PHYSICAL PHARMACY

Dr. U. B. HADKAR

NIRALI PRAKASHAN
ADVANCEMENT OF KNOWLEDGE

A Book Of

PHYSICAL PHARMACY

for

B. Pharmacy Students

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PREFACE TO THE TWELFTH EDITION

I am extremely pleased to present the Twelfth edition of my book "**A TEXT BOOK OF PHYSICAL PHARMACY**". This edition covers the syllabus in the subject of physical pharmacy at the undergraduate level, implemented in most of the Indian Universities. An additional chapter on Mole Concept has been included in this edition to help the students understand the calculations in solving numerical problems.

I would like to thank the teachers and the students of pharmacy colleges in India, without whose support this New Edition of this book would not have been possible. I am extremely grateful to my colleagues at the PKMK College of Pharmacy, Worli, Mumbai, for the knowledge I have gained over the past twenty nine years in the subject of physical pharmacy, the subject I love to teach.

My sincere thanks are due to "Nirali Prakashan", Pune for bringing out such a neatly printed text book and the encouragement received from them and showing confidence in my authorship.

Dr. U. B. Hadkar

CONTENTS

1…

Chemical Kinetics

In every day life, we come across a number of chemical reactions. Thus, we observe burning of coal, rusting of iron etc. Some of the reactions are so fast that we can not measure the rate of the reaction. For example, hydrogen gas, burns in air to form water. Some of the reactions are so slow that it may take years to measure the rate. The rusting of iron at room temperature for instance is a slow reaction, and may take months to measure its rate. Between these two extreme type of reactions, there are reactions which proceed at a measurable rate and the kinetics of the reactions could be studied conveniently in the laboratory.

"Chemical Kinetics" is the branch of chemistry which deals with the rate of chemical reactions.

The words rate, speed, velocity are used synonymously in this chapter.

The rate of a chemical reaction is the *change in the concentration of a reactant per unit time*. The rate of a chemical reaction may also be stated as the change in the concentration of a product in unit time.

As defined above, the rate of a chemical reaction will be different with respect to different reactants. Consider the reaction :

$1 A + 2 B \rightarrow$ products.

Here for every 1 mole of A that reacts, 2 moles of B react. Thus the rate of the chemical reaction w.r.t. B will be twice that w.r.t. A. To make the rate of the chemical reaction independent of the reactant, the concentration term is divided by the number of molecules entering into the reaction. For the reaction, $n_1 A + n_2 B \rightarrow$ products.

The rate $= \frac{1}{n_1} \frac{d[A]}{dt} = \frac{1}{n_2} \frac{d[B]}{dt}$, where [A] and [B] are concentrations of A and B respectively, and this rate is independent of the reactant used to express the rate.

The unit of rate of reaction is mole litre^{-1} time^{-1} i.e. mole litre^{-1} sec^{-1} or mole litre^{-1} min^{-1} or mole litre^{-1} hr^{-1} etc.

Guldberg and Waage stated the **Law of Mass action :** The rate of a chemical reaction is directly proportional to the active mass of the reacting substances. The term "active mass" may be considered as the molecular concentration.

Obviously, as the reaction proceeds, the concentration of the reactants goes on decreasing and hence the rate of the reaction also goes on decreasing.

Consider the general reaction,

$n_1 A + n_2 B + n_3 C + \ldots\ldots\ldots \rightarrow$ products.

The rate of the reaction according to the law of mass action is R

$$\text{Rate} \ \alpha \ [A]^{n_1} \cdot [B]^{n_2} \cdot [C]^{n_3} \ . \ldots\ldots$$

$$\therefore \qquad \text{Rate} = k \ [A]^{n_1} \cdot [B]^{n_2} \cdot [C]^{n_3} \ \ldots\ldots\ldots$$

where, k is the proportionality constant and is known as the **specific reaction rate constant** or simply **rate constant** or **velocity constant**. Hence, specific reaction rate constant is numerically equal to the rate of the reaction when concentrations of all the reactants is unity i.e. $[A] = [B] = [C] = \ldots\ldots\ldots = 1$ mole/litre.

Note : Although, rate of reaction at a given temperature in general, decreases with time the value of k remains constant.

Molecularity of a reaction : The molecularity of a reaction is the *number of atoms or molecules or ions that take part in the reaction*.

Thus, for the reaction, 1 A → products, molecularity is 1, unimolecular.

