

- Q1. A substance with initial concentration 'a' follows zero order kinetics with rate constant k $\text{mol L}^{-1} \text{S}^{-1}$. In how much time will the reaction go to completion?
- Q2. Express the relation between the half life period of a reactant and its initial concentration for a reaction of n^{th} order.
- Q3. Define activation energy of a reaction.
- Q4. Express the relation between the half life period of a reaction and its initial concentration if the reaction involved is of second order.
- Q5. The rate of reaction $X \longrightarrow Y$ becomes 8 times when the concentration of the reaction X is doubled. Write the rate law of the reaction.
- Q6. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of the reaction?
- Q7. For the reaction $A \longrightarrow B$, the rate of reaction becomes twenty-seven times, when the concentration of A is increased three times. What is the order of the reaction?
- Q8. Express the rate of the following reaction in terms of disappearance of hydrogen in the reaction:
$$3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$$
- Q9. Define the term order of reaction for chemical reactions.
- Q10. For the reaction $\text{Cl}_2(\text{g}) + 2\text{NO}(\text{g}) \longrightarrow 2\text{NOCl}(\text{g})$, the rate law is expressed as: $\text{rate} = k[\text{Cl}_2][\text{NO}]^2$. What is the overall order of this reaction?
- Q11. For the reaction $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$, how is the rate of reaction expressions $-\frac{d[\text{H}_2]}{dt}$ and $-\frac{d[\text{NH}_3]}{dt}$ interrelated?
- Q12. The reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l})$ is thermodynamically feasible. How is it that a mixture of hydrogen and oxygen kept at room temperature shows no tendency to form water?
- Q13. For the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$, express the rate of reaction in terms of formation of ammonia.
- Q14. The rate law for the decomposition of N_2O_5 is: $\text{rate} = k[\text{N}_2\text{O}_5]$. What is the significance of k in this equation?
- Q15. State any one condition under which a bimolecular reaction may be kinetically first order.
- Q16. For the reaction $2X \longrightarrow X_2$, the rate of reaction becomes three times when the concentration of X is increased 27 times. What is the order of the reaction?
- Q17. Give an example of Pseudo first order reaction.
- Q18. In some cases, it is found that a large number of colliding molecules have energy more than threshold value, yet the reaction is slow. Why?

Q19. The reaction $A + B \longrightarrow C$ has zero order. What is the rate equation?

Q20. For the reaction : $A + H_2O \longrightarrow B$, rate $\propto [A]$. What is its (a) molecularity (b) order of the reaction.

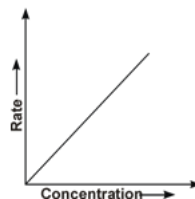
Q21. Why is the instantaneous rate of reaction does not change when a part of the reacting solution is taken out?

Q22. Consider the following equation:



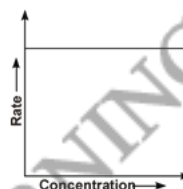
The rate for this reaction is first order w.r.t. H_2 and second order w.r.t. NO . Write the rate law for this reaction.

Q23. Following graph is a plot of rate of reaction vs concentration of the reactant. What is the order of the reaction?



Q24. The rate constant of a reaction is $2 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$. What is the order of the reaction?

Q25. Following graph is a plot of rate of reaction vs concentration of the reactant. What is the order of the reaction?



Q26. For the homogeneous decomposition of N_2O_5 into NO_2 and O_2 .



$$\text{Rate} = -\frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = k[N_2O_5].$$

Find out the order of reaction with respect to N_2O_5 .

Q27. For a reaction $A \longrightarrow B$, the rate of reaction can be denoted by $-\frac{d[A]}{dt}$ or $+\frac{d[B]}{dt}$. State the significance of plus and minus sign.

Q28. For the assumed reaction, $X_2 + 2Y_2$, write the rate equation in terms of the rate of disappearance of Y_2 .

Q29. The half life of reaction is 50 minutes, what will be the order of the reaction if the reaction goes to completion in 100 minutes?

Q30. What is the difference between average rate and instantaneous rate of a chemical reaction?

Q31. The form of the rate law for a reaction is expressed as: $\text{Rate} = k[Cl_2][NO]^2$

Find out the order of reaction with respect to Cl_2 and with respect to NO and also the overall order of reaction.

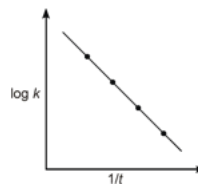
Q32. What will be shape of curve if the concentration of the reaction is plotted against time for a zero order reaction?

Q33. In a reaction $2A \rightarrow \text{Product}$, the concentration of A decreases from 0.5 mole/litre to 0.4 mole/litre in 10 minutes. Calculate the rate during this interval.

Q34. The rate law for the reaction $A + B \rightarrow \text{Product}$ is

$$\text{rate} = -\frac{d[A]}{dt} = +\frac{d[\text{Product}]}{dt} = k[A]^{\frac{3}{2}} [B]^{\frac{1}{2}}. \text{ Find the order.}$$

Q35. What is the shape of graph between $\log k$ vs $\frac{1}{T}$? What is the relationship between slope and activation energy?



