Consequetive or Sequential Reaction

A Typical Example : In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.

 $A \xrightarrow{k_1} B \xrightarrow{k'_1} C$

Let the initial concentration of A be $[A]_0$ and let after time t, the concentrations of A, B and C be [A], [B] and [C], respectively. It is obvious that

 $[A]_0 = [A] + [B] + [C]$ (1) **Differential Rate Law :** The differential rate expressions are

$$-\frac{d[A]}{dt} = k_1[A] \qquad \dots \dots \dots (2)$$

$$\frac{d[B]}{dt} = k_1[A] - k_1'[B] \qquad \dots \dots (3)$$

$$\frac{d[C]}{dt} = k_1'[B] \qquad \dots \dots (4)$$

On integrating equation (2), we get

$$[A] = [A]_0 e^{-k_1 t} \qquad \dots \dots \dots (5)$$

Substituting [A] from equation (5) into equation (3), we get

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_1'[B]$$
$$\frac{d[B]}{dt} + k_1'[B] = k_1[A]_0 e^{-k_1 t}$$

Integrated Rate Law : Multiplying the above expression throughout by exp $(k'_1 t)$, we get

$$\frac{d[B]}{dt} + k_1'[B]e^{k_1't} = k_1[A]_0 e^{-(k_1 - k_1')t}$$

The left side of the above expression is equal to $d([B]e^{k'_1t})/dt$. Hence, the above expression

can written as , $d\{[B]e^{k_1't}\} = k_1[A]_0 e^{-(k_1-k_1')t}dt$ Integrating the above expression with [B] = 0 at t = 0, we get

$$[B]e^{k't} = k_1[A]_0 \left[\frac{e^{-(k_1 - k_1')t}}{-(k_1 - k_1')} + \frac{1}{k_1 - k_1'} \right]$$

$$[B] = k_1[A]_0 \left[\frac{e^{-k_1 t}}{-(k_1' - k_1)} + \frac{e^{-k_1' t}}{k_1 - k_1'} \right]$$

$$[B] = k_1[A]_0 \left(\frac{k_1}{k_1' - k_1} \right) \{e^{-k_1 t} - e^{-k_1' t}\} \qquad \dots \dots (6)$$

Substituting equations (5) and (6) in equation (1), we get

$$[A]_{0} = [A]_{0} e^{-k_{1}t} + [A]_{0} \left(\frac{k_{1}}{k_{1}' - k_{1}}\right) (e^{-k_{1}t} - e^{-k_{1}'t}) + [C]$$

$$[C] = [A]_{0} \left[1 - \frac{1}{k_{1}' - k_{1}} (k_{1}'e^{-k_{1}t} - k_{1}e^{-k_{1}'t})\right] \qquad \dots \dots (7)$$

or

Figure (1) Illustrates the general appearance of the variations of concentrations of A, B and C



Fig. 1: Typical variations of concentration of A, B and C during the progress of the reaction A? B? C. The actual variations on the values of k₁ and k'.

In general concentration of A decreases exponentially, the concentration of B initially increases up to a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value $[A]_0$, when all A has changed into C.

Maximum Concentration of B: Equation (6) is

At the maximum concentration of B, we have

$$\frac{\mathrm{d[B]}}{\mathrm{dt}} = 0$$

Hence, differentiating equation (6) with respect to t, we get

$$\frac{d[B]}{dt} = [A]_0 \left(\frac{k_1}{k_1' - k_1}\right) \{-k_1 e^{-k_1 t} + k_1' e^{-k_1' t}\} \qquad \dots \dots (8)$$

Equating equation (8) to zero, we get

$$-k_1 e^{-k_1 t_{max}} + k_1' e^{-k_1' t_{max}} = 0$$

or

 $\frac{k_1}{k'_1} = e^{(k_1 - k'_1)t_{max}}$ $\ln\left(\frac{k_1}{k'_1}\right) = (k_1 - k'_1)t_{max}$

or

or

$$t_{\max} = \frac{1}{k_1 - k_1'} \ln\left(\frac{k_1}{k_1'}\right) \qquad \dots \dots (9)$$

substituting equation (9) in equation (6), we get

Catalyst

Berzelius used the term catalyst for the first time for the substances which accelerate the rate of chemical reaction. Now the term catalyst has been used for the foreign substances which influence the rate of a reaction and the phenomenon is known as catalysis. Usually two terms are used for catalysis :

Positive Catalysis : The phenomenon in which presence of catalyst accelerates the rate of reaction.

Negative catalysis : The phenomenon in which presence of catalyst retards the rate of reaction. Such substances are also known as inhibitors or negative catalyst.

Characteristics Of Catalyst

- (i) A catalyst remains unchanged chemically at the end of reaction, however its physical state may change. e.g. MnO_2 used as catalyst in granular form for the decomposition of KClO₃, is left in powder form at the end of reaction.
- (ii) A catalyst never initiate a chemical reaction. It simply influences the rate of reaction. Exception : combination of H, and Cl, takes place only when moisture (catalyst) is present.
- (iii) A small quantity of catalyst is sufficient to influence the rate of reaction e.g. 1 g atom of Platinum is sufficient to catalyse 108 litre of H₂O₂ decomposition.
- (iv) A catalyst does not influence the equilibrium constant of reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward & backward reactions equally.
- (v) A catalyst normally does not alter the nature of products in a reaction. However some exceptions are found to this characteristic.

(a) HCOOH
$$\xrightarrow{\text{AlCl}_3}$$
 H₂O + CO, HCOOH $\xrightarrow{\text{Cu}}$ H₂ + CO₂

(b)
$$CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$$
, $CO + 2H_2 \xrightarrow{ZnO} CH_3OH$
 $CO + H \xrightarrow{Cu} HCHO$

It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.

- (vi) A catalyst does not make reaction more exothermic
- (vii) Catalyst's activity is more or less specific : A catalyst for one reaction is not necessary to catalyse the another reaction.

Type of catalyst

- 1. **Homogeneous catalysis :** The reaction in which catalyst and the reactants have same phase. It includes two types.
 - (a) **Gaseous phase catalysis :** When reactants and catalyst are in gaseous phase e.g. chamber process for H_2SO_4 .

 $2SO_2(g) + O_2(g) \xrightarrow{NO} 2SO_3(g)$

(b) **Solution phase catalysis :** The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.

 $\operatorname{RCOOR}'_{(l)} + \operatorname{H}_2\operatorname{O}_{(l)} \xrightarrow{H^+} \operatorname{RCOOH} + \operatorname{R'OH}$

2. Heterogeneous catalysis : The reactions in which catalyst and reactants form phase ≥ 2 .

(a) Solid-liquid catalysis : Reactant : Liquid Catalyst : Solid

 $2H_2O_{2(l)} \xrightarrow{MnO_{2(s)}} 2H_2O + O_2$

(b) Liquid-Liquid catalysis ::

Reactant : Liquid Catalyst : Liquid

$$2H_2O_{2(l)} \xrightarrow{Hg(l)} 2H_2O + O_2$$

Reactant : gases Catalyst : solid

(c) Solid-gas catalysis :

Two aspects of solid catalyst are more significant, one is activity and the other is selectivity. Activity is the ability of catalyst to accelerate chemical reactions; the degree of acceleration can be as high as 10¹⁰ times in certain reactions. Selectivity is the ability of catalyst to direct reaction to yield particular reaction (excluding others). For example, n-heptane selectivity gives toluene in presence of Pt catalyst. Similarly,

 $CH_3 - CH = CH_2 + O_2$ give $CH_2 = CHCHO$ selectivity over Bismuth molybdate catalyst.

