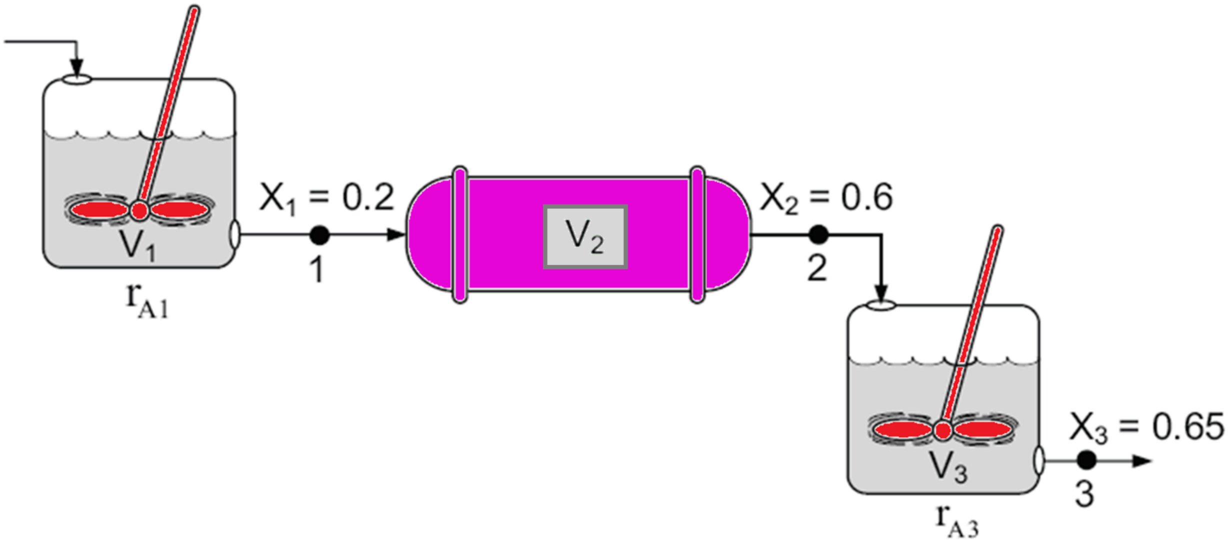
Chemical Kinetics



Chemical kinetics explores various aspects of reactions, including reaction mechanisms, reaction orders, rate laws, and the effect of temperature, concentration, catalysts, and other factors on reaction rates. By studying chemical kinetics, scientists can gain insights into the fundamental nature of reactions, predict reaction outcomes, and design reaction conditions to optimize desired processes in fields ranging from industrial chemistry to environmental science. It is primarily knowledge of chemical kinetics and reactor design that distinguishes the chemical engineer from other engineers. The functions of the chemical engineer therefore in the field of chemical reaction engineering are to specify the size of and geometry of reactors for the production of a given amount of a particular chemical and to appraise the performance of existing reactors.

The study of chemical reaction engineering (CRE) combines the study of chemical kinetics with the reactors in which the reactions occur. Chemical kinetics and reactor design are at the heart of producing almost all industrial chemicals.

Table of Contents

- What is Chemical Kinetics
- Chemical Identity
- Terminology in Chemical Kinetics
- Reaction Rate
- Order of Reaction
- Molecularity and Mechanism of Reaction
- Rate Equation (Rate Law) and Specific Reaction Rate (Rate Constant Or Reaction Velocity)

- Temperature Dependence of Rate Constant (K)
- Stoichiometry of Reaction
- Solved Questions
- Quiz

What is Chemical Kinetics - Click to download it

Chemical kinetics is the branch of chemistry that deals with the study of the speed or rates at which chemical reactions occur and the factors that influence these rates. It involves the investigation of how reactants transform into products over time, and it seeks to understand the underlying mechanisms and principles governing these transformations.

Simply, Chemical kinetics is the study of the rate of reaction and mechanism by which one **chemical species** is converted to another.