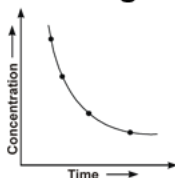
Q36. 87.5% of substance disintegrated in 45 minutes (first order reaction). What is its half life?

Q37. Define threshold energy of activation.

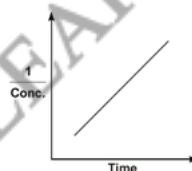
Q38. Define effective collision.

Q39. What is the effect of temperature on activation energy?

Q40. In the reaction $A \longrightarrow B$, if the concentration of A is plotted against time, the nature of the curve obtained will be as shown in the figure. What is the order of the reaction?



Q41. In the decomposition of N_2O_2 the plot between the reciprocal of concentration of the reactant and the time was found to be linear as shown in the figure. Determine the order of the reaction.

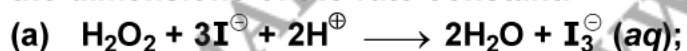


Q42. The reaction of the decomposition of NH_3 on platinum surface is zero order. What are the rate of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ Ms}^{-1}$?

Q43. For the reaction: $2A + B + C \longrightarrow A_2B + C$

the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6} \text{ M}^{-2}\text{s}^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1 \text{ M}$, $[B] = 0.2 \text{ M}$ and $[C] = 0.8 \text{ M}$. If the rate of reverse reaction is negligible then calculate the rate of reaction after $[A]$ is reduced to 0.06 M .

Q44. From rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constant:



$$\text{Rate} = k [H_2O_2] [I^-]$$



$$\text{Rate} = k [CH_3CHO]^{3/2}$$

Q45. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction rate is given by

$$\text{Rate} = k[\text{CH}_3\text{OCH}_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a closed vessel and the rate can also be expressed in terms of the partial pressure of dimethyl ether i.e.,

$$\text{Rate} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

Q46. The half life for radioactive decay of ^{14}C is 5730 y. An archaeological artefact contained wood had only 80% of the ^{14}C in a living tree. Estimate the age of the sample.

Q47. Calculate the half the life period of a first order reaction from their rate constants given below :

(a) 200s^{-1}

(b) 2min^{-1}

Q48. A reaction is first order in A and second order in B .

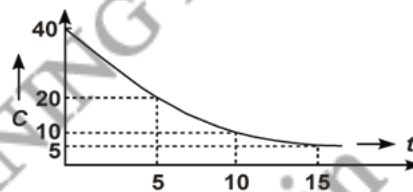
(a) How is the rate affected when the concentration of B is tripled?

(b) How is the rate affected when the concentration of both A and B is doubled?

Q49. The rate constant for a first order reaction is 60s^{-1} . How much time will it take to reduce the initial concentration of the reactant to its $1/16^{\text{th}}$ value?

Q50. For a reaction, a graph was plotted between reactant concentration C and time t as shown in the figure.

Identify the order of the reaction with respect to the reactant. Can the concentration of the reactant be theoretically zero after infinite time?



Q51. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 years. What is the rate constant (in year^{-1}) for the decay? What fraction would remain after 11540 years?

Q52. The rate of reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Q53. The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} \text{ s}^{-1})e^{-28000\text{K}/T} \quad \text{Calculate } E_a.$$

Q54. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2} = 3.0\text{ h}$. What fraction of sample of sucrose remains after 8 hours?

Q55. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5}\text{s}^{-1}$ at 546 K. If the energy of activation is 179.9 kJ mol^{-1} , what will be the value of pre-exponential factor?

Q56. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Q57. Show that time required for 99% completion is twice the time required for the completion of 90% reaction.

Q58. What will be the order of reaction of the type $A \rightarrow \text{Product}$, for which the following data were obtained?

[A]	$\frac{d[A]}{dt}$
(a) 1	1
(b) 2	8
(c) 3	27

Q59. For a reaction at 800°C , $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, the following data were obtained:

$[\text{NO}] \times 10^{-4} \text{ mol/litre}$	$[\text{H}_2] \times 10^{-3} \text{ mole/litre}$	$d[\text{NO}]/dt \times 10^{-4} \text{ mole litre}^{-1} \text{ min}^{-1}$
(a) 1.5	4.0	4.4
(b) 1.5	2.0	2.2
(c) 0.5	2.0	0.24

What is the order of this reaction with respect to NO and H_2 ?

Q60. What is difference between molecularity and order of a reaction.

Q61. Show by using rate laws how much the rate of reaction $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ will change if the volume of the reaction vessel is diminished to $1/3$ of its initial volume.

Q62. The rate constant for the reaction: $\text{CO}_2 + {}^\ominus\text{OH} \rightarrow \text{HCO}_3^\ominus$
In the aqueous solution is $4 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$. Calculate the number of mole of CO_2 and ${}^\ominus\text{OH}$ used up per second when $[\text{CO}_2]$ and $[{}^\ominus\text{OH}]$ are 10^{-6} and $10^{-1} \text{ mol L}^{-1}$. Also predict the mole of HCO_3^\ominus formed per second.

