❖ Rate Law for Consecutive & Parallel Reactions of Ist Order Reactions

In addition to the opposing or reversible reactions, two other types of simultaneous reactions are consecutive and parallel reactions. In this section, we will discuss the kinetic profiles of these two types of reactions up to the first order only.

➢ *Consecutive Reactions*

In many complex reactions, the order of the reaction has not been found equal to the molecularity noted from the stoichiometry. So, these reactions must take place in multiple steps rather than a single step. These multiple steps are individually labeled as consecutive reactions.

The consecutive reactions may be defined as the single-step reactions which can be written to represent an overall reaction.

In order to understand the kinetic profile of consecutive reactions, consider two first-order reactions in which reactant *A* converts to *B* which in turn converts to product *C*.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{85}$$

Where k_1 and k_2 are the rate constants for the first and second steps, respectively. In other words, *A* is the reactant, *B* is simply the intermediate and *C* is the final product.

However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. Now suppose that the initial concentrations of reactant *A* is C_0; while the concentrations of *A*, *B* and *C* after time *t* are C_A, C_B and C_C, respectively. So, we can say that

$$C_0 = C_A + C_B + C_C \tag{86}$$

Now, the rate can be deduced in terms of C_A, C_B and C_C as given below.

1. Rate law in terms of C_A: The rate of disappearance reactant of *A* in the given reaction can be given by the following relation.

$$-\frac{d[C_A]}{dt} = k_1 C_A \tag{87}$$

or

$$-\frac{d[C_A]}{C_A} = k_1 dt \tag{88}$$

Integrating both sides, we get

$$-\ln C_A = k_1 t + I \tag{89}$$

Where *I* is the constant of integration. However, when *t* = 0, C_A = C_0, the equation (89) takes the form

$$-\ln C_0 = I \tag{90}$$

Using the value of integration constant from equation (90) in equation (89), we get

$$-\ln C_A = k_1 t - \ln C_0 \tag{91}$$

or

$$\ln C_0 - \ln C_A = k_1 t \tag{92}$$

or

$$-\ln \frac{C_A}{C_0} = k_1 t \tag{93}$$

or

$$\ln \frac{C_A}{C_0} = -k_1 t \tag{94}$$

or

$$\frac{C_A}{C_0} = e^{-k_1 t} \tag{95}$$

or

$$C_A = C_0 e^{-k_1 t} \tag{96}$$

2. Rate law in terms of C_B: The rate of formation of intermediate B can be given by the following relation.

$$\frac{d[C_B]}{dt} = -k_2 C_B + k_1 C_A \tag{97}$$

or

$$\frac{d[C_B]}{dt} = k_1 C_A - k_2 C_B \tag{98}$$

After putting the value of C_A from equation (96) in equation (98), we get a linear differential equation of first order i.e.

$$\frac{d[C_B]}{dt} = k_1 C_0 e^{-k_1 t} - k_2 C_B \tag{99}$$

Integrating and then rearranging equation (99), both side, we get

$$[C_B] = C_0 \left(\frac{k_1}{k_2 - k_1} \right) \left(e^{-k_1 t} - e^{-k_2 t} \right) \tag{100}$$

3. Rate law in terms of C_C: The overall rate of formation of the product C in the given reaction can be given by the following relation.

$$\frac{d[C_C]}{dt} = k_2 C_B \tag{101}$$

After putting the value of C_A and C_B from equation (96) and equation (100) into equation (86), we get the following result.

$$C_C = C_0 - C_0 e^{-k_1 t} - C_0 \left(\frac{k_1}{k_2 - k_1}\right)\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{102}$$

or

$$= C_0 \left[1 - e^{-k_1 t} - \left(\frac{k_1}{k_2 - k_1}\right)\left(e^{-k_1 t} - e^{-k_2 t}\right)\right] \tag{103}$$

or

$$= C_0 \left[1 - e^{-k_1 t} - \frac{k_1 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1}\right] \tag{104}$$

or

$$= C_0 \left[1 - \left(e^{-k_1 t} + \frac{k_1 e^{-k_1 t}}{k_2 - k_1} - \frac{k_1 e^{-k_2 t}}{k_2 - k_1}\right)\right] \tag{105}$$

or

$$= C_0 \left[1 - \left(\frac{(k_2 - k_1)e^{-k_1 t} + k_1 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1}\right)\right] \tag{106}$$

$$= C_0 \left[1 - \left(\frac{k_2 e^{-k_1 t} - k_1 e^{-k_1 t} + k_1 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1}\right)\right] \tag{107}$$

$$= C_0 \left[1 - \left(\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1}\right)\right] \tag{108}$$

or

$$C_C = C_0 \left[1 - \frac{1}{(k_2 - k_1)}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right] \tag{109}$$

The equation (96), (100) and (109) can be used to plot the time-dependent variation of C_A, C_B and C_C, respectively.