Arrhenius Theory

In 1889 Arrhenius recognised the temperature dependence of rates or rate constant. He has given an emperical relation which can be written as

$$\mathbf{k} = \mathbf{A}\mathbf{e}^{-\mathbf{E}_{a}/\mathbf{R}\mathbf{T}} \qquad \dots \dots (1)$$

k is the rate constant (of any order other than zero order), A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. Activation energy (E_a) is the minimum energy required by a reactant at a certain temperature to undergo transformation into product. Arrhenius clearly assumed that reactions occur because of collisions between atoms and molecules of the reactant.

He assumed the activation energy to be the least value of energy which the colliding molecules must possess for the collision to yield a product. If we plot graph between activation energy and progress of a reaction (expressed as reaction co-ordinate), we get a graph as shown in figure.



Reaction Co-ordinate

The difference between the energies of the reactant and the transition state (TS) is called $(E_a)_f$. $\Delta H = (E_a)_f - (E_a)_b$

A, the pre-exponential factor or the frequency factor or the Arrhenius constant is the number of effective collisions occurring per unit time. Effective collision is the number of collisions occurring per unit time in which orientation of the colliding molecules is proper. $e^{-E_a/RT}$ gives the fraction of the effective collision that have the sufficient activation energy. Therefore the product of A and $e^{-E_a/RT}$ gives the number of collisions per unit time that forms the product and is called its number of productive collisions which is the rate constant, k.

For all practical calculations, we shall assume that E_a and A are temperature independent. Both A and E_a are characteristics of the reaction.

Determination of A and E

First Method :

Taking log of both sides of equation (1)

$$\ln k = \ln A - \frac{E_a}{RT}$$

Converting (natural log) to common log, $\log k = \log A - \frac{E_a}{2.303 \text{ RT}}$

If log k is plotted against 1/T, a straight line is obtained which is shown as below:

The slope of this line is given by slope $= \frac{-E_a}{2.303 \text{ R}}$

Thus, knowing the slope, the E_a can be easily calculated. The intercept of the line will give the value of log A.

Second Method :

The logarithmic form of Arrhenius equation is rearranged as

$$\ln k = -\frac{E_a}{RT} + \ln A$$

Differentiating with respect to temperature, we get :



 $\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$

Integrating with in the limits of temperature T_1 and T_2 , we get

$$\int_{k_{1}}^{k_{2}} d\ln k = \int_{T_{1}}^{T_{2}} \frac{E_{a}}{RT^{2}} dT$$

$$\ln \frac{k_{2}}{k_{1}} = \frac{E_{a}}{R} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}} \right)$$

$$\log \frac{k_{2}}{k_{1}} = \frac{E_{a}}{2.303 R} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}} \right) \qquad \dots (2)$$

or

Where k_1 and k_2 are rate constants at temperatures $T_1 \& T_2$ respectively. Thus, knowing these values E_a can be calculated. When the value of E_a is known, the value of A can be calculated by substituting its value in equation $k = Ae^{-E_a/RT}$. In equation (2), the value of R has to be inserted in the same unit in which E_a is desired.

Temperature Coefficient : "Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by 10°C".

:. Temperature coefficient = $\frac{k_{T+10}}{k_T} \approx 2$ to 3

where k_T is the rate constant at temperature TK and k_{T+10} is the rate constant at temperature (T+10) K. This ratio generally falls between 2 and 3 which means for most of the chemical reactions, the rate becomes two or three folds for every 10°C rise in temperature.

Example 19:

The rate of a reaction triple when temperature changes from 20°C to 50°C. Calculate energy of activation for the reaction ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$).

Solution :

The Arrhenius equation is

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{R \times 2.303} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given $\frac{k_2}{k_1} = 3$; R = 8.314 JK⁻¹ mol⁻¹; T₁ = 20 + 273 = 293 K

and

$$T_2 = 50 + 273 = 323 \text{ K}$$

Substituting the given vlues in the Arrhenius equation,.

$$\log_{10} 3 = \frac{E_a}{8.314 \times 2.303} \left[\frac{323 - 293}{323 \times 293} \right]$$
$$E_a = \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30}$$
$$= 28811.8 \text{ J mol}^{-1}$$
$$= 28.8118 \text{ kJ mol}^{-1}$$

Example 20 :

In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are 4×10^{13} sec⁻¹ and 98.6 kJ mol₋₁ respectively. At what temperature, the reaction will have specific rate constant 1.1×10^{-3} sec⁻¹?

Solution :

According to Arrhenius equation

$$k = Ae^{-E_a/RT}$$

or

$$\log_e k = \log_e A - \frac{E_a}{RT} \log_e e$$

$$2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

or

$$2.303 \log (1.1 \times 10^{-3}) = 2.303 \log (4 \times 10^{13}) - \frac{98.6 \times 10^{3}}{8.314 \times T}$$

$$T = \frac{98.6 \times 10^3}{8.314 \times 2.303 \times 16.56} K = 311 K$$

Example 21:

The rate constant is giveny by Arrhenius equation

 $k = A e^{-E_a/RT}$

Calculate the ratio of the catalysed and uncatalysed rate constant at 25°C if the nergy of activation of a catalysed reaxction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.

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Solution :

Let k_{ca} and k_{un} be the rate constants for catalysed and uncatalysed reactions.

2.303 log10 k_{ca} = 2.303 log₁₀A -
$$\frac{162 \times 10^3}{\text{RT}}$$
(i)

and
$$2.303 \log 10_{\text{un}} = 2.303 \log_{10} \text{A} - \frac{350 \times 10^3}{\text{RT}}$$
(ii)

Substracting Eq. (ii) from Eq.(i)

$$\log_{10} \frac{k_{ca}}{k_{un}} = \frac{10^3}{2.303 \text{RT}} (350 - 162)$$
$$= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95$$
$$\frac{k_{ca}}{k_{un}} = 8.88 \times 10^{32}$$

Example 22 :

At 407 K the rate constant of a chemical reaction is $9.5 \times 10^{-5} s^{-1}$ and at 420 K, the rate constant is $1.9 \times 10^{-4} s^{-1}$. Calculate the frequency factor of the reaction.

Solution :

The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Given $k_1 = 9.5 \times 10^{-5} \text{ s}^{-1}; \quad k_2 = 1.9 \times 10^{-3} \text{ s}^{-1};$
 $R = 8.314 \text{ J} \text{ mol}^{-1} \text{K}^{-1};$
 $T_1 = 407 \text{ K} \text{ and } T_2 = 420 \text{ K}$
Substituting the values in Arrhenius equation.

$$\log_{10} \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} = \frac{E_{a}}{2.303 \times 8.314} \left[\frac{420 - 407}{420 \times 407} \right]$$
$$E_{a} = 75782.3 \text{ J mol}^{-1}$$

Applying now log k₁ = log A - $\frac{E_a}{2.303 \text{ RT}_1}$ log 9.5 ×10⁻⁵ = log A - $\frac{75782.3}{2.303 \times 8.314 \times 407}$ or log $\frac{A}{9.5 \times 10^{-5}} = \frac{75782.3}{2.303 \times 8.314 \times 407}$ = 9.7246 A = 5.04 × 10⁵ s⁻¹

Example 23 :

The energy of activation for a reaction is 100 kJ mol⁻¹. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C, other things being equal ?