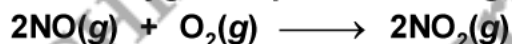
Q63. The rate constant for the reaction, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ is $3.0 \times 10^{-5} \text{ s}^{-1}$. If the rate is $2.40 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$, then calculate the initial concentration of N_2O_5 (in mol L^{-1}).

Q64. For the chemical reaction: $\text{I}^\ominus + \text{OCI}^\ominus \rightarrow \text{Cl}^\ominus + \text{OI}^\ominus$

$$\text{Rate} = \frac{k[\text{OCI}^\ominus][\text{I}^\ominus]}{[{}^\ominus\text{OH}]}$$

- (a) What is the order and molecularity of the reaction?
(b) In the above reaction, what the molecularity and order with respect to $[{}^\ominus\text{OH}]$?

Q65. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide:



The rate law for this reaction is

$$\text{rate} = k [\text{NO}]^2 [\text{O}_2]$$

Propose a mechanism for the above reaction.

Q66. Pseudo first order rate for the reaction $A + B \rightarrow P$

when studies in 0.1 M of B is given by $-\frac{d[A]}{dt} = -k[A]$

where $k = 1.85 \times 10^4 \text{ s}^{-1}$. Calculate the value of second order rate constant.

Q67. Find the two-third life, $t_{2/3}$, of a first order reaction in which $k = 5.4 \times 10^{-14} \text{ s}^{-1}$.

Q68. For a first order reaction, show that time required for completion of 99.9% of reaction is 3 times the time required for completion of 90% of the reaction.

OR

Show that, $t_{99.9\%} = 3t_{90\%}$ for a first order reaction.

Q69. What are photochemical reactions? Give an example to illustrate the course of a photochemical reaction.

Q70. The decomposition of phosphene, $4\text{PH}_3(\text{g}) \longrightarrow \text{P}_4 + 6\text{H}_2(\text{g})$ has rate law, $\text{rate} = k[\text{PH}_3]$. The rate constant is $6.0 \times 10^{-4} \text{ s}^{-1}$ at 300 K and activation energy is $3.05 \times 10^5 \text{ J mol}^{-1}$. What is the value of rate constant at 310 K? ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

Q71. The reaction: $\text{SO}_2\text{Cl}_2 \longrightarrow \text{SO}_2 + \text{Cl}_2$ is a first order gas reaction with $k = 2.2 \times 10^{-5} \text{ sec}^{-1}$ at 320°C . What percentage of SO_2Cl_2 is decomposed on heating this gas for 90 minutes?

Q72. The reaction $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}$ was studied at -10°C , and the following data were obtained:

Initial concentrations (mol L ⁻¹)			Initial rate of formation of NOCl (mol L ⁻¹ min ⁻¹)
Run	[NO]	[Cl ₂]	
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.44

- (a) what is the order of reaction with respect to NO and with respect to Cl₂?
 (b) what is the numerical value of the rate constant at -10°C ?

Q73. Write stoichiometric equation whose mechanism is detailed below



$$k_f = 10^{10} \text{ s}^{-1}; \quad k_b = 10^{10} \text{ s}^{-1}$$



So write: (a) Value of equilibrium constant for the first step. and (b) Rate law equation for the overall reaction in terms of initial concentrations.

Q74. A certain reaction, $\text{X} + \text{Y} \longrightarrow \text{Products}$, is first order w.r.t. each reactant with $k = 5 \times 10^{-3} \text{ s}^{-1}$. Calculate the concentration of X remaining after 100 sec. if initial concentration of X was 0.100 M and that of Y was 10 M. State any approximation that you will make in obtaining the result.

Q75. For a certain reaction, it takes 5 minutes for the initial concentration of 0.5 mole per litre to become 0.25 mole per litre and another 5 minutes to become 0.125 mole per litre. What is the order of this reaction and why is it so? Calculate the rate constant for the reaction.

Q76. Rate constant k of a reaction varies with temperature according to the equation:

$$\log k = \text{constant} - \frac{E_a}{2.303 R T}$$

where E_a is the energy of activation of the reaction, When a graph is plotted for $\log k$ versus $\frac{1}{T}$, a straight line with a slope -6670 K is obtained. Calculate energy of activation for this reaction. State the units ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Q77. In a pseudo first order hydrolysis of ester in water the following results were obtained:

t/s	0	30	60	90
[Ester]/M	0.55	0.31	0.17	0.085

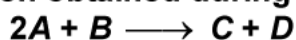
- (a) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
 (b) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Q78. During nuclear explosion, one of the products is ^{90}Sr with half life of 28.1 y. If $1\ \mu\text{g}$ of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

Q79. The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A]/M	[B]/M	Initial rate/M min ⁻¹
I	0.1	0.1	2.0×10^{-2}
II	—	0.2	4.0×10^{-2}
III	0.4	0.4	—
IV	—	0.2	2.0×10^{-2}

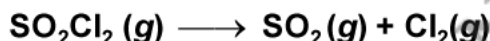
Q80. The following results have been obtained during the kinetic studies of the reaction:



Experiment	[A]/M	[B]/M	Initial rate of formation of D/M min ⁻¹
I	0.1	0.1	$6.0 \times 10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}$
II	0.3	0.2	$7.2 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}$
III	0.3	0.4	$2.88 \times 10^{-1}\ \text{mol L}^{-1}\ \text{min}^{-1}$
IV	0.4	0.1	$2.4 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}$

Determine the rate law and the rate constant for the reaction.