Chemical Identity

A chemical species is said to have reacted when it has lost its chemical identity. The identity of a chemical species is determined by the kind, number, and configuration of that species' atoms. The three (3) basic ways a chemical species may undergo conversion are;

1. **Decomposition** $CH_3CH_3 \rightarrow H_2 + H_2C{=}CH_2$
2. **Combination** $N_2 + O_2 \rightarrow 2\,NO$
3. **Isomerization** $C_2H_5CH{=}CH_2 \rightarrow CH_2{=}C(CH_3)_2$

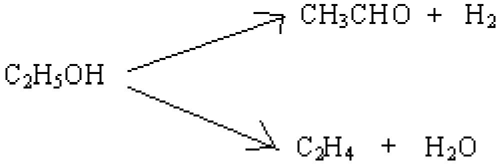
Terminology in Chemical Kinetics

- **Limiting reactant:** if in the reactant system the reactants are not present in the proportions required by the stoichiometric equation then the reactant which is not in excess is the limiting reactant.
- **Fractional conversion (x):** this refers to the fraction of a reactant that has undergone a chemical change at a particular stage of a reaction process.

$$X = \frac{amount(moles).of.reac\tan t.consumed}{amount(moles).of.reac\tan t.fed}$$

Practically, the fractional conversion of the limiting reactant is usually considered. Fractional conversion usually ranges from1 (i.e. 0-100%)

- **Yield:** it is generally defined with respect to a basis e.g.



If ‘a’ moles represent the amount of alcohol fed to the reactor of which a total of ‘q’ moles react to give ‘r’ moles of the aldehyde and s moles of the ethylene. The total conversion is then q/a. the aldehyde yield is either r/a or r/q, depending upon whether one chooses as basis of total alcohol fed or that part of the alcohol which reacts. Similarly the ethylene yield is s/a or s/q

Reaction Rate (Rate Law rA)

The rate of reaction is the mass or moles of a product produced or reactants consumed per unit time. The rate of chemical reaction is only a function of the properties of the reacting material e.g. species concentration, temperature, pressure or type of catalyst used and it is independent of the type of reactor used (batch or continuous reactant). If the reactants are not well stirred then the rate depends on the position in the reactor. Thus, we may write for component A as:

rA = f (state of the system) = f (temperature, pressure, concentration)

Let’s consider this reaction below;

$$pA + qB \longrightarrow wC$$

The rate of change of A is expressed as $-\frac{dN_A}{dt}$, the negative sign indicates that N_A decreases with time. Similarly the rate of change of B and C are expressed as $-\frac{dN_B}{dt}$ and $\frac{dN_C}{dt}$ respectively. The relationship between these three rates is,

$$-\frac{1}{p}\frac{dN_A}{dt} = -\frac{1}{q}\frac{dN_B}{dt} = \frac{1}{w}\frac{dN_C}{dt}$$

$$or$$

$$-\frac{r_A}{p} = -\frac{r_B}{q} = \frac{r_C}{w}$$

Order of Reaction

Generally, the order of reaction refers to the powers to which the concentrations are raised in the rate law. Let's consider this reaction expressed by:

$$pA + qB \longrightarrow wC$$

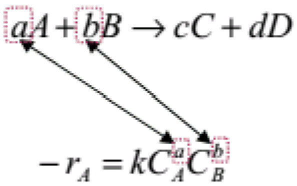
The rate of conversion of A per unit volume of mixture is

$$-r_A = \frac{-dN_A}{dt} = KC_A{}^{\alpha}C_B{}^{\beta}$$

Where α is reaction order with respect to A and β is reaction order with respect to B. the overall order N = α + β. The overall order need not be an integer; it may be 0 or a small positive number which rarely exceeds 3.

- **Elementary Reaction**

A reaction order for which each species is identical to its Stoichiometric coefficient as shown:



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

$$-r_A = kC_A^a C_B^b$$

Where a and b represent the reaction order with respect to the reactant A and B respectively, over all reaction order (n) = a + b

Let’s consider this example below;

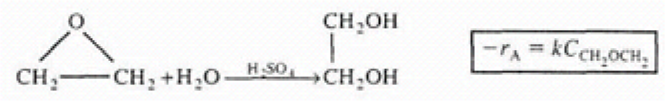
If $2NO + O_2 \rightarrow 2NO_2$ is an elementary reaction, then the rate law is given as;

$$-r_{NO} = KC_{NO}{}^2C_{O_2}$$
$$-rO2 = K^iC_{NO}{}^2C_{O_2}$$
$$r_{NO_2} = K^{ii}C_{NO}{}^2C_{O_2}$$

The reaction is second order with respect to NO and first order with respect to O2 and overall order of 3.

