not consumed and is able to catalyse further reactions. It may appear that the catalyst has not taken part in reaction for this reason but nothing could be further from the truth!

SUMMARY : ROLE OF CATALYSTS

- A catalyst increases the rate of a chemical reaction by providing an *ALTERNATIVE REACTION MECHANISM* of *LOWER ACTIVATION ENERGY*. It takes part in the reaction, ***FORMING INTERMEDIATE COMPOUNDS***, but is ***REGENERATED*** in an unchanged form at the end of the reaction.

SUMMARY:

HIGH REACTION RATE:

- Reactive chemical.
- High temperature.
- Mobile phase (liquid,gas, aqueous).
- High concentration of reactants (high gas pressure, finely divided solids).
- Presence of a catalyst.

LOW REACTION RATE:

- Unreactive or inert chemical.
- Low temperature.
- Resticted phase (solid).
- Low concentration of reactants (low gas pressure, lumpy solids).
- Absence of a catalyst.