Q81. The following data were obtained during the first order thermal decomposition of $\text{SO}_2\text{Cl}_2(\text{g})$ at constant volume.



Experiment	Time/s ⁻¹	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of reaction when total pressure is 0.65 atm.

Q82. For the decomposition of a zoisopropane to hexane and nitrogen at 543 K, the following data is obtained.



T(sec)	p (mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

Q83. The rate constant for the first order decomposition of H_2O_2 is given by the equation:

$$\log k = 14.34 - 1.25 \times 10^4 / \text{K/T}$$

Calculate E_a for this reaction and at what temperature will its $t_{1/2}$ be 256 minutes?

Q84. Consider a certain reaction, $A \rightarrow$ products with $k = 2.0 \times 10^{-2}\ \text{s}^{-1}$. Calculate the concentration of A remaining after 100 s if initial concentration of A is $1.0\ \text{mol L}^{-1}$.

Q85. In a reaction between A and B, the initial rate of reaction was measured for differential initial concentrations of A and B as given below:

A/mol L ⁻¹	0.20	0.20	0.40
B/mol L ⁻¹	0.30	0.10	0.05
r ₀ /mol L ⁻¹ s ⁻¹	5.07 × 10 ⁻⁵	5.07 × 10 ⁻⁵	7.6 × 10 ⁻⁵

What is the order of reaction with respect to A and B?

Q86. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

- (a) doubled (b) reduced to 1/2

Q87. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is 4 × 10¹⁰ s⁻¹, calculate k at 308 K and E_a.

Q88. The decomposition of A into product has value of k as 4.5 × 10³s⁻¹ at 10°C and energy of activation 60 kJ mol⁻¹. At what temperature would k be 1.5 × 10⁴s⁻¹?

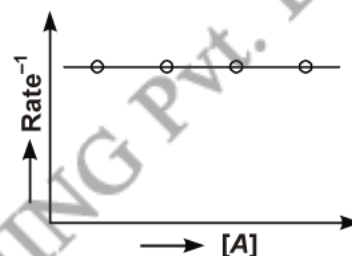
Q89. 2A + 3B → Product

What is order w.r.t. A and B in the following cases:

(a) When $\left(\frac{dx}{dt}\right) = k[A]$ and B is in excess.

(b) when $\left(\frac{dx}{dt}\right) = k[B]^2$ and graph is true.

(c) When the rate is doubled, then the concentration of A is doubled, and the rate is eight times when the concentration of A and B is doubled.



Q90. For 2A + B + C → Products, calculate:

- (a) Rate expression (b) Units of rate and rate constant.
(c) Effect on rate, if the concentration of A is doubled and that of B is tripled.

Q91. The reaction, 2N₂O₅ → 4NO₂ + O₂, is forming NO₂ at the rate of 0.0072 mole/L/s at some time.

- (a) What is the rate of change of [O₂] at this time?
(b) What is the rate of change of [N₂O₅] at this time?
(c) What is the rate of reaction at this time?

Q92. The decomposition of a compound is found to follow a first-order rate law. If it takes 15 minutes for 20 percent of original material to react, calculate (a) the specific rate constant, (b) the time at which 10 percent of the original material remains unreacted, (c) the time it takes for the next 20 percent of the reactant left to react first 15 minutes.

Q93. A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction.

Q94. The catalytic decomposition of hydrogen peroxide was studied by titrating it at different intervals with KMnO₄. Calculate the rate constant from the following data, assuming the reaction to be of first order:

t (secs.)	0	600	1,200
KMnO ₄ (ml.)	22.8	13.8	8.2

Q95. In general, it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If this generalisation holds good for the reaction in the temperature range 295 K to 305 K, what would be the value of activation energy for this reaction? ($R = 9.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

Q96. First order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete?

Q97. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is again 50% complete in 5 minutes at 350 K. Calculate energy of activation if it is a reaction of first order.

Q98. Consider the data for the reaction between A and B.

[A] (mol L ⁻¹)	[B] (mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)	
		At 300 K	At 320 K
2.5×10^{-4}	3.0×10^{-5}	5×10^{-4}	2×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4×10^{-3}	—
1.0×10^{-4}	6.0×10^{-5}	1.6×10^{-2}	—

Calculate:

- (a) order w.r.t. A and B
 (b) rate constant at 300
 (c) the energy of activation
 (d) the pre-exponential factor

Q99. The rate constant for the decomposition of N_2O_5 at various temperature is given below:

T^{10}/C	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between $\ln k$ and $1/T$ and calculate the values of A and E_a . Predict the rate constant at 30° and 50°C.