NB: α and β may or may not be equal to their respective stoichiometric numbers, a and b.

Other examples are shown below:



$$\boxed{-r_A = kC_{CH_2OCH_2}}$$

$$\boxed{-r_A = k_{ONCB}C_{ONCB}C_{NH_3}}$$

Reaction rate constant, k will vary with the order of the reaction as shown:

A → Products

Order	Rate Equation	Units
Zero	$-r_A = k$	$mol.V^{-1}.s^{-1}$
First	$-r_A = kC_A$	s^{-1}
Second	$-r_A = kC_A^2$	$V.mol^{-1}.s^{-1}$
Third	$-r_A = kC_A^3$	$(V.mol^{-1})2.s^{-1}$
nth order	$-r_A = kC_A^n$	$(concentration)^{1-n}.s^{-1}$

Another example of elementary reaction; reversible second order:-

$$2C_6H_6 \underset{k_2}{\overset{k_1}{\longleftrightarrow}} C_{12}H_{10} + H_2 \qquad -r_B = k_1\left(C_B^2 - \frac{C_DC_{H_2}}{K_c}\right)$$

Where Kc is equilibrium constant

All reversible reaction rate laws must reduce to the thermodynamic relationship relating reacting species concentrations at equilibrium. At equilibrium, the net rate of reaction is zero for all species involved in the reaction

$$-r_{ie} = 0$$

- **Non-Elementary Reaction**

Do not follow the Stoichiometric coefficients for the overall reaction

Let’s consider this Homogeneous Reactions below:

1. Gas-phase synthesis of phosgene,

$$CO + Cl_2 \longrightarrow COCl_2 \quad -r_{CO} = k_{CO}C_{CO}C_{Cl_2}^{3/2} \ \mathbf{n=5.5}$$

2. Decomposition of nitrous oxide,

$$2N_2O \longrightarrow 2N_2 + O_2$$

$$-r_{N_2O} = \frac{k_{N_2O}C_{N_2O}}{1+k'C_{O_2}}$$

n depended on C_{O_2} concentration

Also let’s consider Heterogeneous Reactions

Heterogeneous reaction and corresponding rate law is the hydrodemethylation of toluene (T) to form benzene (B) and methane (M) carried out over a solid catalyst.

$$C_6H_5CH_3 + H_2 \xrightarrow{cat.} C_2H_6 + CH_4$$

$$-r'_T = \frac{k\ P_{H_2}P_T}{1+K_BP_P+K_TP_T}$$

$$k = \frac{mol\ toluene}{kg_{cat}.s.kPa^2}$$

Molecularity and Mechanism of Reaction

The term molecularity refers to number of atoms, ions, or molecules involved in the rate-limiting step of the reaction.

- Unimolecular – one reactant involved in reaction
- Bimolecular – two reactants must collide to react
- Termolecular – three reactants must interact for reaction to occur

The mechanism of a reaction is the sequence of individual chemical events whose overall results produce the observed reaction. The molecularity describes the mechanism of chemical reaction and must be an integer. Thus the number of molecules which react at the rate determining step gives the molecularity of the reaction. Consider the overall reaction.

$2A + B \rightarrow C + D$ proceeding by two steps

Step 1 $A + B \rightarrow C + E$ (slow) for rate determining step

Step 2 $A + E \rightarrow D$ (fast)

The Molecularity of the above reaction is 2, because the rate determining step involves the reaction between 1 mole of A and 1 mole of B.

Rate Equation (Rate Law) and Specific Reaction Rate (Rate Constant or Reaction Velocity)

Rate Law or rate equation is an algebraic equation that relates the rate of reaction to the species concentration in the kinetic expression.

e.g. $-r_A = \frac{-dN_A}{dt} = KC_A^{\alpha} C_B^{\beta}$, mole/time for a unit volume of reactor

N_A = moles of A; V = volume (K is only constant with concentration but not with temperature).