Solution :

The arrhenius equation is

$$k = Ae^{-E_a/RT}$$

In absence of catalyst, $k_1 = Ae^{-100/RT}$ In presence of catalyst, $k_2 = Ae^{-25/RT}$

So
$$\frac{k_2}{k_1} = e^{75/RT}$$
 or 2.303 log $\frac{k_2}{k_1} = \frac{75}{RT}$
or 2.303 log $\frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293}$
or log $\frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$

 $\times 10^{13}$

or
$$\frac{k_2}{k_1} = 2.34$$

As the things being equal in presence or absence of a catalyst,

i.e.,
$$\frac{k_2}{k_1} = \frac{\text{rate in presence of catalyst}}{\text{rate in absence of catalyst}}$$
$$\frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

Pressure Change Method :

This method is used for gaseous reactions.

As reaction proceeds there is change in pressure.

For a reaction, $\begin{array}{l} A_{(g)} \longrightarrow B_{(g)} + C_{(g)} \\ \text{Initial pressure at } t = 0 \\ P_0 & 0 \\ \end{array} \\ \begin{array}{l} P_0 \\ P_0$

Example 24 :

The following rate data was obtained for the first order thermal decomposition of $SO_2Cl_{2(g)}$ at a constant volume.

 $\begin{array}{cccc} SO_2C\bar{l}_{2(g)} & \xrightarrow{-\infty} & SO_{2(g)} + C\bar{l}_{2(g)} \\ Exp. & Time (sec^{-1}) & Total pressure (atm) \\ 1. & 0 & 0.5 \\ 2 & 100 & 0.6 \\ Calculate the reaction rate when total pressure is 0.65 atmosphere. \end{array}$

Solution :

Let us say that the pressure of SO_2Cl_2 decreases by x atm, then the increase of pressure of SO_2 and $Cl_2 = x$ atm each. [Q 1 mole of SO_2Cl_2 decomposes to give 1 mole of SO_2 and 1 mole of Cl_2].

 $\begin{array}{ccc} \mathrm{SO}_2\mathrm{Cl}_{2(\mathrm{g})} \longrightarrow \mathrm{SO}_{2(\mathrm{g})} & + & \mathrm{Cl}_{2(\mathrm{g})} \\ 0.5 \ \mathrm{atm} & 0 & & 0 \end{array}$ Pressure at t = 0Pressure at t, (0.5 - x) atm x atm x atm $\mathbf{P}_{\mathrm{T}} = \mathbf{P}_{\mathrm{SO}_{2}\mathrm{Cl}_{2}} + \mathbf{P}_{\mathrm{SO}_{2}} + \mathbf{P}_{\mathrm{Cl}_{2}}$ Since total pressure =(0.5-x)+x+x $P_{T} = 0.5 + x \text{ or } x = P_{T} - 0.5$ $P_{SO_{2}Cl_{2}} = 0.5 - (P_{T} - 0.5)$ Hence $= 0.5 - P_{T} + 0.5 = 1.0 - P_{T}$ Since, at t = 100 sec, $P_T = 0.6 \text{ atm}$ $P_{SO,Cl_2} = 1.0 - 0.6 = 0.4$ atm Evaluation of k **(a)** $k = \frac{2.303}{t} \log \frac{\text{Initial pressure}}{\text{Pressure at time t}}$ $=\frac{2.303}{100}\log\frac{0.5}{0.4}=\frac{2.303}{100}\log 1.25=\frac{2.303}{100}\times 0.0969=2.23\times 10^{-3}\ \mathrm{sec^{-1}}$ Rate at $P_{T} = 0.65$ atm **(b)** P_{SO,Cl_2} at total pressure of 0.65 atm = 1.0 - 0.65 = 0.35 atm

Rate = $k[N_2O_5] = 2.23 \times 10^{-3} \times 0.35 = 7.8 \times 10^{-4}$ atm sec⁻¹

Example 25 :

For a homogeneous gaseous phase reaction: $2A \longrightarrow 3B + C$, the initial pressure of reactant was P° while pressure at time 't' was P. Find the pressure after time 2t. Assume I order reaction.

3B + CSolution : $2A \longrightarrow$ P° Initial Pressure 0 0 $P^{\circ} - 2a$ Pressure at t = t3a а $P^{\circ} - 2x$ Pressure at t = 2t3x Х $P^{\circ} - 2a + 3a + a = P$ Given(1) $P^{\circ} + 2a = P$...

Now for I order reaction at time t

$$K = \frac{2.303}{t} \log \frac{P^{\circ}}{P^{\circ} - 2a} = \frac{2.303}{t} \log \frac{P^{\circ}}{2P^{\circ} - P} \qquad \dots \dots \dots (2)$$

Let total pressure at t = 2t be A, then $P^{\circ} - 2x + 3x + x = A$ or $P^{\circ} + 2x = A$

$$K = \frac{2.303}{2t} \log \frac{P^{\circ}}{P^{\circ} - 2x} = \frac{2.303}{2t} \log \frac{P^{\circ}}{2P^{\circ} - A} \qquad \dots \dots (3)$$
$$K = \frac{2.303}{t} \log \left[\frac{P^{\circ}}{2P^{\circ} - A} \right]^{1/2} \qquad \dots \dots (4)$$

By equations (2) and (4)

$$\begin{bmatrix} \frac{P^{\circ}}{2P^{\circ} - P} \end{bmatrix}^{2} = \begin{bmatrix} \frac{P^{\circ}}{2P^{\circ} - A} \end{bmatrix}$$

$$\begin{bmatrix} 2P^{\circ} - A \end{bmatrix} \cdot P^{\circ} = \begin{bmatrix} 2P^{\circ} - P \end{bmatrix}^{2}$$

$$P^{\circ} \cdot A = 2 (P^{\circ})^{2} - (2P^{\circ} - P)^{2}$$

$$A = 2P^{\circ} - \frac{(2P^{\circ} - P)^{2}}{P^{\circ}}.$$

Example 26 :

The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is of I order. After 55 sec at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate :

(a) The rate constant.

(b) Pressure of
$$Cl_2O_7$$
 after 100 sec.

Solution :
Cl₂O₇ → Cl₂ +
$$\frac{7}{2}$$
O₂
Mole at t = 0 a 0 0
Mole at t = 55 sec. (a - x) x 7x/2
(a) Since Pressure of Cl₂O₇ is given and therefore,
a ∝ 0.062
(a - x) ∝ 0.044
Q K = $\frac{2.303}{t} \log_{10} \frac{0.062}{0.044}$
K = 6.23 × 10⁻³ sec⁻¹.
(b) Let at t = 100 sec, (a - x) ∝ P
 \therefore 6.23 × 10⁻³ = $\frac{2.303}{100} \log_{10} \frac{0.062}{P}$ = P = 0.033 atm.

