Synopsis

1. Meaning of reaction rate
2. Reaction rate and concentration and time
3. Models for reaction rate
4. Reaction rate and temperature
5. Catalysis
6. Reaction mechanisms

Rates of Reactions

Rates of reactions are usually expressed in units of moles per liter per unit time. If we know the chemical equation for a reaction, its rate can be determined by following the change in concentration of any product or reactant that can be detected quantitatively.

The rate of reaction is a positive quantity that expresses how the concentration of a reactant or product changes with time.

Chemical kinetics is the area of chemistry concerned with the speeds, or rates, at which a chemical reaction occurs. The word “kinetic” suggests movement or change; and it refers to the rate of a reaction, or the reaction rate, which is the change in the concentration of a reactant or a product with time (M/s).

On a practical level, a knowledge of reaction rates is useful in drug design, in pollution control, and in food processing. Industrial chemists often place more emphasis on speeding up the rate of a reaction rather than on maximizing its yield.

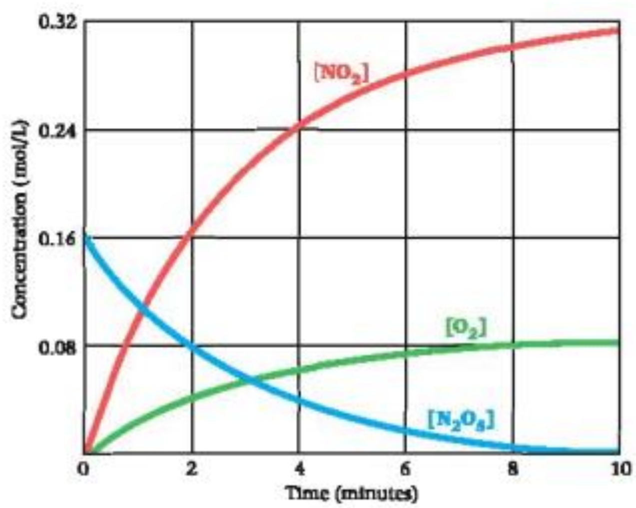
The reaction can be represented by the general equation

$$\text{Reactants} \longrightarrow \text{Products}$$

This equation tells us that during the course of a reaction, reactants are consumed while products are formed. Thus, the progress of a reaction can be monitored either by the decrease in concentration of the reactants or the increase in concentration of the products.

To illustrate what this means, consider the reaction

$$N_2O_{5(g)} \rightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$$



The concentrations of N_2O_5 decreases with time; the concentration of NO_2 and O_2increases. When one mole of N_2O_5 decomposes, two moles of NO_2 and one-half mole of O_2 are formed. This means that

$$-\Delta[N_2O_5] = \frac{\Delta[NO_2]}{2} = \frac{\Delta[O_2]}{\frac{1}{2}}$$

Where $\Delta[\quad]$ refers to change in concentration in mole per liter. The minus sign in front of the N_2O_5 term is necessary because $[N_2O_5]$ decreases as the reaction takes place, the numbers in the denominator of the terms are the coefficients of these species in the balanced equation.

The rate of reaction can now be defined by dividing by the change in time, Δt:

$$rate = \frac{-\Delta[N_2O_5]}{\Delta t} = \frac{\Delta[NO_2]}{2\Delta t} = \frac{\Delta[O_2]}{\frac{1}{2}\Delta t}$$

The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive. On the other hand, the rate of product formation does not require a minus sign because $\frac{\Delta[NO_2]}{2\Delta t}$ and $\frac{\Delta[O_2]}{\frac{1}{2}\Delta t}$ are positive quantity (the concentration of NO_2 & O_2 increases with time).

More generally, for the reaction

$$aA + bB \rightarrow cC + dD$$

Where A, B, C, and D represent substances in the gas phase (g) or in aqueous solution (aq), and a, b, c, d are their coefficients in balanced equation,

$$rate = \frac{-\Delta[A]}{a\Delta t} = \frac{-\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{c\Delta t}$$

Suppose that for the formation of ammonia

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

The molecular nitrogen is disappearing at the rate of 0.10 mol/L per minute, that is $\Delta[N_2]/\Delta t = -0.10\frac{mol}{Lmin}$.