2 A → products, molecularity is 2, bimolecular.

2 A + 1 B → products, molecularity is 3, termolecular.

Most of the chemical reactions are unimolecular or bimolecular whereas a few are termolecular reactions. The reactions of higher molecularity are rare. This is because, for the reaction to occur, the molecules must colloid. The probability of collision decreases with increase in the molecularity of the reaction.

The order of a chemical reaction is the *number of atoms or molecules or ions whose concentration determines the rate or the kinetics of the reaction.*

The reaction $H_{2(g)} + I_{2(g)} \rightarrow 2\,HI_{(g)}$ is a second order reaction, since the rate of formation of HI is proportional to the concentration of H_2 and I_2.

The order of a reaction may also be defined as the *sum of powers of the concentration terms involved in the "rate equation".*

Note : "Rate equation" includes the reactants which undergo appreciable change in the concentrations. Thus if for the reaction,

$nA + mB \rightarrow$ products,

the rate $= k[A]^n \cdot [B]^m$,

and the order of the reaction is $(m + n)$.

The order and molecularity of a reaction need not be the same.

For example, in the formation of HI in the reaction given above, the order as well as the molecularity is two. The acid catalysed hydrolysis of ethyl acetate ester is a bimolecular reaction, however, its order is one. The reaction is thus called **pseudo-first order reaction** (some authors prefer to call it a pseudo – unimolecular reaction).

$$1\ CH_3COOC_2H_5 + 1\ H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

This reaction is studied in the laboratory at 20 to 40°C by mixing 5 ml of the ester with 100 ml 0.5 N HCl. Hence there is a large excess of water as compared to the ester concentration in the reaction mixture. The change in the concentration of water during the progress of the reaction is negligible as compared to the change in the concentration of the ester. Thus,

$$\text{rate} \propto [CH_3COO\,C_2H_5]\ [H_2O] \quad \text{… as per the law of mass action.}$$

$$\therefore \quad \text{rate} = k'\,[CH_3COOC_2H_5]\,[H_2O]$$

$$= k\,[CH_3COOC_2H_5]$$

Hence, the rate of the reaction depends only on the concentration of ester and is a first order reaction. Another example of pseudo first order reaction is the acid hydrolysis of sucrose :

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

The rate determining step : The overall reaction may go through a number of steps. Consider the reactions,

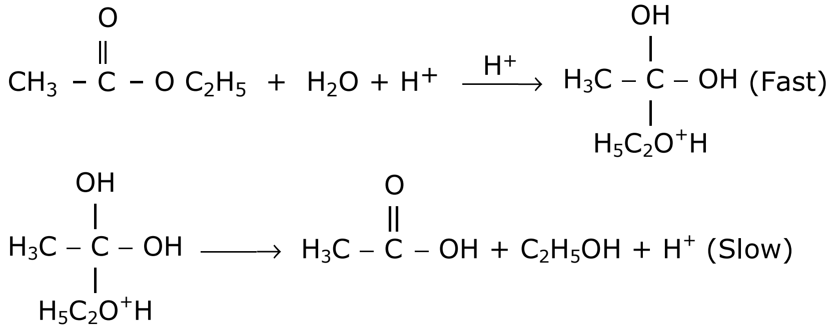
$$A \rightarrow B$$

$$B \rightarrow C$$

$$\underline{C \rightarrow D}$$

The overall reaction is A → D. The rate of this overall reaction will be determined by **the slowest step,** out of the three steps, and is called the rate determining step.

The ester hydrolysis in presence of an acid, is infact two-step reaction. First step the protonation of the ester molecule which is fast and the second step is the formation of acetic acid and alcohol molecule, which is a slow step.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O\,C_2H_5 + H_2O + H^+ \xrightarrow{H^+} H_3C-\underset{\underset{\displaystyle H_5C_2O^+H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-OH \text{ (Fast)}$$

$$H_3C-\underset{\underset{\displaystyle H_5C_2O^+H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-OH \longrightarrow H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH + C_2H_5OH + H^+ \text{ (Slow)}$$

This mechanism shows that the second step decides the overall rate of hydrolysis of the ester.

First Order Reactions : Consider a first order reaction,

$$A \longrightarrow \text{products.}$$

At $t = 0$ a moles/l.

At $t = t$ $(a - x)$ moles/l i.e. c mole/l.