Q100. The experimental data for decomposition of N_2O_5 [$2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$] in gas phase at 318 K are given below :

Time/seconds	0	400	800	1200	1600
$10^{-2} \times [\text{N}_2\text{O}_5]/\text{M}$	1.65	1.36	1.14	0.93	0.78
Time/seconds	2000	2400	2800	3200	
$10^{-2} \times [\text{N}_2\text{O}_5]/\text{M}$	0.64	0.53	0.43	0.35	

- (a) Plot (N_2O_5) against t.
 (b) Find the half life period for the reaction.
 (c) Calculate the half life period from k and compare it with answer (b).

- S1.** $k = \frac{a}{t}$ or $t = \frac{a}{k}$, In time $\frac{a}{k}$ the reaction will be completed.
- S2.** $t_{1/2} \propto \frac{1}{[R]_0^{n-1}}$.
- S3.** It is the extra energy which must be supplied to the reactants so that they can change into the products after crossing the activated complex.
- S4.** $t_{1/2} \propto \frac{1}{[R]_0}$, where $[R]_0$ is initial concentration.
- S5.** $\frac{dx}{dt} = k[X]^3$.
- S6.** It is first order. In first order reactions, $t_{75\%} = 2t_{50\%}$.
- S7.** Order = 3
- S8.** $-\frac{1}{3} \frac{d[H_2]}{dt}$
- S9.** Sum of the powers of concentration of the reactants in the rate law expression is called the order of that chemical reaction.
- S10.** Order = 3
- S11.** $-\frac{1}{3} \frac{d[H_2]}{dt} = +\frac{1}{2} \frac{d[NH_3]}{dt}$.
- S12.** They require activation energy to give the product.
- S13.** $+\frac{1}{2} \frac{d[NH_3]}{dt}$.
- S14.** k is the rate constant. It is equal to the rate of reaction when the concentrations of reactants are unity.
- S15.** If one of the reactants is in excess, its concentration does not change. Therefore, the reaction may be first order.
- S16.** Order of the reaction = $\frac{1}{3}$.
- S17.** $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
- S18.** In such cases, the molecules do not collide in proper orientation.

S19. $\frac{dx}{dt} = k[A]^0[B]^0$.

S20. Molecularity = 2; Order of reaction = 1.

S21. Instantaneous rate is measured over a very small interval of time. Therefore, it is not affected on taking out a part of reacting solution.

S22. $\frac{dx}{dt} = k[H_2][NO]^2$

S23. First order.

S24. From the unit of rate constant, we can identify that it is a second order reaction.

S25. Zero order reaction.

S26. First order with respect to N_2O_5 .

S27. Concentration of A (reaction) decreases with time and concentration of B (product) increase with time.

S28. Rate of reaction = $-\frac{1}{2} \frac{d[Y_2]}{dt}$.

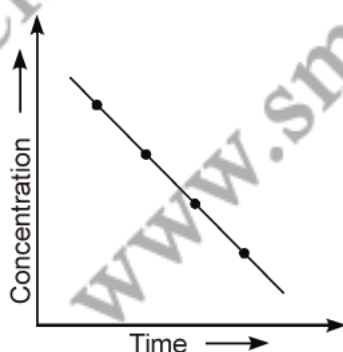
S29. Zero order. $t_{100\%} = 2t_{50\%}$

S30. When change in concentration is measured over long period of time, we get average rate of reaction.

When change in concentration is measured over a very small period of time, or at a particular instant, it is instantaneous rate.

S31. Order with respect to $Cl_2 = 1$
 Order with respect to $NO = 2$
 Over all order = 3

S32.



S33. Rate = rate of disappearance of A per mole.

$$= -\frac{1}{2} \frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{(0.5 - 0.4)}{10} = -0.005$$

The negative sign simply indicates the fall in concentration of A. Thus ignoring the negative sign, the rate of the reaction is 0.005 mole/litre/minute.

S34. The order of the reaction by definition is equal to,

$$\frac{3}{2} + \frac{1}{2} = 2$$

S35. Slope of the line = $-\frac{E_a}{2.303R}$

S36. $\frac{12.5}{100} = \left(\frac{1}{2}\right)^n$ or $\left(\frac{1}{2}\right)^n = \frac{1}{8}$ or $n = 3$, Number of half lives = 3

$$\therefore t_{1/2} = \frac{45}{3} = 15 \text{ minutes}$$

S37. Minimum energy that must be possessed by molecules in order to give the product is called threshold energy.

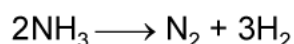
S38. Collisions between molecules which result in the formation of products are effective collisions.

S39. No effect of temperature on activation energy.

S40. First order reaction.

S41. Second order reaction.