From balanced equation above, we see that the concentration of H_2 must be decreasing three times as fast: is $\Delta[H_2]/\Delta t = -0.30\frac{mol}{Lmin}$ and the concentration of NH_3 must be increasing at the rate of $2 \times 0.10\frac{mol}{Lmin}$

$$rate = \frac{-\Delta[N_2]}{\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} = \frac{\Delta[NH_3]}{2\Delta t} = 0.10\frac{mol}{Lmin}$$

Example

EXAMPLE 16-1 *Rate of Reaction*

At some time, we observe that the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is forming NO_2 at the rate of $0.0072\ \frac{\text{mol}}{\text{L·s}}$.

(a) What is the rate of change of $[O_2]$, $\frac{\Delta[O_2]}{\Delta t}$, in $\frac{\text{mol}}{\text{L·s}}$, at this time?

(b) What is the rate of change of $[N_2O_5]$, $\frac{\Delta[N_2O_5]}{\Delta t}$, in $\frac{\text{mol}}{\text{L·s}}$, at this time?

(c) What is the rate of reaction at this time?

Plan

We can use the mole ratios from the balanced equation to determine the rates of change of other products and reactants. The rate of reaction can then be derived from any one of these individual rates.

Solution

(a) The balanced equation gives the reaction ratio 1 mol $\frac{O_2}{4}$ mol NO_2.

$$\text{rate of change of } [O_2] = \frac{\Delta[O_2]}{\Delta t} = \frac{0.0072 \text{ mol } NO_2}{\text{L·s}} \times \frac{1 \text{ mol } O_2}{4 \text{ mol } NO_2} = \boxed{0.0018\ \frac{\text{mol } O_2}{\text{L·s}}}$$

(b) The balanced equation shows that 2 mol N_2O_5 is *consumed* for every 4 mol NO_2 that is *formed*. Because $[N_2O_5]$ is decreasing as $[NO_2]$ increases, we should write the reaction ratio as $\frac{-2 \text{ mol } N_2O_5}{4 \text{ mol } NO_2}$.

$$\text{rate of change of } [N_2O_5] = \frac{\Delta[N_2O_5]}{\Delta t} = \frac{0.0072 \text{ mol } NO_2}{\text{L·s}} \times \frac{-2 \text{ mol } N_2O_5}{4 \text{ mol } NO_2}$$

$$= \boxed{-0.0036\ \frac{\text{mol } N_2O_5}{\text{L·s}}}$$

The rate of *change* of $[N_2O_5]$ with time, $\frac{\Delta[N_2O_5]}{\Delta t}$, is $-0.0036\ \frac{\text{mol } N_2O_5}{\text{L·s}}$, a *negative* number, because N_2O_5, a reactant, is being used up.

(c) The rate of reaction can be calculated from the rate of decrease of any reactant concentration or the rate of increase of any product concentration.

$$\text{rate of reaction} = -\frac{1}{2}\left(\frac{\Delta[N_2O_5]}{\Delta t}\right) = -\frac{1}{2}\left(-0.0036\ \frac{\text{mol}}{\text{L·s}}\right) = \boxed{0.0018\ \frac{\text{mol}}{\text{L·s}}}$$

$$\text{rate of reaction} = \frac{1}{4}\left(\frac{\Delta[NO_2]}{\Delta t}\right) = \frac{1}{4}\left(0.0072\ \frac{\text{mol}}{\text{L·s}}\right) = \boxed{0.0018\ \frac{\text{mol}}{\text{L·s}}}$$

$$\text{rate of reaction} = \frac{1}{1}\left(\frac{\Delta[O_2]}{\Delta t}\right) = \boxed{0.0018\ \frac{\text{mol}}{\text{L·s}}}$$

Factors that influence reaction rate

Four factors have marked effects on the rates of chemical reactions. They are (1) nature of the reactants, (2) concentrations of the reactants, (3) temperature, and (4) the presence of a catalyst.