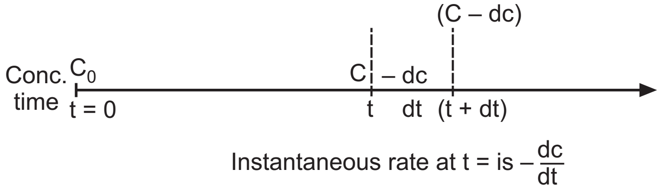


Fig. 1.1 : Instantaneous Rate of a Chemical Reaction

Let the initial concentration of the reactant i.e. at t = 0 be a moles/litre. Let at any time t from the start of the reaction, the decrease in the concentration of A be x mole/l; the concentration of A remaining at time t will be $(a - x)$ mole/l i.e. c moles/l. If $-dc$ is the change in the concentration at time t, in time dt, then (**Note :** the negative sign indicates, decrease in the concentration) the rate of the reaction is given by the general equation,

$$-\frac{dc}{dt} \propto c \quad \text{(Law of mass action)}$$

$$\therefore \quad -\frac{dc}{dt} = k.c. \qquad \dots (1.1)$$

$$\therefore \quad -\frac{d\,(a - x)}{dt} = k \cdot (a - x).$$

$$\therefore \quad \frac{dx}{dt} = k\,(a - x) \qquad \left\{\because a \text{ is a constant, } \frac{da}{dt} = 0\right\} \qquad \dots (1.2)$$

$$\therefore \quad \frac{dx}{(a - x)} = k \cdot dt$$

Integrating the above equation

$$\therefore \quad \int \frac{dx}{(a - x)} = k \int dt + I_0 \qquad \{I_0 \text{ is the constant of integration}\}$$

$$\therefore \quad -ln\,(a - x) = kt + I_0 \qquad \dots (1.3)$$

At t = 0, the change in the concentration x is zero.

$$\therefore \quad -ln\,a = I_0$$

Substituting this value of I_0 in equation (1.3), we get,

$$-ln\,(a - x) = kt - ln\,a$$

$$\therefore \quad ln\,\frac{a}{(a - x)} = k.t. \qquad \dots (1.4)$$

$$\therefore \quad k = \frac{1}{t}\,ln\,\frac{a}{(a - x)}$$

$$\therefore \quad \boxed{k = \frac{2.303}{t}\,\log_{10}\frac{a}{(a - x)}} \qquad \dots (1.5)$$

Equation (1.4) and (1.5) may also be written as,

$$(a - x) = a\, e^{-k \cdot t} \qquad \dots (1.6)$$

Equation (1.5) is the most suitable expression for the velocity constant or specific reaction rate constant of a first order reaction. To determine the value of k, experimentally, one has to determine the concentration of the reacting substance at various time intervals from the start of the reaction.

Units of k for the first order reaction : It is time^{-1} i.e. sec^{-1} or min^{-1} or hr^{-1} etc.

$$k = \frac{2.303}{t} \log \frac{a}{(a - x)}$$

$$= \frac{2.303}{\text{time}} \log \frac{a}{(a - x)} \frac{\text{mole}/l}{\text{mole}/l}$$

$$\therefore \quad = \text{time}^{-1}$$

Second Order Reactions :

Case I : Second Order Reaction of the type

$$2A \longrightarrow \text{products.}$$

At $t = 0$ a mole/l.

At $t = t$ $(a - x)$ mole/l.

Let the initial concentration of the reactant A be a moles/l. Let at any time t from the start of the reaction, the decrease in the concentration of A be x moles/l; the concentration of A remaining at time t will be $(a - x)$ moles/l. i.e. c mole/l. If $- dc$ is the change in the concentration at time t in time dt, then (**Note :** the – ve sign indicates decrease in the concentration) the rate of the reaction is given by the equation,

$$-\frac{dc}{dt} \propto [A]^2 \qquad \dots \text{(by Law of mass action)}$$

$$\therefore \quad -\frac{dc}{dt} = k\,[A]^2$$

$$\therefore \quad -\frac{dc}{dt} = k\,c^2$$

$$\therefore \quad -\frac{d\,(a - x)}{dt} = k\,(a - x)^2$$

$$\therefore \quad \frac{dx}{dt} = k\,(a - x)^2$$

$$\therefore \quad \frac{dx}{(a - x)^2} = k\,dt$$

Integrating the above equation

$$\therefore \quad \int \frac{dx}{(a - x)^2} = k \cdot \int dt + I_0$$ where, I_0 is the constant of integration.