S42. The reaction for decomposition of NH_3 is



Rate of reaction,

$$\frac{dx}{dt} = \frac{1}{2} \frac{d(\text{NH}_3)}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k$$

(k is rate constant and reaction is of zero order)

$$\therefore \text{rate of reaction, } \frac{dx}{dt} = \frac{d(\text{N}_2)}{dt} = k = 2.5 \times 10^{-4} \text{ Ms}^{-1}$$

or rate of production of N_2 , i.e.,

$$\frac{d(\text{N}_2)}{dt} = k = 2.5 \times 10^{-4} \text{ Ms}^{-1}$$

Rate of production of H_2 , is given by

$$\begin{aligned} \frac{d(\text{H}_2)}{dt} &= 3 \frac{d(\text{N}_2)}{dt} = 3 \times 2.5 \times 10^{-4} \text{ Ms}^{-1} \\ &= 7.5 \times 10^{-4} \text{ Ms}^{-1} \end{aligned}$$

S43. In the reaction $2A + B + C \longrightarrow A_2B + C$, there is no change in C , therefore its concentration does not affect the rate of the reaction.

$$\text{Initial rate} = k[A][B]^2$$

But, $[A] = 0.1 \text{ M}$; $[B] = 0.2 \text{ M}$ and $k = 2 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$.

$$\therefore \text{Initial rate} = 2 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1} \times (0.1 \text{ M}) \times (0.2 \text{ M})^2 = 8 \times 10^{-9} \text{ Ms}^{-1}$$

From the equation $2A + B + C \longrightarrow A_2B + C$ it is clear that when 2 moles of A are used then 1 mol of B is used in the same time. Therefore, when A has been reduced to 0.06 M (0.04 M of A have reacted and hence 0.02 M of B). Thus

$$\text{Conc. of } A \text{ left} = [A] = 0.06 \text{ M}$$

$$\text{Conc. of } B \text{ left} = [B] = [0.2 \text{ M} - 0.02 \text{ M}] = 0.18 \text{ M}$$

$$\text{Rate} = k[A][B]^2$$

$$= 2 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1} \times (0.06 \text{ M}) (0.18 \text{ M})^2 = 3.89 \times 10^{-9} \text{ Ms}^{-1}$$

S44. (a) $\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^\ominus]$

Overall order of reaction = $1 + 1 = 2$

$$\text{Rate constant, } k = \frac{\text{Rate}}{[\text{H}_2\text{O}_2][\text{I}^\ominus]} = \frac{\text{Conc. / time}}{\text{Conc.}^2}$$

$$= \frac{1}{\text{Conc.} \times \text{time}} = \frac{1}{\text{mol L}^{-1} \text{ s}}$$

$$= \text{L mol}^{-1} \text{ s}^{-1}$$

The dimensions of the rate constant, k are : $\text{L mol}^{-1} \text{ s}^{-1}$

(b) $\text{Rate} = k[\text{CH}_3\text{CHO}]^{3/2}$

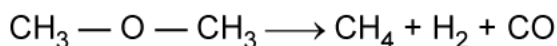
Overall order of reaction = 1.5

$$\text{Rate constant, } k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^{3/2}} = \frac{\text{Conc. / time}}{\text{Conc.}^{3/2}} = \frac{1}{\text{Conc.}^{1/2} \times \text{s}}$$

$$= \frac{1}{(\text{mol L}^{-1})^{1/2} \text{ s}} = \text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$$

The dimensions of rate constant, k are : $\text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$

S45. The reaction for decomposition of dimethyl ether can be written as:



The rate of reaction,

$$\left(\frac{dx}{dt}\right) = \frac{d[\text{CH}_3\text{OCH}_3]}{dt} = \frac{d[\text{CH}_4]}{dt} = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{CO}]}{dt}$$

$$= k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

The unit of rate is : bar min⁻¹ or bar s⁻¹

The unit of rate constant, k is : bar s⁻¹/bar^{-3/2} = bar^{-1/2} s⁻¹

$$\left[\therefore k = \frac{\text{rate}}{(P_{\text{CH}_3\text{OCH}_3})^{3/2}} \right]$$

S46. Given, $t_{1/2} = 5730$ years; $\frac{N}{N_0} = 80\% = 0.80$

Decay constant, $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} = 1.21 \times 10^{-4} \text{ year}^{-1}$

All radioactive nuclear decay are first order reactions, hence

\therefore Decay constant, $\lambda = \frac{2.303}{t} \log \frac{N_0}{N}$

$$\lambda = \frac{2.303}{t} \log \frac{10}{8}$$

or time, $t = \frac{2.303}{\lambda} \log 1.25$

$$t = \frac{2.303}{1.21 \times 10^{-4}} \times 0.0969 = 1845 \text{ years}$$

Age of sample $t = 1845$ years.

S47. For the first order reaction,

$$t_{1/2} = \frac{0.693}{k}$$

(a) $k = 200 \text{ s}^{-1}$ $\therefore t_{1/2} = \frac{0.693}{200} = 3.465 \times 10^{-3} \text{ s}$

(b) $k = 2 \text{ min}^{-1}$ $\therefore t_{1/2} = \frac{0.693}{2} = 0.3465 \text{ min.}$

S48. (a) $\frac{dx}{dt} = k[A][B]^2$... (i)

When conc. of B is tripled, it means conc. of B becomes $[3 \times B]$

\therefore new rate of reaction,

$$\frac{dx'}{dt} = k[A][3B]^2$$

$$= 9k[A][B]^2 = 9 \left(\frac{dx}{dt} \right)$$

[From Eq. (i)]

i.e., rate of reaction will become 9 times.

- (b) When conc. of A is doubled and that of B is also doubled, then conc. of A becomes [2A] and that of B becomes [2B].

$$\text{rate of reaction, } \frac{dx'}{dt} = k[2A][2B]^2 = 8k[A][B]^2$$

i.e., the rate of reaction will become 8 times the rate as in Eq. (i).

