CHEMICAL KINETICS

TEMPERATURE DEPENDENCE OF THE RATE OF A REACTION

FACTOR AFFER RATES OF CHEMICAL REACTION (PART I) :-

Factors Affecting the Rate of Chemical Reaction

The rate of a chemical reaction is the pace at which a chemical reaction occurs. Learn about how reaction rate is calculated and what factors it depends on.

The rate of a chemical reaction is defined as how much of the reacting substance is consumed in a given amount of time. Alternatively, it can also be defined as how much of the resulting product is produced in a given amount of time.

Defining The Rate of A Chemical Reaction

The rate of a chemical reaction is the pace at which the reaction takes place. It is directly influenced by the decrease in concentration of a reactant in a given amount of time or the increase in the concentration of a product in a unit time.

Reaction rates vary across a very wide range. For example, a piece of iron exposed to the atmosphere rusts over a very long period of time. On the other hand, combustion in a car engine occurs in fractions of seconds.

Normally, the rate of a chemical reaction reduces with time. The reaction rate is calculated by measuring the change in the concentration of reacting substances or the products generated, over time.

Rate Law or Rate Equation

The Rate law or rate equation explains how the rate of a chemical reaction is impacted by the concentration of its reactants. It is generally written as:

Rate = k[A]x[B]y

where,

k = rate constant,

[A] & [B] = molar concentration of the reactant substances A & B,

x & y = reaction orders

The rate constant k and the exponents x and y are calculated by examining how the rate of a reaction changes with the change in concentrations of the reactants. The rate constant k does not depend on the concentration of reactants A or B. However, it does change with other factors like temperature and surface area.
Summation of x and y is called the order of the reaction. It is usually a whole number (0, 1, 2 etc.), though it can also be fractions at times. When x + y = 0, it means the reaction is not dependent on the concentration of the reacting substances.

Formula For Rate Of Reaction

Consider a chemical reaction as below:
aA + bB pP + qQ
Here, the letters in lowercase (a, b, p, q) represent the stoichiometric coefficients. Capital letters (A, B) represent the reactants, while (P, Q) denote the products.

IUPAC's Gold Book defines the reaction rate v for a chemical reaction as:

v=-1ad[A]dt=-1bd[B]dt=1pd[P]dt=1qd[Q]dt
The above holds true only for a chemical reaction that occurs in a closed system and at a constant volume, without the generation of intermediates in the reaction.

Average Rate Of A Reaction

We know that the rate of a chemical reaction is defined as the pace at which the products are formed or the speed at which the reacting substances are consumed.
Thus,
Rate of disappearance of reactant (R)

= (Decrease in concentration of R) / (Time taken)

= – [R]/ T

The -ve sign is added in order to make the rate a positive quantity since R is negative.

Alternately,

Rate of appearance of product (P)

= (Increase in concentration of P) / (Time taken)

= [P]/ T

These are called the average rate of a reaction as they give the reaction rate over the entire time period T.

From the equation, it is clear that the units of rate of reaction are concentration per unit time. Hence, if concentration is measured in Mol/L, then the rate of reaction will be measured as Mol/ L/sec.

Instantaneous Rate of A Reaction

The average rate is not suitable for determining the rate of a reaction at any given moment of time. To convey the rate at a specific point in time, we determine the instantaneous rate.

We saw above that,

Average Rate of Reaction = – [R]/ T = [P]/ T

As, T 0,

Instantaneous Rate of Reaction = – [R]/ dT = [P]/ dT

= – d[R]/ dT = d[P]/ dT

Factors Affecting The Rate Of Chemical Reaction

The rate of chemical reaction depends on the nature of the substances undergoing the reaction, the nature of chemical transformation taking place, pressure, temperature and several other factors. Generally, reactions involving combining of ions or atoms occur at a rapid pace, while reactions involving the breaking of covalent bonds are slower.

The rate of a chemical reaction depends on a few generic factors such as:

Temperature of the system

When we increase the temperature, we are delivering more energy into the system. This increases the collision frequency between particles, thus, resulting in an increase in the reaction rate.

This happens because with increase in temperature, a greater number of colliding particles attain the activation energy (minimum amount of energy needed to undergo the chemical change) needed for the collisions to be successful.

Concentration of the reactants

As explained by the rate law and collision theory, the rate of chemical reaction changes with the change in concentration of reactant—the rate reduces with the reduction in the concentration of the reacting substances. This occurs because the collision frequency between particles increases when we increase the concentration.