$$\therefore \quad \frac{1}{(a - x)} = k \cdot t + I_0 \qquad \dots (1.7)$$

$\therefore$ At t = 0, x = 0 and equation (1.7) gives,

$$I_0 = \frac{1}{a}$$

and

$$\frac{1}{(a-x)} = kt + \frac{1}{a}$$

$$\therefore \quad k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right] \quad \text{... (1.8)}$$

$$\therefore \quad k = \frac{x}{t\,a\,(a-x)} \quad \text{... (1.9)}$$

The equations (1.8) and (1.9) give the expression for the velocity constant (specific rate constant) of second order reaction of the type 2A → products.

Units of k for the second order reaction : It is mole^{-1} litre time^{-1}

$$k = \frac{x}{t\,a\,(a-x)} = \frac{\text{mole/litre}}{\text{time} \cdot \text{mole/litre} \cdot \text{mole/litre}}$$

$$= \text{mole}^{-1}\ \text{litre}\ \text{time}^{-1}$$

Case II : Second Order Reaction of the type :

$$A + B \rightarrow \text{products.}$$

Let the initial concentrations of A and B be a mole/l and b mole/l.

Case (II A) : The reactants are in equal concentrations (i.e. equimolar conc.) at the start of the reaction i.e. a = b.

$$A + B \rightarrow \text{products.}$$

At t = 0 a mole/l. b mole/l.
At t = t (a − x) (a − x) mole/l. $(\because\ a = b)$

Let at time t from the start of the reaction, the decrease in the concentration of A and hence that of B be x mole/l'; the concentration of A and B remaining at time t will be (a − x) mole/l. i.e. c mole/l. If − dc is the change in the concentration, at time t, in time dt, then (**Note :** the negative sign indicates, decrease in the concentration) the rate of the reaction is given by the general equation :

$$-\frac{dc}{dt} \propto [A]\ [B] \quad \text{... (law of mass action)}$$

$$\propto (c)\ (c)$$

$$\therefore \quad -\frac{dc}{dt} = kc^2$$

$$\therefore \quad -\frac{d\,(a-x)}{dt} = k\,(a-x)^2$$

$$\therefore \quad \frac{dx}{dt} = k\,(a-x)^2$$

This can be integrated as in case (I) to give the equations (1.8) and (1.9).

$$\therefore \quad k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

or

$$k = \frac{x}{t \cdot a \cdot (a-x)}$$

Case (II B) : Second Order Reaction in which a ≠ b and a > b

$$\begin{array}{llll} & A \quad + & B \quad \rightarrow & \text{products.} \\ \text{At } t = 0 & a \text{ mole}/l; & b \text{ mole}/l. & \\ \text{At } t = t & (a - x) \text{ mole}/l; & (b - x) \text{ mole}/l. & \end{array}$$

Let the initial concentration of the reactants A and B be a mole/l and b moles/l.

Let at any time t from the start of the reaction, the decrease in the concentration of A and hence that of B, be x mole/l; the concentration of A and B remaining at time t will be (a − x) and (b − x) mole/l; respectively. If − dc is the change in the concentration at time t, in time dt then (**Note :** the negative sign indicates decrease in the concentration) the rate of the reaction is given by

$$\frac{-\,dc}{dt} \propto [A]\ [B]$$

$$\therefore \quad \frac{-\,dc}{dt} = k \cdot [A]\,[B]$$

$$\therefore \quad \frac{-\,d\,(a-x)}{dt} = k \cdot (a-x)\,(b-x)$$

$$\therefore \quad \frac{dx}{dt} = k \cdot (a-x)\,(b-x) \qquad \ldots (1.10)$$

$$\therefore \quad \frac{dx}{(a-x)\,(b-x)} = k\cdot dt.$$

Integrating the above equation

$$\therefore \quad \int \frac{dx}{(a-x)\,(b-x)} = k \cdot \int dt + I_0, \quad \text{where } I_0 = \text{Constant of integration.}$$

$$\therefore \quad \int \frac{dx}{(a-x)\,(b-x)} = k\cdot t + I_0 \qquad \ldots (1.11)$$