DALAL INSTITUTE
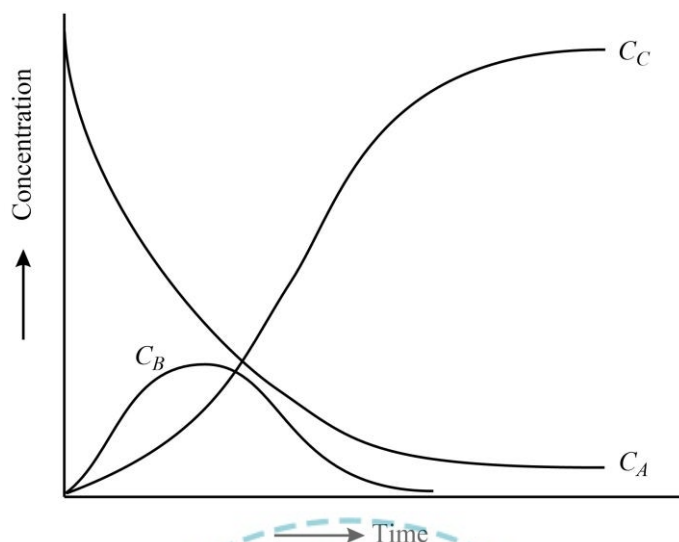
Figure 7. The plot C_A, C_B and C_C as a function of time in a typical consecutive reaction.

It can be clearly seen that the concentration of A decreases exponentially, while the concentration of B increases first and then declines. The concentration of C increases continuously and finally becomes equal to the concentration of A.

Maxima in the concentration of B: In addition to the time-dependent concentration variation of different species, one more important parameter to measure is the maximum B concentration. Since, for this the value of $[dC_B]/dt = 0$, the differentiation of equation (100) and then putting equal to zero gives

$$\frac{d[C_B]}{dt} = C_0 \left(\frac{k_1}{k_2 - k_1}\right)\left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right) = 0 \tag{110}$$

$$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0 \tag{111}$$

or

$$k_1 e^{-k_1 t} = k_2 e^{-k_2 t} \tag{112}$$

or

$$\frac{k_1}{k_2} = \frac{e^{-k_2 t}}{e^{-k_1 t}} \tag{113}$$

$$\frac{k_1}{k_2} = e^{(k_1 - k_2)t} \tag{114}$$

Taking logarithm both side, we get

$$\ln\frac{k_1}{k_2} = \ln e^{(k_1 - k_2)t} \tag{115}$$

$$\ln\frac{k_1}{k_2} = (k_1 - k_2)t \tag{116}$$

$$t_{max} = \frac{1}{(k_1 - k_2)} \ln\frac{k_1}{k_2} \tag{117}$$

Now putting the value of *t* from equation (117) in equation (100), we get

$$[C_B] = C_0 \left(\frac{k_1}{k_2 - k_1}\right)\left[\exp\left\{\frac{-k_1\ln(k_1/k_2)}{k_1 - k_2}\right\} - \exp\left\{\frac{-k_2\ln(k_1/k_2)}{k_1 - k_2}\right\}\right] \tag{118}$$

Simplifying and then rearranging the above equation, we get

$$[C_B]_{max} = C_0 \left(\frac{k_2}{k_1}\right)e^{k_2/(k_1 - k_2)} \tag{119}$$

Rate law in special cases: In addition to the typical consecutive reaction i.e. $k_1 = k_2$, two special cases also arise from the nature of the step reactions discussed below.