 In the reaction; A + 2B → 3C + D which of the following expressions does not descrichanges in the concentration of various species as a function of time: (A) d[C]/dt = -3d[A]/dt (B) 3d[D]/dt = d[C]/dt (C) 3d[B]/dt = -2d[C]/dt (D) 2d[B]/dt = d[A]/dt Which of the following statement is correct for a reaction X + 2Y → prodcuts: (A) The rate of disappearance of X = twice the rate of disappearance of Y (B) The rate of disappearance of X = 1/2 rate of appearance of Y (D) The rate of appearance of products = 1/2 the rate of disappearance of Y (D) The rate of appearance of products = 1/2 the rate of disappearance of Y (D) The rate of appearance of B is one fourth the rate of disappearance of A (B) The rate of disppearance of C is half the rate of disappearance of A (B) The rate of formation of C and D are equal For the reaction 2A + B → C + D, -d[A]/dt = k[A]² [B]. The expression for -d[B]/dt v be: (A) K[A]² [B] (B) 1/2K[A]²[B] (C) K[A]²[2B] (D) K[2A]²[B] Which is correct relation in between dC/dt, dt/dt and dP/dt where C, n, P, represents concentratimole and pressure terms for gaseous phase reactant A(g) → product. (A) - dC/dt = - 1/V dn/dt = - 1/RT dP/dt (B) dC/dt = -dn/dt = -dP/dt (C) dC/dt = RT/dt dt = -dP/dt (D) All Which is found to be 3.5 × 10⁻² mol dm⁻³ s⁻¹ during a measured time interval. Calculate rate of appearance of intric oxide and water. The following reaction was carried out at 44^oC N₂O₃ → 2NO₂	Dail	y Practice Problem 1
 (A) d[C]/dt = -3d[A]/dt (B) 3d[D]/dt = d[C]/dt (C) 3d[B]/dt = -2d[C]/dt (D) 2d[B]/dt = d[A]/dt 2. Which of the following statement is correct for a reaction X + 2Y → products : (A) The rate of disappearance of X = twice the rate of disappearance of Y (B) The rate of disappearance of x = 1/2 rate of appearance of Y (C) The rate of appearance of products = 1/2 the rate of disappearance of X 3. For the reaction, 4A + B → 2C + 2D, The statement not correct is : (A) The rate of appearance of C is half the rate of disappearance of A (B) The rate of appearance of C is half the rate of disappearance of B (C) The rate of formation of D is half the rate of disappearance of B (C) The rate of formation of C and D are equal 4. For the reaction 2A + B → C + D, -d[A]/dt = k[A]² [B]. The expression for -d[B]/dt v be: (A) K[A]² [B] (B) 1/2K[A]² [B] (C) K[A]² [2B] (D) K[2A]² [B] 5. Which is correct relation in between dC/dt, dn/dt and dP/dt where C, n, P, represents concentrate mole and pressure terms for gaseous phase reactant A(g) → product. (A) - dC/dt = -1/V dn/dt = -1/RT dP/dt (B) dC/dt = dn/dt = -dP/dt (C) dC/dt = RT/dt dn = -dP/dt (D) All 6. When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance of nitric oxide and water. 7. The following reaction was carried out at 44°C N₂O₃ → 2NO₂ + ½ O₂ The concentration of NO₂ over the first ten minutes of the reaction. 8. The oxidation of iOdd ei on by arsenic acid. H.AsO., is described by the balance equation	1.	In the reaction; $A + 2B \longrightarrow 3C + D$ which of the following expressions does not describe changes in the concentration of various species as a function of time:
 Which of the following statement is correct for a reaction X + 2Y → products : (A) The rate of disappearance of X = twice the rate of disappearance of Y (B) The rate of disappearance of products = 1/2 the rate of disappearance of Y (D) The rate of appearance of products = 1/2 the rate of disappearance of Y (D) The rate of appearance of products = 1/2 the rate of disappearance of X For the reaction, 4A + B → 2C + 2D, The statement not correct is : (A) The rate of disppearance of B is one fourth the rate of disappearance of A (B) The rate of off formation of D is half the rate of consumption of A (D) The rate of formation of C and D are equal For the reaction 2A + B → C + D, -d[A]/dt = k[A]² [B]. The expression for -d[B]/dt veloce (A) K[A]² [B] (B) 1/2K[A]² [B] (C) K[A]² [2B] (D) K[2A]² [B] Which is correct relation in between dC/dt, dt/dt and dP/dt where C, n, P, represents concentrate mole and pressure terms for gaseous phase reactant A(g) → product. (A) - dC/dt = - 1/V dn/dt = - 1/RT dP/dt (B) dC/dt = dn/dt = - dP/dt (C) dC/dt = RT/V dn/dt = - dP/dt (D) All When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance are of appearance of and water. The following reaction was carried out at 44°C N₂O₃ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction. The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction. 		(A) $\frac{d[C]}{dt} = \frac{-3d[A]}{dt}$ (B) $\frac{3d[D]}{dt} = \frac{d[C]}{dt}$ (C) $\frac{3d[B]}{dt} = \frac{-2d[C]}{dt}$ (D) $\frac{2d[B]}{dt} = \frac{d[A]}{dt}$
 For the reaction, 4A + B → 2C + 2D, The statement not correct is : (A) The rate of disppearance of B is one fourth the rate of disappearance of A (B) The rate of appearance of C is half the rate of disappearance of B (C) The rate of formation of D is half the rate of consumption of A (D) The rates of formation of C and D are equal For the reaction 2A + B → C + D, -d[A]/dt = k[A]² [B]. The expression for -d[B]/dt v be: (A) K[A]² [B] (B) 1/2K[A]²[B] (C) K[A]²[2B] (D) K[2A]²[B] Which is correct relation in between dC/dt, dn/dt and dP/dt where C, n, P, represents concentration mole and pressure terms for gaseous phase reactant A(g) → product. (A) - dC/dt = -1/V dn/dt = -1/RT dP/dt (B) dC/dt = dn/dt = -dP/dt (C) dC/dt = RT/V dn/dt = -dP/dt (D) All When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance and mole and veter. The following reaction was carried out at 44°C N₂O₅ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction calculate the rate of production of NO₂ over the first ten minutes of the start of the reaction calculate the rate of production of NO₂ over the first ten minutes of the start of the reaction calculate the rate of production of NO₂ over the first ten minutes of the reaction. 	2.	Which of the following statement is correct for a reaction $X + 2Y \longrightarrow prodcuts$:(A)The rate of disappearance of X = twice the rate of disappearance of Y(B)The rate of disappearance of $X = 1/2$ rate of appearance of products(C)The rate of appearance of products = $1/2$ the rate of disappearance of Y(D)The rat of appearance of products = $1/2$ the rate of disappearance of X
 For the reaction 2A + B → C + D, -d[A]/dt = k[A]² [B]. The expression for -d[B/dt v be: (A) K[A]² [B] (B) 1/2K[A]²[B] (C) K[A]²[2B] (D) K[2A]²[B] Which is correct relation in between dC/dt, dn/dt and dP/dt where C, n, P, represents concentrate mole and pressure terms for gaseous phase reactant A(g) → product. (A) - dC/dt = -1/V dn/dt = -1/RT dP/dt (B) dC/dt = dn/dt = -dP/dt (C) dC/dt = RT/V dn/dt = -dP/dt (D) All When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance ammonia is found to be 3.5 × 10⁻² mol dm⁻³ s⁻¹ during a measured time interval. Calculate rate of appearance of nitric oxide and water. The following reaction was carried out at 44°C N₂O₅ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction. The oxidation of iodide ion by arsenic acid. H. AsO, is described by the balance equation 	3.	For the reaction, $4A + B \longrightarrow 2C + 2D$, The statement not correct is : (A) The rate of disppearance of B is one fourth the rate of disappearance of A (B) The rate of appearance of C is half the rate of disappearance of B (C) The rate of formation of D is half the rate of consumption of A (D) The rates of formation of C and D are equal
 be: (A) K[A]²[B] (B) 1/2K[A]²[B] (C) K[A]²[2B] (D) K[2A]²[B] 5. Which is correct relation in between dC/dt, dn/dt and dP/dt where C, n, P, represents concentration mole and pressure terms for gaseous phase reactant A(g) → product. (A) - dC/dt = -1/V dn/dt = -1/RT dP/dt (B) dC/dt = dn/dt = -dP/dt (C) dC/dt = RT/V dn/dt = -dP/dt (D) All 6. When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance ammonia is found to be 3.5 × 10⁻² mol dm⁻³ s⁻¹ during a measured time interval. Calculate rate of appearance of nitric oxide and water. 7. The following reaction was carried out at 44°C N₂O₅ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction. 8. The oxidation of iodide ion by arsenic acid. H.AsO., is described by the balance equation 	4.	For the reaction $2A + B \longrightarrow C + D$, $-\frac{d[A]}{dt} = k[A]^2 [B]$. The expression for $\frac{-d[B]}{dt}$ will
 5. Which is correct relation in between dC/dt , dn/dt and dP/dt where C, n, P, represents concentration mole and pressure terms for gaseous phase reactant A(g) → product. (A) - dC/dt = -1/V dn/dt = -1/RT dP/dt (B) dC/dt = dn/dt = -dP/dt (C) dC/dt = RT/V dn/dt = -dP/dt (D)All 6. When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance ammonia is found to be 3.5 × 10⁻² mol dm⁻³ s⁻¹ during a measured time interval. Calculate rate of appearance of nitric oxide and water. 7. The following reaction was carried out at 44°C N₂O₅ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction. 8. The oxidation of iodide ion by arsenic acid. H.AsO., is described by the balance equation 		be: (A) $K[A]^2[B]$ (B) $1/2K[A]^2[B]$ (C) $K[A]^2[2B]$ (D) $K[2A]^2[B]$
 mole and pressure terms for gaseous phase reactant A(g) → product. (A) - dC/dt = -1/V dn/dt = -1/RT dP/dt (B) dC/dt = dn/dt = -dP/dt (C) dC/dt = RT/V dn/dt = -dP/dt (D)All 6. When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance ammonia is found to be 3.5 × 10⁻² mol dm⁻³ s⁻¹ during a measured time interval. Calculate rate of appearance of nitric oxide and water. 7. The following reaction was carried out at 44°C N₂O₅ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction. 8. The oxidation of iodide ion by arsenic acid. H.AsO, is described by the balance equation 	5.	Which is correct relation in between $\frac{dC}{dt}$, $\frac{dn}{dt}$ and $\frac{dP}{dt}$ where C, n, P, represents concentration,
 (A) - dC/dt = -1/V dn/dt = -1/RT dP/dt (B) dC/dt = dn/dt = -dP/dt (C) dC/dt = RT/V dn/dt = -dP/dt (D) All 6. When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance ammonia is found to be 3.5 × 10⁻² mol dm⁻³ s⁻¹ during a measured time interval. Calculate rate of appearance of nitric oxide and water. 7. The following reaction was carried out at 44°C N₂O₅ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction. 8. The oxidation of iodide ion by arsenic acid. H.AsO., is described by the balance equation 		mole and pressure terms for gaseous phase reactant $A(g) \longrightarrow product$.
 (C) dC/dt = RT/V dn/dt = - dP/dt (D)All 6. When ammonia is treated with O₂ at elevated temperatures, the rate of disappearance ammonia is found to be 3.5 × 10⁻² mol dm⁻³ s⁻¹ during a measured time interval. Calculate rate of appearance of nitric oxide and water. 7. The following reaction was carried out at 44°C N₂O₅ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction Calculate the rate of production of NO₂ over the first ten minutes of the reaction. 8. The oxidation of iodide ion by arsenic acid. H.AsO., is described by the balance equation 		$(A) - \frac{dC}{dt} = -\frac{1}{V} \frac{dn}{dt} = -\frac{1}{RT} \frac{dP}{dt} \qquad (B) \frac{dC}{dt} = \frac{dn}{dt} = -\frac{dP}{dt}$
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 7. The following reaction was carried out at 44°C N₂O₅ → 2NO₂ + ½ O₂ The concentration of NO₂ is 6.0 × 10⁻³ M after 10 minutes of the start of the reaction Calculate the rate of production of NO₂ over the first ten minutes of the reaction. 8. The oxidation of iodide ion by arsenic acid. H.AsO., is described by the balance equation 	6.	When ammonia is treated with O_2 at elevated temperatures, the rate of disappearance of ammonia is found to be 3.5×10^{-2} mol dm ⁻³ s ⁻¹ during a measured time interval. Calculate the rate of appearance of nitric oxide and water.
8. The oxidation of iodide ion by arsenic acid. H.AsO., is described by the balance equation	7.	The following reaction was carried out at 44°C $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$ The concentration of NO ₂ is 6.0×10^{-3} M after 10 minutes of the start of the reaction. Calculate the rate of production of NO ₂ over the first ten minutes of the reaction.
(a) $3I^{-}(aq) + H_3AsO_4(aq) + 2H^{+}(aq) \longrightarrow I_3^{-}(aq) + H_3AsO_3(aq) + H_2O(l)$ (a) $If - \Delta[I^{-}] / \Delta t = 4.8 \times 10^{-4} \text{ M/s}$, what is the value of $\Delta[I_3^{-}] / \Delta t$ during the same tir interval?	8.	The oxidation of iodide ion by arsenic acid, H_3AsO_4 , is described by the balance equation : $3I^-(aq) + H_3AsO_4(aq) + 2H^+(aq) \longrightarrow I_3^-(aq) + H_3AsO_3(aq) + H_2O(l)$ (a) If $-\Delta[I^-] / \Delta t = 4.8 \times 10^{-4}$ M/s, what is the value of $\Delta[I_3^-] / \Delta t$ during the same time interval ?
(b) What is the average rate of consumption of H^+ during that time interval ?		(b) What is the average rate of consumption of H^+ during that time interval ?
9. In a reaction, the rate expression is, rate = $K[A] [B]^{2/3} [C]^0$, the order of reaciton is : (A) 1 (B) 2 (C) 5/3 (D) Zero	9.	In a reaction, the rate expression is, rate = $K[A] [B]^{2/3} [C]^0$, the order of reaciton is : (A) 1 (B) 2 (C) 5/3 (D) Zero