To solve the integral on the L.H.S., the method of integration by parts is used. Thus,

$$\frac{1}{(a-x)\,(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)} \qquad \ldots (1.12)$$

$$\therefore \quad \frac{1}{(a-x)\,(b-x)} = \frac{A\,(b-x) + B\,(a-x)}{(a-x)\,(b-x)}$$

$$\therefore \quad 1 = A\,(b-x) + B\,(a-x)$$

When x = b; $1 = 0 + B\,(a-b)$ and $B = \frac{1}{(a-b)}$

If x = a; $1 = A\,(b-a) + 0$ and $A = \frac{1}{(b-a)} = \frac{-1}{(a-b)}$

Substituting these values of constants in equation (1.12) we get,

$$\frac{1}{(a-x)\,(b-x)} = \frac{-\,1}{(a-b)\,(a-x)} + \frac{1}{(a-b)\,(b-x)}$$

Substitution in equation (1.11) we get,

$$\int \frac{-\,dx}{(a-b)\,(a-x)} + \int \frac{dx}{(a-b)\,(b-x)} = k{\cdot}t + I_0$$

$$\therefore \quad \frac{-1}{(a-b)} \int \frac{dx}{(a-x)} + \frac{1}{(a-b)} \int \frac{dx}{(b-x)} = k{\cdot}t + I_0$$

$$\therefore \quad \frac{1}{(a-b)}\, ln\;(a-x) - \frac{1}{(a-b)}\; ln\;(b-x) = kt + I_0 \qquad \dots (1.13)$$

To get the constant of integration,

At t =0, x = 0

$$\therefore \quad \frac{ln\;a}{(a-b)} - \frac{ln\;b}{(a-b)} = I_0$$

$$\therefore \quad I_0 = \frac{1}{(a-b)}\, ln\left(\frac{a}{b}\right)$$

Substitution in equation (1.13) gives,

$$\frac{1}{(a-b)}\, ln\;(a-x) - \frac{1}{(a-b)}\, ln\;(b-x) = kt + \frac{1}{(a-b)}\, ln\left(\frac{a}{b}\right)$$

$$k \cdot (a-x) - ln\;(b-x) = k\,(a-b)\,t + ln\left(\frac{a}{b}\right)$$

$$\therefore \quad k \cdot (a-b)\,t = ln\;\frac{(a-x)}{(b-x)} + ln\;\frac{b}{a}$$

$$\therefore \quad k\,(a-b)\,t = ln\;\frac{b\,(a-x)}{a\,(b-x)}$$

$$\therefore \quad k = \frac{2.303}{(a-b)\,t}\;\log_{10}\;\frac{b\,(a-x)}{a\,(b-x)} \qquad \dots (1.14)$$

Equation (1.14) gives the expression for the specific reaction rate constant of a second order reaction for which a > b. It is thus possible to determine the value of k experimentally, by determining the concentrations of A and B namely (a − x) and (b − x) at various time intervals t.

Units of k for the second order reaction for which a > b, can be seen from equation (1.14) as

$$k = \text{mole}^{-1}\;\text{litre time}^{-1}.$$

Time required for completion of a first order reaction : We have, $(a-x) = a\,e^{-kt}$ where, (a − x) is the concentration of the reactant A at any time t from the start of the reaction. When the reaction goes to completion, (a − x) = 0 and we get,

$$0 = a\,e^{-kt}$$

$$\therefore \quad t = \infty$$

$\therefore$ Time required for completion of a first order reaction is infinity. The nature of the plot (a − x) Vs. t is as shown in the Fig. 1.2. i.e. (a − x) decreases asymptotically with time.

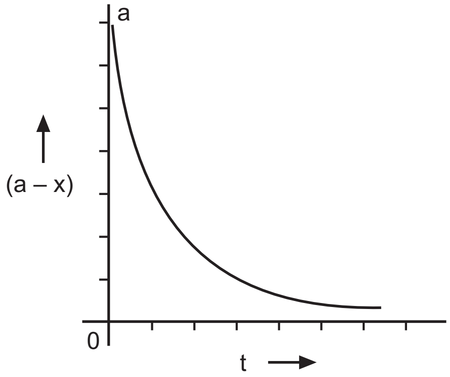


Fig. 1.2 : Plot of (a – x) Vs. t

Note : By considering equations for the second order reactions, it can be shown that the time required for the completion of second order reaction is also infinity.