- S49.** Rate constant of reaction, $k = 60 \text{ s}^{-1}$

$$t_{1/16} = ?$$

Rate constant of first order reaction is given as,

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

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

when $1/16^{\text{th}}$ of reaction is over, if $a = 1 \text{ M}$, then $a - x = 1/16 \text{ M}$

Hence,

$$\begin{aligned} t_{1/16} &= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{1/16} \\ &= \frac{2.303}{60} \log 16 = \frac{2.303}{60} \times 1.2041 \text{ s} \\ &= 0.046 \text{ s} = 4.6 \times 10^{-2} \text{ sec.} \end{aligned}$$

- S50.** From the graph we see that the concentration reduces from 40 to 20 in 5 minutes, reduces from 20 to 10 in 5 minutes, and reduces from 10 to 5 in again 5 minutes, which shows that half-life period is independent of concentration which is the characteristic of a first order reaction. In a first order reaction the concentration of the reactant can never be theoretically zero.

- S51.** Disintegration constant, $k = \frac{0.6932}{t_{1/2}}$

(or rate constant) $k = \frac{0.6932}{5770} = 0.00012 \text{ yr}^{-1}$.

Again, for the radioactive disintegration process say,



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

$$0.00012 = \frac{2.303}{11540} \log \frac{a}{(a-x)}$$

$$\log \frac{a}{(a-x)} = \frac{0.00012 \times 11540}{2.303} = 0.6013$$

Taking antilog, $\frac{a}{(a-x)} = 3.993$

$$\therefore \text{Fraction of A remained} = \frac{(a-x)}{a} = \frac{1}{3.993} \approx \frac{1}{4}$$

S52. $T_1 = 293 \text{ K}; T_2 = 313 \text{ K}$

According to Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$E_a = 2.303 R \times \left(\frac{T_1 T_2}{T_2 - T_1} \right) \log \frac{k_2}{k_1}$$

Now, $\frac{T_1 T_2}{T_2 - T_1} = \frac{293 \times 313}{313 - 293} = 4585.45 \text{ k}$

and $\log \frac{k_2}{k_1} = \log \frac{4}{1} = \log 4 = 0.6021$

$$\therefore E_a = 2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 4585.45 \text{ k} \times 0.6021$$

$$= 52863.33 \text{ J mol}^{-1} = 52.86 \text{ kJ mol}^{-1}$$

S53. According to Arrhenius equation, $k = A \cdot e^{-E_a/RT}$

Comparing the given value of $k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K}/T}$, we get

$$-\frac{E_a}{RT} = -\frac{28000 \text{ K}}{T}$$

Hence, $E_a = 28000 \text{ K} \times R = 28000 \text{ K} \times 8.3145 \text{ K}^{-1} \text{ mol}^{-1}$

$$= 232792 \text{ J mol}^{-1} = 232.79 \text{ kJ mol}^{-1}$$

S54. For a first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3} = 0.231 \text{ h}^{-1}$$

Say initial conc. of sucrose = 1.0 mol

Conc. after 8 h = (1.0 - x)

Hence, $\frac{kt}{2.303} = \log \frac{1}{1-x}$

or
$$\log \frac{1}{1-x} = \frac{0.231 \times 8}{2.303} = 0.802$$

Hence,
$$\frac{1}{1-x} = \text{antilog } 0.802 = 6.345$$

or
$$1 = 6.346 (1-x), x = \frac{5.345}{6.345} = 0.842$$

\therefore Conc. after 8 hours = $1.0 - 0.842 = 0.158 \text{ M}$

S55.
$$\log A = \log k + \frac{E_a}{2.303 RT}$$

$$= \log 2.418 \times 10^{-5} \text{ s}^{-1} + \frac{179900 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 546 \text{ K}}$$

$$= -4.6184 + 17.21$$

$$\log A = -4.6184 + 17.21 = 12.5916$$

Taking antilog of both sides

$$A = \text{Antilog } 12.5916 = 3.9 \times 10^{12} \text{ s}^{-1}.$$

S56.
$$t_{0.3} = \frac{2.303}{k} \log \frac{[A]_0}{0.7[A]_0} = \frac{2.303}{k} \log \frac{10}{7} = \frac{2.303}{k} \times 0.155$$

or
$$k = \frac{2.303}{40} \times 0.155 = 8.92 \times 10^{-3} \text{ min}^{-1}.$$

Now,
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.92 \times 10^{-3}} = 77.69 \text{ min}.$$

S57. For any first order reaction the time required for completion of a particular fraction is given as

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

(All terms in expression have usual meaning)

Accordingly,

$$t_{0.99} = \frac{2.303}{k} \log \frac{[A]_0}{0.01[A]_0} = \frac{2.303}{k} \log 10^2$$

