CHEMICAL KINETICS

TEMPERATURE DEPENDENCE OF THE RATE OF A REACTION

FACTORS AFFECTING RATE OF CHEMICAL REACTION (PART I):

Factors Affecting the Rate of Chemical Reaction

The pace at which a chemical reaction takes place is referred to as the reaction rate. Explore the calculation of reaction rate and the factors influencing it. This rate is quantified by the amount of the reacting substance consumed or the resulting product produced within a specified time frame.

Defining The Rate of A Chemical Reaction

The reaction rate in a chemical process signifies the speed at which the reaction unfolds. It is directly influenced by the decline in the concentration of a reactant over a specific period or the increase in the concentration of a product within a unit of time.

Reaction rates exhibit considerable variation; for instance, the oxidation of iron in the atmosphere progresses over an extended timeframe, while combustion in a car engine transpires within fractions of seconds. Typically, the rate of a chemical reaction diminishes as time elapses. The calculation of the reaction rate involves measuring the alteration in the concentration of reactants or the produced products over time.

Rate Law or Rate Equation

The rate law or rate equation elucidates how the rate of a chemical reaction is influenced by the concentrations of its reactants. Typically, it is expressed as:

Rate $= k[A]x[B]y$

where,

k = rate constant,

[A] and [B] represent the molar concentrations of the reactant substances A and B, while x and y denote the reaction orders. The determination of the rate constant (k) and the exponents x and y involves analyzing how the reaction rate varies with changes in the concentrations of the reactants. Notably, the rate constant k remains independent of the concentrations of reactants A or B, although it is influenced by factors such as temperature and surface area.

The sum of x and y is referred to as the order of the reaction, typically expressed as a whole number (0, 1, 2, etc.), although it can occasionally be fractional. When $x + y$ equals 0, it indicates that the reaction is not contingent on the concentration of the reacting substances.

Formula For Rate of Reaction

Consider a chemical reaction as below:

$$aA + bB\ pP + qQ$$

In this context, the lowercase letters (a, b, p, q) signify the stoichiometric coefficients, where the capital letters (A, B) represent reactants and (P, Q) denote products. The reaction rate 'v' for a chemical reaction is defined by the International Union of Pure and Applied Chemistry (IUPAC) Gold Book as:

v=-1ad[A]dt=-1bd[B]dt=1pd[P]dt=1qd[Q]dt

The statement is applicable solely to a chemical reaction taking place within a closed system, maintaining a constant volume, and without the formation of intermediates during the reaction.

Average Rate of A Reaction

We understand that the rate of a chemical reaction is characterized by the speed at which products are produced or the rate at which the reacting substances are utilized.

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 referred to as the average rate of a reaction as they provide the reaction rate over the entire time period 'T.' The equation makes it evident that the units of the rate of reaction are concentration per unit time. Therefore, if the concentration is measured in Mol/L, the rate of reaction will be expressed as Mol/L/sec.

Instantaneous Rate of A Reaction

The average rate is inadequate for ascertaining the rate of a reaction at any particular moment. To depict the rate at a specific point in time, we calculate 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 a chemical reaction is influenced by various factors, including the nature of the substances involved, the type of chemical transformation occurring, pressure, temperature, and several other elements. Typically, reactions involving the combination of ions or atoms tend to occur rapidly, whereas reactions involving the breaking of covalent bonds tend to be slower. The rate of a chemical reaction is determined by a set of fundamental factors, such as:

Temperature of the system

Elevating the temperature entails supplying additional energy to the system, leading to a heightened collision frequency among particles and consequently an acceleration in the reaction rate. This phenomenon arises because, with a temperature increase, a larger proportion of colliding particles achieve the activation energy required for successful collisions – the minimum amount of energy needed for chemical changes to occur.

Concentration of the reactants

As elucidated by the rate law and collision theory, the rate of a chemical reaction varies in response to alterations in the concentration of the reactant. The rate diminishes as the concentration of the reacting substances decreases. This is attributed to the heightened collision frequency between particles, which occurs when the concentration is increased.

Presence of catalyst

A catalyst enhances the speed of a chemical reaction by providing an alternative reaction pathway with a lower activation energy. Conversely, an inhibitor has the ability to decelerate reaction rates.

Light or Electromagnetic radiation

Electromagnetic radiation, like visible light, represents a form of energy. Exposure to this radiation has the potential to elevate the energy of particles, consequently accelerating reaction rates.

Surface area of reactants

In the presence of liquids or solids, the reaction takes place at the interface, specifically at the boundary or surface of the reactants. Therefore, when a solid is crushed into a powder, its surface area expands, leading to an augmentation in the reaction rate. This explains why you may have noticed that a sizable piece of wood smolders when ignited, while smaller pieces burn more swiftly, and sawdust tends to burn almost explosively.

Pressure of the gases

In a gas, atoms or molecules are dispersed with ample space. Elevating the pressure diminishes the available volume for gas molecules to disperse. By compressing the molecules, collision frequency between them intensifies, leading to an upsurge in reaction rates.

Conclusion

In this article, we have gained an understanding that the rate of a chemical reaction is synonymous with the pace at which the reacting substances are utilized. The rate law clarifies the relationship between the rate and the concentration of the reactants. Furthermore, we have explored the influence of factors such as temperature, concentration, pressure, surface area, and more on the rate of a chemical reaction.

Arrhenius equation (part i):

The Arrhenius equation plays a vital role in determining the rate of a reaction and is an essential component of chemical kinetics. It aids in comprehending the influence of temperature on the reaction rate. This equation was initially introduced by Svante Arrhenius in 1889.
In the equation,

A = Frequency factor

K = Rate constant

$$R = \text{Gas constant}$$
$$Ea = \text{Activation energy}$$
$$T = \text{Kelvin temperature}$$

The collision theory forms the basis of the Arrhenius equation. According to this theory, a reaction fundamentally involves the collision of two molecules (either of the same or different substances) to produce an intermediate. This intermediate is transient and unstable, existing for a brief period. Subsequently, the intermediate decomposes, yielding two molecules of the final product. The energy expended in forming this intermediate is referred to as 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

By examining the graph, we can deduce that there is a direct correlation between the rate of reactions and temperature. As the temperature rises, the rate of reaction generally increases. The escalation in temperature corresponds to an augmented kinetic energy. Consequently, when the temperature is elevated, there is an increase in the number of molecules possessing kinetic energy surpassing the activation energy threshold. This results in an overall boost in the reaction rate, facilitated by the decrease in activation energy.
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.

$$\ln\ K1 = \frac{-E}{RT_1} + \ln\ A \qquad \dots (1)$$
$$\ln\ K2 = \frac{-Ea}{RT_2} + \ln\ A \qquad \dots (2)$$

Now we subtract 1 from 2

$$\text{In K2 - In K1 equals to } \frac{Ea}{RT_1} - \frac{Ea}{RT_2}$$
$$\ln \frac{K_2}{K_1} = \left(\frac{Ea}{R}\right) \frac{1}{T_1} - \frac{1}{T_2}$$

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 tends to spoil more quickly when stored at room temperature as opposed to being refrigerated. Eggs tend to boil faster when at sea level compared to higher altitudes, such as mountains. Butter has a tendency to turn rancid more swiftly in summer than in winter. Cold-blooded animals, such as reptiles and insects, become more sluggish during colder days.

Significance of Arrhenius Equation

This equation allows for the consideration of factors influencing the rate of reaction that cannot be determined by the rate law alone. It aids in assessing the effects of the energy barrier, collision frequency, temperature, collision orientation, and the presence of a catalyst.