I. nature of the reactants: The physical states of reacting substances are important in determining their reactivities. A puddle of liquid gasoline can burn smoothly, but gasoline vapors can burn explosively. Two immiscible liquids may react slowly at their interface, but if they are intimately mixed to provide better contact, the reaction speeds up. White phosphorus and red phosphorus are different solid forms (allotropes) of elemental phosphorus. White phosphorus ignites when exposed to oxygen in the air. By contrast, red phosphorus can be kept in open containers for long periods of time without noticeable reaction.
II. concentrations of the reactants:

There are four factors namely

1. Concentration: Molecules must collide to react, a major factor influencing the rate of a given reaction is reactant concentration, a reaction can occur only when the reactant molecules collide. Thus the reaction rate is proportional to the concentration of reactants:
$$rate \propto collision\ frequency \propto concentration$$
2. Physical State: molecules must mix to collide. The frequency of collisions between molecules also depend on the physical states of the reactants. When the reactants are in the same phase, as in an aqueous solution, random thermal motion brings them into contact. When they are in different phases., contacts occur only at the interface, so vigorous stirring and grinding may be needed. In these cases, the more finely divided is solid and liquid reactants, the greater its surface area per unit volume, the more contact it makes with the other reactants and the faster. the reaction occurs.
3. Temperature.; Molecules must collide with enough energy to react. Temperature usually has a major effect on the speed of your reaction. Recall that molecules in his sample of gas have a range of speeds, With the most probable speed depends on the temperature. Thus, at higher temperature, Molecule collision occur in a given time. At the higher temperature, more of the, sufficiently energetic collisions occur. Thus, Raising the temperature increases the reaction rate by increasing the number and especially the energy of collisions.
4. Catalyst.; speeding up a chemical reaction. Hey, catalysis is a substance. That increases the rate without being consumed in the reaction, because Catalysts are not consumed., only very small., non-stoichiometric quantities are generally required.

Rate Expression and Rate constant

The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

For the general reaction:

$$aA + bB \rightarrow cC + dD$$

the rate law takes the form

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

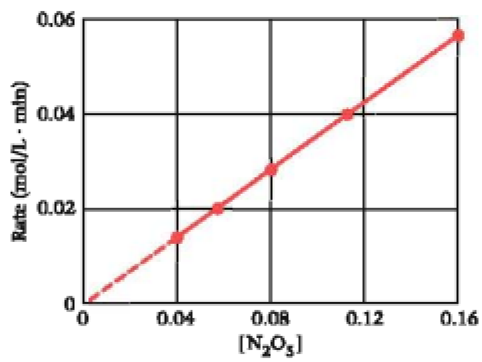
where x and y are numbers that must be determined experimentally. Note that, in general, x and y are not equal to the stoichiometric coeffi cients a and b.

Reaction order, defined as the sum of the powers to which all reactant concentrations appearing in the rate law are raised. The overall reaction order is $x + y$. Alternatively, we can say that the reaction is xth order in A, yth order in B, and $(x + y)$th order overall. Reaction order enables us to understand how the reaction depends on reactant concentrations.

Suppose, for example, that for the general reaction $aA + bB \rightarrow cC + dD$ we have $x = 1$ and $y = 2$. The rate law for the reaction is

$$Rate = k[A][B]^2$$

The dependency of reaction rates on concentration is readily determined for the decomposition. Of N_2O_5. the plots of rate versus Concentration is a straight line through the origin which means that the rates must be directly proportional to the concentration.



$$rate = k[N_2O_5]$$

This equation is referred to as the rate expression for the decomposition of N_2O_5 and the proportionality constant k is called rate constant. The rate constant is independent of other quantities in the equation. The rate expression can take various forms, depending on the nature of the reaction. An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.

The power (exponent) of concentration *n* or *m* in the rate law is usually a small whole number integer (1, 2, 3) or fractional. The proportionality constant *k* is called the **rate constant** for the reaction.

Examples of rate law :

	REACTIONS	RATE LAW
(1)	$2N_2O_5 \longrightarrow 4NO_2 + O_2$	rate = $k[N_2O_5]$
(2)	$H_2 + I_2 \longrightarrow 2HI$	rate = $k[H_2][I_2]$
(3)	$2NO_2 \longrightarrow 2NO + O_2$	rate = $k[NO_2]^2$
(4)	$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$	rate = $k[H_2][NO]^2$