Presence of catalyst

A catalyst increases the rate of a chemical reaction. Its presence enables an alternative reaction path that requires lower activation energy.

Similarly, an inhibitor can slow down the reaction rates.

Light or Electromagnetic radiation

Electromagnetic radiation, such as visible light, is a form of energy. Exposure to it can increase the energy of the particles, thus, speeding up the reaction rates.

Surface area of reactants

When liquids or solids are involved, the reaction occurs at the interface (boundary or surface) of the reactants. Hence, when a solid is crushed into a powder, its surface area increases and the reaction rate increases.

This is why you would have observed that a large piece of wood shoulders when ignited, whereas smaller pieces burn more rapidly and sawdust burns almost explosively.

Pressure of the gases

We know that, in a gas, the atoms or molecules are loosely spread out. When we increase the pressure, we are reducing the volume available for the gas molecules to spread. By squeezing the molecules together, we increase the frequency of collisions between them, resulting in an increase in reaction rates.

Conclusion

In this article, we learned that the rate of a chemical reaction is the speed at which the reacting substances are consumed. The rate law explains the dependency of the rate on the concentration of the reactants. We also learned how temperature, concentration, pressure, surface area, etc. affect the rate of a chemical reaction.

Arrhenius equation (part i):-

The Arrhenius equation is used for calculating the rate of reaction. It is a crucial part in chemical kinetics. It helps to understand the impact of temperature on the rate of reaction. This equation was first introduced by Svelte Arrhenius in 1889.

In the equation,

A = Frequency factor

K = Rate constant

R = Gas constant

Ea = Activation energy

T = Kelvin temperature

The collision theory is the foundation for the Arrhenius equation. As per this theory, the reaction is essentially a collision involving two molecules (of same or different substances) to form the intermediate. This intermediate that is formed is unstable, and itt exists for a short duration of time. The intermediate breaks down thereby giving out two molecules of product. The energy that is used for forming this intermediate is called the activation energy.

If we look at log on both sides of the equation, the equation becomes

Ln is the natural algorithm, and these values can be picked up from a logarithmic table.

For the graphical representation,

When we compare this equation with the straight-line equation, we get

$X = \frac{1}{T}$

$Y = \ln k$

$M = \frac{-Ea}{R}$

$C = \ln A$

This provides the straight-line graph but has a negative slope.

Plotting the

$kv/s(\frac{1}{T})$

Impact of Temperature

With the help of the graph, we can conclude that the rate of reactions and temperature are proportional. As temperature increases, the rate of reaction also tends to increase. There is an increase in kinetic energy with temperature. So when the temperature is increased, the number of molecules having kinetic energy higher than activation energy also increases. This leads to a rise in the rate of overall reaction as the activation energy decreases.

For the 10K shift in temperature, the rate is almost doubled.

Let us consider the Arrhenius equation at times T1 and T2 where the rates of reaction are denoted by K1 and K2 respectively.

$\ln K1 = \frac{-Ea}{RT_1} + \ln A \qquad \ldots (1)$

$\ln K2 = \frac{-Ea}{RT_2} + \ln A$ ... (2)

Now we subtract 1 from 2

In K2 - In K1 equals to $\frac{Ea}{RT_1} - \frac{Ea}{RT_2}$

$$\ln \frac{K_2}{K_1} = \left(\frac{Ea}{R}\right)\frac{1}{T_1} - \frac{1}{T_2}$$

Converting to log,

$$\log(\frac{Ea}{2.303R})\frac{T_2 - T_1}{T_1 T_2}$$

The Arrhenius equation also suggests that uncatalyzed reaction is more impacted by temperature in comparison to the catalyzed reaction.

Real-Life Examples of This Theory:

Milk gets sour faster when it is kept at room temperature instead of being kept in the refrigerator. Eggs tend to hard boil faster when they are at sea level in comparison to mountains or elevated levels. The butter tends to become rancid at a faster rate in summer than it does in winter Cold-blooded animals or species like reptiles and insects become more lethargic during colder days.

Significance of Arrhenius Equation

his equation enables the accounting of factors that have an effect on the rate of reaction and which is not possible to be determined by the rate law.

It helps in finding the impact of energy barrier, frequency, temperature, the orientation of collisions, and presence of catalyst using the equation.