10. For the reaction, $H_2(g + Br_2(g) = 2HBr(g))$, the reaction rate = K [H₂] [Br₂]^{1/2}. Which statement is true about this reaction : (A) The reaction is of second order (B) Molecularity of the reaction is 3/2(C) The unit of K is sec^{-1} (D) Molecularity of the reaction is 2 11. The dimensions of the rate constant of a sceond order reaction involves : (A) Neither time nor concentration (B) Time and concentration (C) Time and square of concentration (D) Only time The rate constant for a reaction is 10.8×10^{-5} mol litre⁻¹ sec⁻¹. The rection obeys : 12. (B) Zero order (C) Second order (D) Half order (A) First order 13. Which statement about the order of reaction is correct? The order of reaction must be a positive integer (A) **(B)** A second order reaction is also bimolecular The order of reaction increases with increasing temperature. (C) The order of reaction can only be determined by experiment (D) The rate of the reaction $A + B + C \longrightarrow P$ is given by : 14. $r = \frac{d[A]}{dt} = k [A]^{1/2} [B]^{1/2} [C]^{1/4}$. The order of the reaction is: The reaction is : (C) 1/2 (D) 5/4 (A) 1 (B) 2 Bromomethane is converted to methanol in an alkaline solution : 15. $CH_{2}Br(aq) + OH^{-}(aq) \longrightarrow CH_{2}OH(aq) + Br^{-}(aq)$ The reaction is first order in each reactant. Write the rate law. **(a) (b)** How does reaction rate change if the OH⁻ concentration is decreased by factor of 5? (c) What is the change in rate if the concentrations of both reactants are doubled? 16. The oxidation of Br^- by BrO_3^- in acidic solution is described by the equation $5\mathrm{Br}^{-}(\mathrm{aq}) + \mathrm{BrO}_{3}^{-}(\mathrm{aq}) + 6\mathrm{H}^{+}(\mathrm{aq}) \longrightarrow 3\mathrm{Br}_{2}(\mathrm{aq}) + 3\mathrm{H}_{2}\mathrm{O}(l)$ The reaction is first order in Br^- , first order in BrO_3^- , and second order in H^+ . **(a)** Write the rate law **(b)** What is the overall reaction order? How does the reaction rate change if the H⁺ concentration is tripled ? (c) (d) What is the change in rate if the concentrations of both Br⁻ and BrO₃⁻ are halved ? For the reaction: $2A + B_2 + C \longrightarrow A_2B + BC$, the rate law expression has been determined 17. experimentally to be $R = k [A]^2 [C]$ with , $k = 3.0 \times 10^{-4} M^{-2} min^{-1}$. Determine the initial rate of the reaction, started with concentration (i) $[A] = 0.1 \text{ M}, [B_2] = 0.35 \text{ M} \& [C] = 0.25 \text{ M}$ (ii) What is the effect on rate of reaction and rate constant on changing the volume to 1/4th of initial value. 18. For the reaction $2NO + Cl_2 \longrightarrow 2NOCl$, it is found that doubling the concentration of both reactants increases the rate by the factor of 8, but doubling the Cl₂ concentration alone, only doubles the rate What is the order of the reaction with respect to NO and Cl₂? 19. For the reaction, $2A + B + C \longrightarrow A_{a}B + C$ the rate = k[A] [B]² with k = 2.0×10^{-6} M⁻² s⁻¹. Calculate the initial rate of the reaction when [A] = 0.1 M, [B] = 0.2 M and [C] = 0.8 M.