If the reactor has a volume V, then the rate of conversion of A is

$$-r_A = \frac{-dN_A}{dt} = VC_A^{\alpha} C_B^{\beta}$$

If the volume is constant then dividing through by V,

$$-\frac{1}{V}\frac{dN_A}{dt} = KC_A^{\alpha} C_B^{\beta}$$

$$\Rightarrow \frac{-d\dfrac{N_A}{V}}{dt} = KC_A{}^{\alpha}C_B{}^{\beta}$$

$$\frac{-dC_A}{dt} = KC_A{}^{\alpha}C_B{}^{\beta} \quad \text{Where } C_A = \frac{N_A}{V}$$

But if V is varying, eliminating N_A (i.e. $N_A = C_AV$)

$$\Rightarrow -\frac{d(C_AV)}{dt} = KVC_A{}^{\alpha}C_B{}^{\beta}$$

$$-V\frac{dC_A}{dt} - C_A\frac{dV}{dt} = KVC_A{}^{\alpha}C_B{}^{\beta}$$

K = specific reaction rate or rate constant or rate coefficient or velocity constant. Its dimensions vary with the order of the reaction.

Units of K

Order of reaction	Dimension of K	Unit of K
Zero order (n = 0)	$[\text{CONC}][\text{TIME}]^{-1}$	g-mol$\text{L}^{-!}$sec^{-1}
First order (n = 1)	$[\text{TIME}]^{-1}$	sec^{-1}
Second order (n = 2)	$[\text{CONC}]^{-1}[\text{TIME}]^{-1}$	L g-mol^{-1} sec^{-1}
nth order (n)	$[\text{TIME}]^{-1}[\text{CONC}]^{1-n}$	$[\text{g-mol/L}]^{(1-n)}$ sec^{-1}

Let’s deduce the units of K for an nth order reaction

$$-r_A = KC_A{}^n$$

$$\text{g-mol L}^{-!}\text{sec}^{-1} = K\,(\text{g-mol L}^{-1})^n$$

$$K = \frac{g - molL^{-1}\sec^{-1}}{\left(g - molL^{-1}\right)^n} = \left(g - molL^{-1}\right)^{1-n}\sec^{-1}$$

Also let’s consider Rate equation using Partial Pressures

$pA + qB \longrightarrow wC$ for a gas phase reaction

In terms of partial pressures, the rate law

$-r_A = K_p P_A^{\alpha} P_B^{\beta}$ ………… eqn.1

From the ideal gas law

$$C_A = \frac{P_A}{RT} \quad \text{……………eqn.2}$$

$$C_B = \frac{P_B}{RT} \quad \text{………………eqn.3}$$

But $-r_A = K_C C_A^{\alpha} C_B^{\beta}$ ………eqn.4

Substitute (2) and (3) into (4)

$$-r_A = K_C \left(\frac{P_A}{RT}\right)^{\alpha} \left(\frac{P_B}{RT}\right)^{\beta}$$

$$-r_A = \frac{K_C P_A^{\alpha} P_B^{\beta}}{(RT)^{\alpha+\beta}} \quad \text{……….eqn.5}$$

Comparing equations (1) and (5)

$$K_P = \frac{K_C}{(RT)^{\alpha+\beta}} = \frac{K_C}{(RT)^{n}}$$

Units of K_P in this case becomes

$(\text{sec}^{-1})(\text{mol L}^{-1})\,\text{atm}^{-(\alpha+\beta)}$

Note: Use R in units of L.atm/mol.K

Temperature Dependence of Rate Constant (K)

K(T) is not a true constant but mainly independent of the concentration of species involved in the reaction. It is strongly dependent upon temperature but other variable such as pressure and catalyst weight will exhibit much less effect on the rate constant.