Time required for the completion of a definite fraction "y" of First order reaction : Consider a fraction y of the reaction i.e. $x = y \cdot a$

Substituting this value of x in the equation (1.5), we get

$$k = \frac{2.303}{t_{(y)}} \log \frac{a}{(a - y \cdot a)}$$

$$\therefore \quad t_{(y)} = \frac{2.303}{k} \log \frac{1}{(1 - y)} \qquad \ldots (1.15)$$

For half fraction, $y = \frac{1}{2}$ and we get,

$$(t)_{(1/2)} = \frac{2.303}{k} \cdot \log 2$$

$$\therefore \quad t_{(1/2)} = \frac{0.693}{k}$$

Equation (1.15) shows that for a given fraction, "y" is constant and since k is a constant $t_{(y)}$ is also a constant. **Thus, time required for completion of a definite fraction of a first order reaction is independent of the initial concentration "a" of the reactant.**

[**Note :** The term "a" is absent in equation (1.15)].

For a second order reaction in which a = b, we have from equation (1.9),

$$t = \frac{x}{k \cdot a \cdot (a - x)}$$

and

$$t_{(y)} = \frac{a \cdot y}{k \cdot a\,(a - ay)}$$

$$\therefore \quad t_{(y)} = \frac{y}{k \cdot a \cdot (1 - y)}$$

For a given fraction, y is a constant and hence, for a second order reaction for which a = b,

$$t_{(y)} = \frac{\text{constant}}{a'} \qquad \dots (1.16)$$

It could in general be shown that for a reaction of order n, in which reactants, at the start of the concentration are in the equimolar concentrations,

$$t_{(y)} = \frac{\text{constant}}{a^{(n-1)}} \qquad \dots (1.17)$$

For first order reaction, $n = 1$ and $t_{(y)} = \text{constant}$

For second order reaction, $n = 2$ and $t_{(y)} = \frac{\text{constant}}{a'}$

Zero Order Reaction : (Derivation for the reaction rate constant) : If the *rate of the chemical reaction remains constant during the progress of the reaction*, it is called zero order reaction.

Ex. :

1. *The photo chemical reaction between hydrogen and chlorine over water is a zero order reaction. The HCl formed dissolves in water and the pressure remains constant, and thus the rate remains constant, at any time t.*
2. *Another example is that of suspensions – a system in which a solid drug is in equilibrium with the drug in solution. As the drug in the solution decomposes, more of the solid dissolves and the concentration of the solution remains constant at any time "t". The decomposition of suspension is apparent zero order reaction. For a zero order reaction, the rate is*

$$\frac{-\,dc}{dt} = \text{constant}$$

or $\frac{dx}{dt} = k$, where, k is the velocity constant.

$$\therefore \quad dx = k \cdot dt$$

Integrating the above equation

$$\therefore \quad \int dx = k \int dt + I_0$$

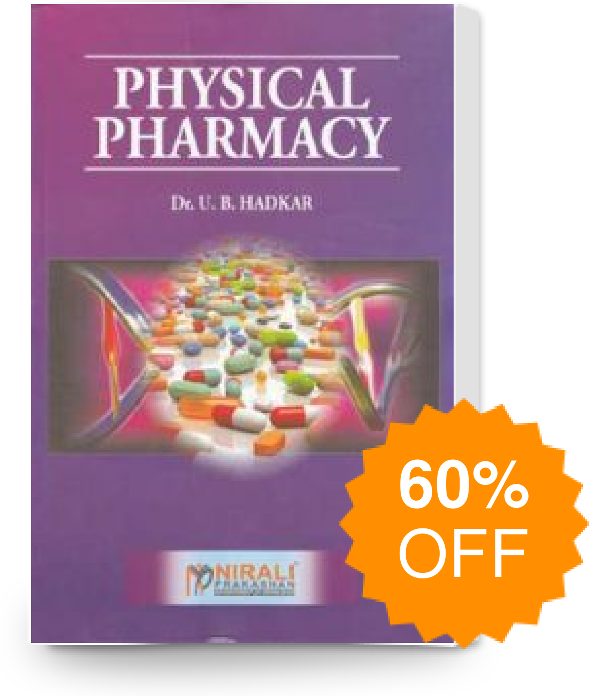
$$\therefore \quad x = k \cdot t + I_0 \qquad \dots (1.18)$$

At = 0, x = 0, hence equation (1.18) gives, $I_0 = 0$ and

$$x = k\,t$$

$$\therefore \quad k = \frac{x}{t} \qquad \dots (1.19)$$

Physical Pharmacy



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