- 20. If the pressure of gaseous reactant is changed by 3 times the rate of reaction changes by 5.2 times. Determine
 - order of reaction unit of rate constant (i) (ii)
 - effect on rate of reaction if volume of container is reduced to $\frac{1}{16}$ th of the original (iii)

2. **Daily Practice Problem Sheet**

- 1. The rate law for the single-step reaction, $2A + B \longrightarrow 2C$, is given by: (A) Rate = K[A]. [B] (B) Rate = $K[A]^2$. [B] (C) Rate = K[2A]. [B] (D) Rate = $K[A]^2 \cdot [B]^0$
- 2. The correct expression the rate of reaction of elementary reaction, $A + B \longrightarrow C$ is

(A)
$$\frac{d[C]}{dt} = K[A]$$
 (B) $\frac{d[C]}{dt} = K[B]$ (C) $\frac{-d[A]}{dt} = K[A][B]$ (D) $\frac{-d[A]}{dt} = K[A]$

3. Select the intermediate in the following reaction mechanism :

(A)
$$O_3(g)$$
 (B) $O_2(g) + O(g)$, $O_3 + O \longrightarrow 2O_2$
(B) $O(g)$ (C) $O_2(g)$ (D) None

The elementary step of the reaction, $2Na + Cl_2 \longrightarrow 2NaCl$ is found to follow III order 4. kinetics, its molecularity is : (\mathbf{A})

5. For the reaction $2NO_2 + F_2 \longrightarrow 2NO_2F$, following mechanism has been provided :

 $NO_2 + F_2 \xrightarrow{slow} NO_2F + F$ $NO_2 + F \xrightarrow{fast} NO_2F$ Thus rate expression of the above reaction can be written as : (A) $r = k [NO_2]^2 [F_2]$ (B) $r = k [NO_{2}][F_{2}]$ (C) $r = k [NO_2]$ (D) $r = k [F_2]$

The reaction $2NO + Br_2 \longrightarrow 2NOBr$, Obey's the following mechanism: 6.

 $NO + Br_2 \xrightarrow{fast} NOBr_2$; $NOBr_2 + NO \xrightarrow{slow} 2NOBr$ The rate expression of the above reaction can be written as: (A) $r = k [NO]^2 [Br_2]$ (B) r = k [NO] [Br₂] (D) $r = k [NOBr_2]$ (C) $r = k [[NO] [Br_2]^2$

The reaction $2A \longrightarrow B + C$ follows zero order kinetics. The differential rate equation for the 7. reaction is:

(A)
$$\frac{dx}{dt} = K [A]^0$$
 (B) $\frac{dx}{dt} = K [A]^2$ (C) $\frac{dx}{dt} = K [B] [C]$ (D) $\frac{dx}{dt} = K [A]$

- For the elementary step, $(CH_3)_3$. $CBr(aq) \longrightarrow (CH_3)_3 C^+(aq) + Br^-(aq)$ the molecularity is: 8. (A) Zero **(B)** 1 (D) cannot ascertained (C) 2
- 9. Following mechanism has been proposed for a reaction,

 $2 A + B \longrightarrow D + E$ $A + B \longrightarrow C + D$ (slow) $A + C \longrightarrow E$ (fast) The rate law expression for the reaction is: (A) $r = K[A]^{2}[B]$ (B) r = K[A][B] (C) $r = K[A]^{2}$ (D) r = K[A][C]

10.	A reaction, $A_2 + B_2$ $A_2 \longrightarrow A + B_2 - A + B - B_2$ Its order would be	$B_{2} \longrightarrow 2AB \text{ occur}$ $A + A$ $\longrightarrow AB + B$ $\longrightarrow AB$ Def:	rs by the following med (slow) (fast) (fast)	chanism;		
	(A) 3/2	(B) 1	(C) zero	(D) 2		
11.	The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows : $O_3 \rightleftharpoons O_2 + O$ (fast) $O + O_3 \longrightarrow 2O_2$ (slow) The rate law expression should be: (A) $r = K [O_3]^2$ (B) $r = K[O_3]^2 [O_2]^{-1}$ (C) $r = K [O_3][O_2]$ (D) Unpredictable					
12.	The following two step mechanism has been proposed for the gas-phase decomposition of nitrous oxide (N ₂ O): Step I : $N_2O(g) \longrightarrow N_2(g) + O(g)$ Step II : $N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g)$ (a) Write the chemical equation for overall reaction. (b) Identify any reaction intermediates. (c) What is the molecularity of each of the elementary reactions ? (d) What is the molecularity of the overall reaction ?					
13.	What is the order of reaction, $A_2 + B_2 \longrightarrow 2 AB$; having following mechanism $A_2 \rightleftharpoons A + A$ (fast) $A + B_2 \longrightarrow AB + B$ (slow) $A + B \longrightarrow AB$ (fast)					
14.	The following reaction has a second-order rate law : $H_2(g) + 2ICl(g) \longrightarrow I_2(g) + 2HCl(g)$ Rate = k[H ₂] [ICl] Devise a possible reaction mechanism.					
15.	Initial rate data at 25°C are listed in the table for the reaction $NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$					
	Experiment No.	Initial [NH4 ⁺]	Initial [NO ₂ ⁻]	Initial rate of consumption of NH4 ⁺ (M/s)		
	1.	0.24	0.10	7.2×10^{-6}		
	2.	0.12	0.10	$3.6 imes 10^{-6}$		
	3.	0.12	0.15	$5.4 imes 10^{-6}$		

- (a) What is the rate law?
- (b) What is the value of the rate constant?
- (c) What is the reaction rate when the concentrations are $[NH_4^+] = 0.39$ M and $[NO_2^-] = 0.052$ M?
- **16.** Find :
 - (i) rate law expression
 - (ii) order of reaction with respect to each reactant and overall order of reaction
 - (iii) value and unit of rate constant
 - (iv) effect on rate of reaction on changing the volume to $1/8^{th}$ of the original.