Rate constant dependent on temperature is given by;

- **Arrhenius equation** base on the collision theory of molecules

  $K(T) = Ae^{-E/RT}$

Where

A = frequency factor

E = Activation energy

R = universal gas constant
T = absolute temperature in Kelvin

- **Transition state theory:** this theory regards the reaction rate to be governed by the rate of decomposition of the intermediate

  $K(T) = A'T^n e^{-E/RT},\ 0 \leq n \leq 1$

Stoichiometry of Reaction

Consider the reaction of the form

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

Where a, b, c and d are the stoichiometric coefficient, using A as reference, we can rewrite this as:

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$

Therefore, expressing their rates, we have

$$-r_B = \frac{b}{a}(-r_A)\ldots\ldots\ldots\ldots(1) \qquad\qquad -r_A = \frac{a}{b}(-r_B)$$

$$r_C = \frac{c}{a}(-r_A)\ldots\ldots\ldots\ldots\ldots(2) \quad \text{Make } -r_A \text{ the subject} \quad -r_A = \frac{a}{c}(r_C)$$

$$r_D = \frac{d}{a}(-r_A)\ldots\ldots\ldots\ldots\ldots(3) \qquad\qquad -r_A = \frac{a}{d}(r_D)$$

Equating them

$$-r_A = \frac{a}{b}(-r_B) = \frac{a}{c}(r_C) = \frac{a}{d}(r_D)$$

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

Let's consider this example: If a = 1, b = 2, c = 3 and d = 0

i.e. $A + 2\,B \rightarrow 3\,C$

$$\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{3} \quad \text{if } r_A = 0.3 \text{ mol/min. find } r_B \text{ and } r_C$$

Writing the rate law for the reaction above, we have

In terms of A

$-r_A = K^1 C_A C_B^2$ In terms of B $-r_B = K^{11} C_A C_B^2$

In terms of C

$-r_B = K^{111} C_A C_B^2$

But

$$-r_A = \frac{-r_B}{2} = \frac{r_C}{3}$$

$$\frac{K^1 C_A C_B{}^2}{1} = \frac{K^{11} C_A C_B{}^2}{2} = \frac{K^{111} C_A C_B{}^2}{3}$$

$$\therefore \frac{K^1}{1} = \frac{K^{11}}{2} = \frac{K^{111}}{3}$$

If $-r_A = 0.6\, C_A C_B^2$, find $-r_B$ and r_C

$$\frac{K^1}{1} = \frac{K^{11}}{2} = \frac{0.6}{1} \text{ , } K'' = 1.2$$

$$\therefore\ -r_B = 1.2\, C_A C_B^2$$

Solved Questions

1. Given that:

   $2NO_2 + \frac{1}{2} O_2 \rightarrow N_2O_5$

   What is the relation between the rates of formation and disappearance of the three component of the reaction?
2. For a gas phase reaction at 400K the rate is reported as:

   $$\frac{-dP_A}{dt} = 3.66 P_A{}^2$$

   Determine the units of rate constant.

Solution

1. $\frac{-r_{NO2}}{2} = \frac{-r_{O2}}{½} = \frac{r_{N_2O_5}}{1}$

2. $\frac{atm}{hr} = 3.66(atm)^2$

$= 3.66$ [=] $atm^{-1}hr^{-1}$

Fractional conversion or conversion (x)

$$x = \frac{amount.reacted}{amount.fed\,(initial.amount)}$$

$$x = \frac{moles.of.A.reacted}{initial.moles.of.A.fed}$$

$$x = \frac{N_{AO} - N_A}{N_{AO}}$$

If volume is constant

$N_{AO} = VC_{AO}$, $N_A = VC_A$

$$x = \frac{VC_{AO} - VC_A}{VC_{AO}} = \frac{C_{AO} - C_A}{C_{AO}}$$

$C_{AO} - C_A = XC_{AO}$, $C_A = C_{AO}(1-x)$

For flow process, we use Fi in place of Ni

$$x = \frac{Fio - Fi}{Fio}$$

$$x = \frac{F_{AO} - F_A}{F_{AO}} \Rightarrow F_{AO} - F_A = xF_{AO}$$

$$F_A = F_{AO}(1-x)$$

Quiz

a. Chemical kinetics is the study of the rate of reaction and mechanism by which a………is converted to another.
b. The principle of chemical kinetics can also be applied to living systems. True/false
c. What are the three basic ways species can undergo in chemical reaction?
d. State the units of the rate constant if rate law of a reaction is

$-r_A = 0.2\ C_A^n$, mol/(L.s)

Where n is 2.

Click to download it