i) When $k_2 \ggg k_1$: In these types of reactions, the value of k_1 can be neglected. Therefore, the equation (109) takes the form

$$C_c = C_0\left(1 - e^{-k_1 t}\right) \tag{120}$$

Graphically,
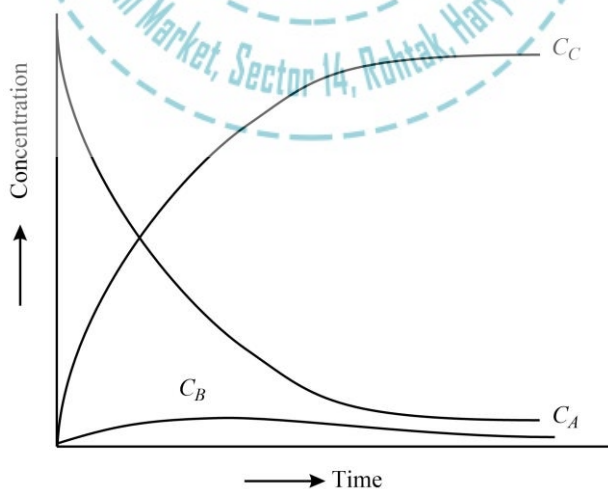
Figure 8. The plot C_A, C_B and C_C vs time in a typical consecutive reaction when $k_2 \ggg k_1$.

It can be clearly seen that the concentration of the intermediate practically remains constant, and therefore, the steady-state approximation can be applied in this case.

ii) When $k_1 \ggg k_2$: In these types of reactions, the value of k_2 can be neglected. Therefore, the equation (109) takes the form

$$C_C = C_0\big(1 - e^{-k_2 t}\big) \tag{121}$$

Graphically,
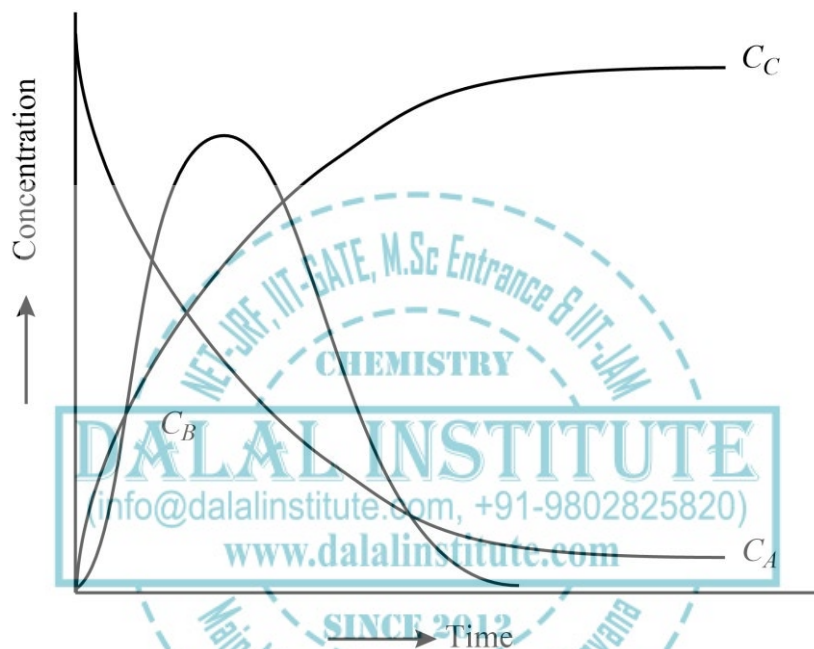
Figure 9. The plot C_A, C_B and C_C vs time in a typical consecutive reaction when $k_1 \ggg k_2$.

➢ *Parallel Reactions*

In many reactions, the reactant reacts to form more than one product simultaneously. If the amount of one the reaction product is very large in comparison to the others, then we can simply neglect these other reactions. However, if the amount of the product formed by other reactions are significant, we must refine the overall rate equation to represent this.

The parallel or side reactions may simply be defined as the reactions in which initial species react to give multiple products simultaneously.

In order to understand the kinetics of parallel reactions of the first order, suppose that a reactant *A* reacts to form product *B* and *C* simultaneously. A typical depiction of the parallel or side reaction with two pathways is given below.
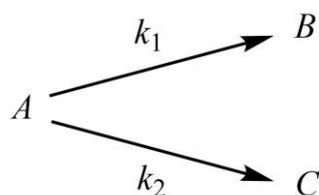
Where k_1 and k_2 are the rate contents. Now suppose that a is the initial concentration of the reactant A, while x is the decrease in the concentrations of the reactant after 't' time. Hence, the rates of first (R_1) and second reaction (R_2) can be given as:

$$R_1 = \frac{d[B]}{dt} = k_1[A] = k_1(a - x)$$

(122)

or

$$R_2 = \frac{d[C]}{dt} = k_2[A] = k_2(a - x)$$

(123)