For the reaction , $A + B + C \longrightarrow product$

given:

Experiment No.	[A] ₀ 10 ⁻⁴ (m/l)	[B] ₀ 10 ⁻² (m/l)	[C] ₀ 10 ⁻¹ (m/l)	Initial rate × 10 ⁻⁶ (m/l/s)
1	7	3	5	9
2	7	6	5	12.7
3	7	6	2	12.7
4	14	3	5	4.51

17. Initial rate data at 25°C are listed in the table for reaction, $A_2 + B_2 \longrightarrow 2AB$

Experiment No.	$[A_2]_0 (m/l)$	$[B_2]_0 (m/l)$	Initial rate (m/l/s)
1	1.5×10^{-3}	3.2×10^{-4}	$8.1 imes 10^{-8}$
2	$4.5 imes 10^{-3}$	9.6×10^{-4}	6.56×10^{-6}
3	3×10^{-3}	1.6×10^{-4}	3.24×10^{-7}

using that, determine

- (i) rate law
- (ii) order of reaction with respect to A_2 and B_2 and overall order of reaction
- (iii) value and unit of rate constant
- (iv) effect on rate of reaction on doubling the volume of container.

18. The data given below are for the reacion of NO and Cl₂ to form NOCl at 295 K.

[Cl,]	[NO]	Initial rate (mol litre ⁻¹ sec ⁻¹)
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

- (a) What is the order w.r.t. NO and Cl_2 in the reaction
- (b) Write the rate expression
- (c) Calculate the rate constant
- (d) Determine the reaction rate when conc. of Cl_2 and NO are 0.2 M and 0.4 M respectively.
- 19. The decomposition of NH_3 on tungsten surface follows zero order kinetics. The half life is 5 minutes for an initial pressure of 70 torr of NH_3 . If the initial pressure had been 0.25 atm, what would the total pressure after 3 minutes ? What is the half life ?
- **20.** In a reaction, the decrease in reactant's concentration is 20 % in 20 minute and 40 % in 40 minute. Calculate order of reaction and rate constant.

3. Daily Practice Problem Sheet

- 1. Show that for a first order reaction, $R \longrightarrow P$ the concentration of product can be represented as a function of time by, $[P] = at + bt^2 + ct^3 + \dots$ and express a, b and c in terms of $[R]_0$ and K.
- 2. (i) Substance A decomposes by the first order reaction. Starting initially with [A] = 2.00 M, after 200 minutes [A] = 0.25 M. For this reaction what is $t_{1/2}$ and k?
 - (ii) A first order reaction is 40% complete after 8 min. How long will it take before it is 90% complete ? What is the value of the rate constant ?

- (iii) For a certain reaction it takes 20 minutes for the initial concentrations of 34.8 mol L^{-1} to become 17.4 mol L^{-1} and another 20 minutes to become 8.7 mol L^{-1} . Calculate the rate constant of the reaction.
- (iv) For a first order reaction in which $k = 5.48 \times 10^{-1} \text{ sec}^{-1}$. Find : (a) $t_{1/3}$ (b) $t_{2/3}$
- 3. Show that for a first order reaction

(i) $t_{25\%} = 0.415t_{1/2}$ (ii) $t_{87.5\%} = 3t_{1/2}$ (iii) $t_{90\%} = 3.33 t_{1/2}$ (iv) $t_{99\%} = 6.66t_{1/2}$ (v) $t_{99.9\%} = 10t_{1/2}$ (vi) $t_{99\%} = 2t_{90\%}$ (vii) $t_{99.9\%} = 3t_{90\%}$

- 4. The solution of H_2O_2 of normality 0.73 is catalytically decomposed. What will be the concentration at the end of 45 minute, assuming the decomposition to follow first order rate law if half life is 15 minute?
- 5. The change, $A \longrightarrow B$ shows I order :
 - (a) How will the rate of reaction change when the concentration of A is tripled?
 - (b) What will be the change in half life period in doing so?
- 6. The virus prepared in a chemical bath shows inactivation process obeying I order. Calculate the rate constant for the viral inactivation if in the beginning 1.5% of the virus is inactivated per minute. Also calculate the time required for its,
 (a) 50% inactivation
 (b) 80% inactivation.
- 7. Show that for I order reaction, the time required for 99.9 % decomposition of the reaction is ten folds to the time required for half of the reaction.
- 8. The time required for 20 % completion for a reaction is 10 minute for I order reaction. Calculate :
 - (a) specific reaction rate. (b) Time required for 75 % completion
- 9. The half life for a I order reaction A → Product, is 10 minute. What % of A remains after
 (i) 1/2 hour
 (ii) 2/3 hour
 (iii) 1 hour
- 10. The reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ obeys I order kinetics with rate const. $3.2 \times 10^{-5} \text{ sec}^{-1}$ at 320 °C. What % of SO_2Cl_2 will be decomposed on heating gas for 90 minute ?
- 11. For the first order reaction, $A \longrightarrow B$, shown in the figure, what is the significance of the point at which the two curves cross each other. How is the slopes of the two curves be related at this point ?



- 12. A first order gaseous reactions has $K = 1.5 \times 10^{-6} \text{ sec}^{-1}$ at 200 °C. If the reaction is allowed to run for 10 hour, what percentage of initial concentration would have changed into products. What is the half life period of reaction?
- **13.** Thermal decomposition of a compound is of first order. If 50 % sample of the compound is decomposed in 120 minute, how long will it take for 90 % of the compound to decompose ?
- 14. A substance is reduced to one third of its original concentration in 100 minute. Calculate the time in which it will be reduced to one ninth of its original value. Assume I order .

- 15. For the decomposition of N_2O_5 , the rate constant is $6.2 \times 10^{-4} \text{ sec}^{-1}$ at 45°C. It begins with one mole of N_2O_5 in a litre flask, how long would it take for 20% N_2O_5 to decompose and how long for 50 %?
- In the decomposition of oxalic acid following data were obtained: Time in minute 0 300 600 Pressure in mm 22.0 17.0 13.4 Determine the net operator K and helf life period if recetion above L

Determine the rate constant K and half life period, if reaction obeys I order kinetics.

- 17. Decomposition of $N_2O_5(g)$ into $NO_2(g)$ and $O_2(g)$ is a first order reaction. If the initial concentration of $N_2O_5(g)$, i.e., $[N_2O_5]_0$ is 0.030 mol litre⁻¹, what will be its concentration after 30 minute? Rate constant of reaction is $1.35 \times 10^{-4} \text{ sec}^{-1}$.
- 18. For a homogeneous gaseous reaction, $A \longrightarrow B + C + D$, the initial pressure was P_0 while pressure after time t was P. Derive an expression for rate constant K in terms of P_0 , P and t. assume I order reaction.
- **19.** Acetone on heating gives CO and other hydrocarbons at 600°C. The reaction obeys I order kinetics w.r.t. acetone concentration. The half life period is 81 sec. Calculate the time in which acetone taken in a container at 600 °C reduces its pressure from 0.5 atm to 0.4 atm.
- 20. Dimethyl ether gaseous phase decomposition is : $CH_3OCH_3 \longrightarrow CH_4 + H_2 + CO$ at 750 K having rate constant 6.72×10^{-3} min⁻¹. Calculate the time in which initial pressure of 400 mm in closed container becomes 750 mm.
- **21.** The decomposition of Cl_2O_7 at 400 K in gaseous phase to Cl_2 and O_2 is of I order reaction. After 55 sec at 400 K, the pressure of reaction mixture increase from 0.62 to 1.88 atm. Calculate the rate constant of reaction. Also calculate the pressure of reaction mixture after 100 second.
- 22. In the vapour phase decomposition of ethylene oxide, $C_2H_4O \longrightarrow CH_4 + CO$ at 414.5°C, the initial pressure and the pressure after 5 minute were 116.51 mm and 122.56 mm of Hg respectively. If the reaction follows I order kinetics, what must be the pressure after 12 minutes?
- 23. Calculate the partial pressures of reactants and products, when azomethane decomposes at an initial pressure of 200 mm for 30 minute according to $(CH_3)_2 N_2 \longrightarrow C_2 H_6 + N_2$. The rete constant is $2.5 \times 10^{-4} \text{ sec}^{-1}$.
- 24. Rate constant of a first order reaction A \longrightarrow B is 6.93 ×10⁻² minute. If initial concentration of reactant is 1 M. Then calculate :
 - (i) Initial rate (ii) Rate after 600 seconds
 - (iii) Rate after 75 % of the reaction is completed
 - (iv) Rate after 30 minutes.
- **25.** In a first order reaction concentration of reactant decreases from 10 M to 2.5 M in 500 seconds . Calcualte :
 - (i) $t_{1/2}$ of the reaction
 - (ii) rate of reaction when concentration is 5 M.
- **26.** Rate constant of a first order reaction is 10^{-3} sec. Calculate time in seconds when concentration is changing from :

(i) $2 \text{ M to } 0.25 \text{ M}$ (ii) $16 \text{ M to } 1$
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(iii) 6.4 M to 1.6 M (iv) 4 M to 0.125 M

ANSWERS

Daily Practice Problems 1

	1. (D)	2. (C)	3. (B)	4. (B)	5. (A)	
	$6. \ \frac{\Delta[\text{NO}]}{\text{dt}} =$	$3.5 \times 10^{-2} \text{ mol}$	$dm^{-3} s^{-1} \frac{\Delta [H_2]}{dt}$	$\frac{O}{2} = 5.3 \times 10^{-1}$	2 mol dm ⁻³ s ⁻¹	
	7. 6.0×10^{-4}	$mol L^{-1} min^{-1}$		8. (a) 1.6 × 1	0 ⁻⁴ M/s ; (b) 3.	$2 \times 10^{-4} \text{ M/s}$
	9. (C)	10. (D)	11. (B)	12. (B)	13. (D)	14. (D)
	15. (a) Rate (c) rate w	$= k[CH_3Br] [C]$ ill increase by t	OH⁻] (b) rat factor of 4	e will decrease	by factor of 5	
	 16. (a) k[Br⁻] [BrO₃⁻] [H⁺]² (b) 4 (c) rate will increase by the factor of 9 (d) rate will decrease by factor of 1/4 17. (i) 7.5 × 10⁻⁷ M min⁻¹ (ii) rate increased by 64 times 					the factor of 9
	18. order w.r	.t. [NO] = 2 ; o	order w.r.t. [Cl ₂] = 1 19. 8 ×	$10^{-9} \ M^{-2} \ s^{-1}$	
	20. (i) 3/2	(ii) atm ^{-1/2} tim	ne ⁻¹ (iii) in	creased by 64 t	imes	
Daily	Practice P	roblems 2				
	1. (B) 7. (A)	2. (C) 8. (B)	3. (B) 9. (B)	4. (C) 10. (B)	5. (B) 11. (B)	6. (A)
	12. (a) 2 N ₂ C (c) (i) uni	$(g) \longrightarrow 2 N_2(g)$ molecular (ii)	$(g) + O_2(g)$ bimolecular	(b) oxygen a(d) not defin	tom ed	
	13. 3/2					
	15. (a) Rate	$= k[NH_4^+][NC_4^+]$	D_2^{-1} (b) 3	$.0 \times 10^{-4}$ M/s	(c) 6.1 ×	10^{-6} M/s
	16. (i) $r = k[$	$[A]^{-1} [B]^{1/2}$	(ii) wrt : $A = -$	-1, B = 1/2, C =	= 0 ,overall ord	ler = -1/2
	(iii) k =	$\frac{63}{\sqrt{3}} \times 10^{-9}$	(iv) rate of rea	action increases	s by $2\sqrt{2}$ times	
	17. (i) k[A ₂]	$^{3}[B_{2}]$	(ii) order wrt	$A_2 = 3$; O. wrt	$B_2 = 1$, overall	l order = 4
	(iii) k = 7	$1.5 \times 10^{3} (\text{mol/l})^{-1}$	it) ⁻³ /sec	(iv) rate of rea	action decrease	e to $\frac{1}{16}$
	18. (a) 2 and	1 (b) $r = K[C]$	$[1_2]^1[NO]_2$ (c)	8 litre ² mol ⁻² s	ec^{-1} (d) 0.25	6 mol litre ⁻¹ sec ⁻¹

19. 211 torr, 13.57 min **20.** Zero order

Daily Practice Problems 3

2. (i) $a = R_0 K$, $b = \frac{R_0 K^2}{2}$, $c = \frac{R_0 K^3}{6}$ 2. (i) $t_{1/2} = 66.66 \text{ min}$, $k = 0.01039 \text{ min}^{-1}$ (ii) $k = 0.06386 \text{ min}^{-1}$; t = 36.06 min(iii) 0.03465 min^{-1} (iv) (i) 0.740 s (ii) 2.005 s4. 0.09 5. (a) 3 (b) No change 6. $K = 2.5 \times 10^{-4} \text{ sec}^{-1}$, 7. (a) 46.2 minute (b) 107.3 minute

CHEMICAL KINETICS		45
8. (a) $2.232 \times 10^{-2} \min^{-1}$ (b) 62.12 min	ute 9. (i) 12.5	%, (ii) 6.25 %, (iii) 1.56%
10. 15.86 % 11. Time at	this point is $t_{1/2}$ because	se [A] = [B]: Also $\frac{d[A]}{dt} + \frac{d[B]}{dt} = 0$
12. 5.25 %, 128.33 hr	14. 200 minute	15. 3.59×10^2 , 1.1×10^3 sec
 16. 8.6× 10⁻⁴ sec; 13.43 minute 19. 26 sec 	17. 0.023 mol/L20. 85.64	18. K = $\frac{2.303}{t} \log_{10} \frac{2P_0}{3P_0 - P}$ 21. 1.58 ×10 ⁻² , 233 atm
22. 130.41	23. $P'_{(CH_3)_2N_2} = 12$	27.55 mm , $P'_{C_2H_6} = 72.45 \text{ mm}$
24. (i) 6.93 × 10 ⁻² M/min.(ii) 3.46 25. (i) 250 seconds (ii) 0.01386 26. (i) 2079 sec (ii) 2772 sec, (iii)	$55 \times 10^{-2} \text{ M/min (iii)} 1.55 \text{ M} \text{ sec}^{-1}$ i) 1386 sec. (iv	7325 × 10 ⁻² M/min.(iv) 8.67 × 10 ⁻³) 3465 sec.