The overall reaction rate can be obtained by adding equation (122) and equation (123) as

$$\frac{dx}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt} = k_1(a - x) + k_2(a - x)$$

(124)

or

$$\frac{dx}{dt} = (k_1 + k_2)(a - x)$$

(125)

or

$$\frac{dx}{(a - x)} = (k_1 + k_2)dt$$

(126)

Integrating the equation (126) and then rearranging, we get

$$k_1 + k_2 = \frac{1}{t}\ln\frac{a}{(a - x)}$$

(127)

Also, dividing equation (122) by (123), we get

$$\frac{R_1}{R_2} = \frac{k_1(a - x)}{k_2(a - x)}$$

(128)

Which implies that

$$\frac{R_1}{R_2} = \frac{k_1}{k_2}$$

(129)

Hence, the value of rate constants involved, i.e., k_1 and k_2 can easily be obtained from the use of equation (127) and equation (129).
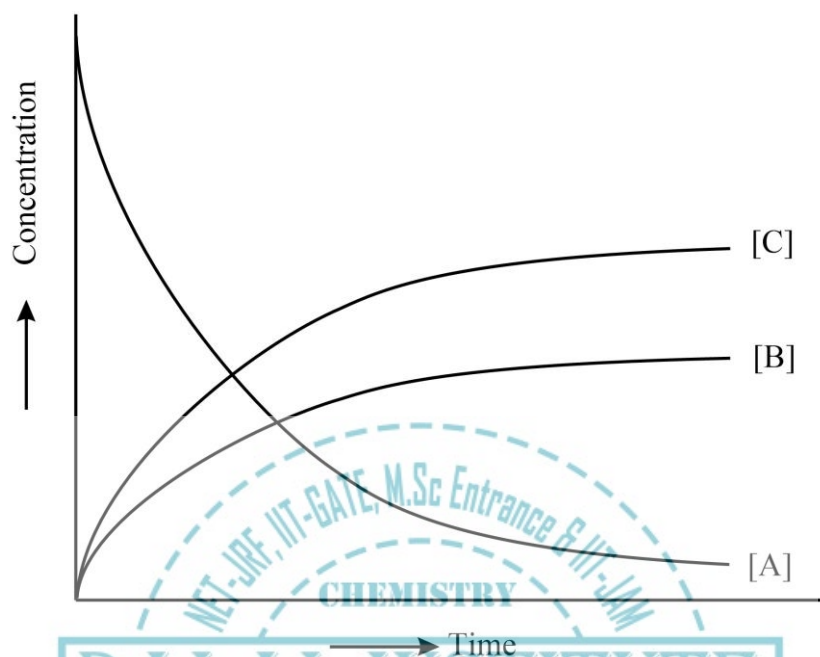
Figure 10. The variation of the concentrations of reactants and products as a function of time in a typical parallel reaction.

It should also be noted from the equation (129) that the ratio of the concentration of products remains the same with time. Furthermore, the percentage of both products can also be obtained from the knowledge of rate constants using the relations given below.

$$Fractional\ Quantum\ Yield\ of\ A = \frac{k_1}{k_1 + k_2} \tag{130}$$

also

$$Fractional\ Quantum\ Yield\ of\ B = \frac{k_2}{k_1 + k_2} \tag{131}$$

The percentage is obtained by multiplying corresponding fractional quantum yields by 100. Similarly, parts per thousand (ppt) and parts per million (ppm) can be obtained by multiplying equations (130) and (131) by 10^3 and 10^6, respectively.

CLASSES

BOOKS

VIDEOS

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM

Want to study chemistry for CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

READ MORE

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute ?

READ MORE

Video Lectures

Want video lectures in chemistry for CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

READ MORE

Home: https://www.dalalinstitute.com/
Classes: https://www.dalalinstitute.com/classes/
Books: https://www.dalalinstitute.com/books/
Videos: https://www.dalalinstitute.com/videos/
Location: https://www.dalalinstitute.com/location/
Contact Us: https://www.dalalinstitute.com/contact-us/
About Us: https://www.dalalinstitute.com/about-us/

Postgraduate Level Classes
(NET-JRF & IIT-GATE)
Admission

Regular Program	Distance Learning
Test Series	Result

Undergraduate Level Classes
(M.Sc Entrance & IIT-JAM)
Admission

Regular Program	Distance Learning
Test Series	Result

A Textbook of Physical Chemistry – Volume 1

"A Textbook of Physical Chemistry – Volume 1 by Mandeep Dalal" is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.
READ MORE

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

Sign Up

International Edition

A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL
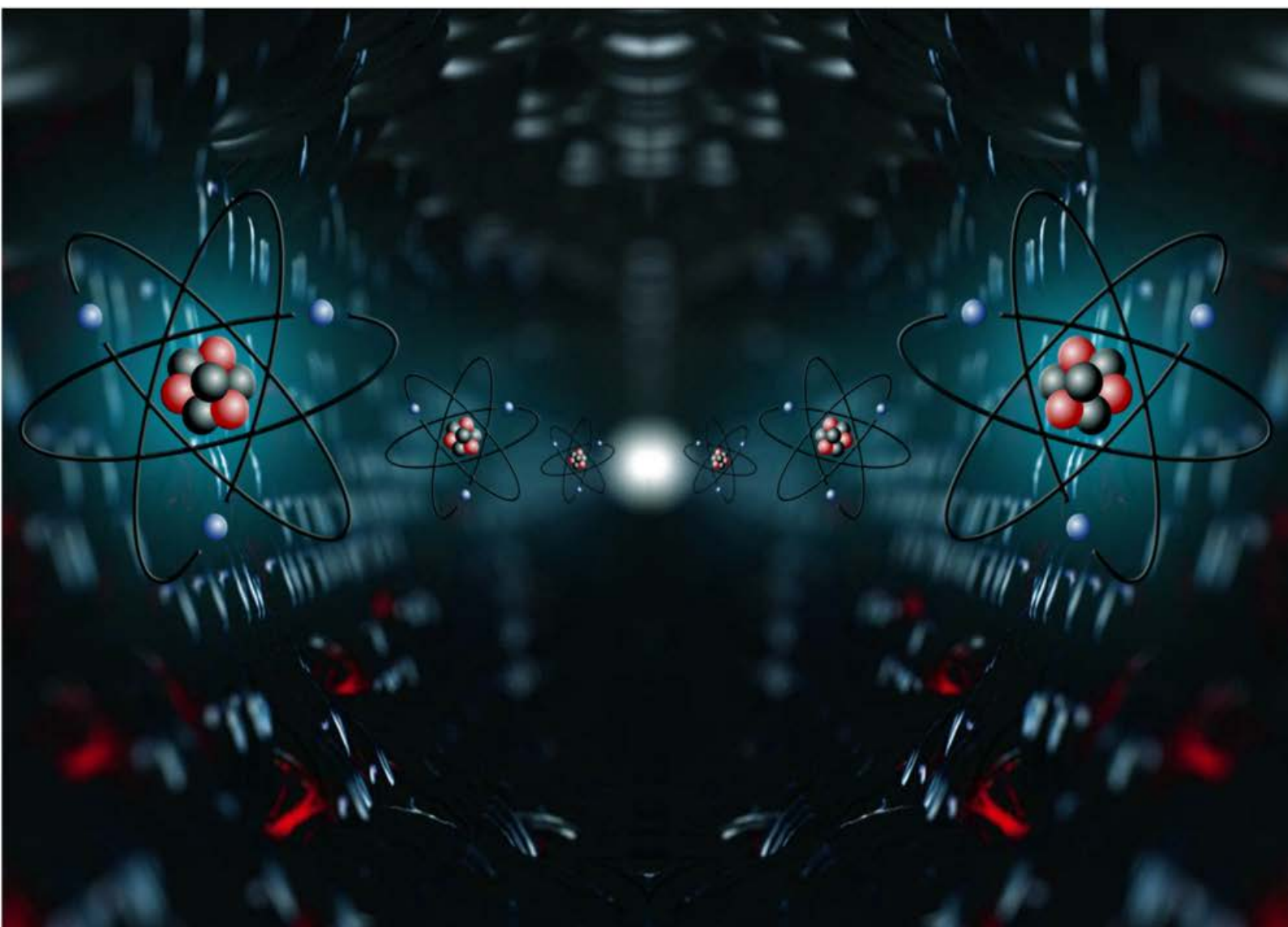
First Edition

DALAL INSTITUTE

Table of Contents

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

DALAL INSTITUTE
Main Market, Sector-14, Rohtak, Haryana-124001
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com