Similarly,
$$t_{0.90} = \frac{2.303}{k} \log \frac{[A]_0}{0.1[A]_0} = \frac{2.303}{k} \log 10$$

or
$$\frac{t_{0.99}}{t_{0.90}} = \frac{2.303}{k} \log 10^2 \times \frac{k}{2.303} \times \frac{1}{\log 10} = \frac{2}{1}$$

or
$$t_{0.99} = 2 t_{0.90}$$

S58. Since the specific reaction rate k is the rate when the reactant concentration is unity, we see from data (a)

$$k = 1 \text{ as}$$

$$d[A]/dt = 1 \text{ at } [A] = 1$$

From data (b) or (c), we thus have,

$$\frac{d[A]}{dt} = k[A]^m; \text{ (} m \text{ is the order)}$$

$$8 = 1 \cdot (2)^m$$

or $2^3 = 2^m$ or $m = 3$

Again, $27 = 1 \times (3)^m$

$$3^3 = 3^m$$

or $m = 3$

Hence the order is three.

S59. From the data (a) and (b), we see that when the concentration of H_2 is halved, the rate is also halved, the rate is also halved at constant concentration of NO.

Hence the reaction is of first order with respect to H_2 . Let us now consider the data (b) and (c) to determine the order with respect to NO as $[H_2]$ is constant.

The rate law of the above reaction is

$$\text{rate} = -\frac{1}{2} \times \frac{d[NO]}{dt} = k[NO]^m [H_2]^1$$

where m is the order with respect to NO

or $-\frac{d[NO]}{dt} = 2k[NO]^m [H_2]$

Substituting data (b) and (c), we get

$$2.2 \times 10^{-4} = 2k(1.5 \times 10^{-4})^m \cdot (2 \times 10^{-3}) \quad \dots \text{ (i)}$$

$$0.24 \times 10^{-4} = 2k(0.5 \times 10^{-4})^m \cdot (2 \times 10^{-3}) \quad \dots \text{ (ii)}$$

Dividing (i) by (ii),

$$\frac{2.2}{0.24} = \frac{(1.5 \times 10^{-4})^m}{(0.5 \times 10^{-4})^m} = 3^m$$

or $\frac{220}{24} = 3^m$

Taking log, $\log 220 - \log 24 = m \log 3$

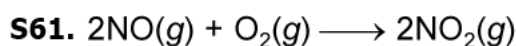
$$2.3424 - 1.3802 = m \times 0.4771$$

or $0.9622 = 0.4771 m$

or
$$m = \frac{0.9622}{0.4771} \approx 2$$

Hence, the reaction is of second and first order with respect to NO and H₂ respectively.

S60.	Molecularity	Order of a reaction
	1. It is the number of reacting species undergoing simultaneous collision in an elementary or simple reaction.	1. It is the sum of powers of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentration in the rate law equation.
	2. It is a theoretical concept and can be calculated by simply adding the molecules of the slowest step.	2. It is determined experimentally only and cannot be calculated.
	3. It is always a whole number value only, <i>i.e.</i> , 1, 2, 3, etc.	3. It need not to be a whole number, <i>i.e.</i> , it can be fractional, zero or integer.
	4. It is applicable for elementary reactions and has no meaning for complex reactions, <i>i.e.</i> , it is only the slowest step whose molecularity has significance for the over all reactions	4. It is applicable for both elementary as well as complex reaction, <i>i.e.</i> , it is for overall reactions and no separate steps are written to obtain it.
	5. It is independent on pressure and temperature.	5. It depends upon pressure and temperature.



Using rate law, as given theoretically *i.e.*,

$$r_1 = k[\text{NO}]^2[\text{O}_2]$$

When the volume is reduced to one-third of initial value, the concentration becomes three times.

$$\therefore r_2 = k[3\text{NO}]^2[3\text{O}_2]$$

$$\therefore \frac{r_2}{r_1} = 27$$

$$r_2 = 27r_1$$

S62. Rate of reaction = $\frac{-d[\text{CO}_2]}{dt} = \frac{-d[\text{OH}^-]}{dt} = \frac{d[\text{HCO}_3^-]}{dt}$

Also the unit of *k* suggests it to be II order. Thus, rate of reaction

$$= k[\text{CO}_2][\text{OH}^-] = 4 \times 10^{-3} \times 10^{-6} \times 10^{-1}$$

$$= 4 \times 10^{-10} \text{ mol L}^{-1} \text{ s}^{-1}$$

S63. Rate = $k[\text{N}_2\text{O}_5]$

$$2.4 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1} = (3.0 \times 10^{-5} \text{ s}^{-1})[\text{N}_2\text{O}_5]$$

$$[\text{N}_2\text{O}_5] = \frac{2.4 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}}{3.0 \times 10^{-5} \text{ s}^{-1}} = 0.8 \text{ mol L}^{-1}$$

Since the unit of k is s^{-1} , hence the decomposition of N_2O_5 is first order reaction.

S64. (a)
$$\text{Rate} = \frac{k[\text{OCI}^\ominus][\text{I}^\ominus]}{[\text{OH}^\ominus]}$$

Order of reaction = $1 + 1 - 1 = 1$

Molecularity of reaction = $1 + 1 = 2$

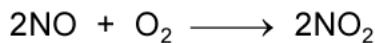
(b) Molecularity w.r.t. $[\text{OH}^\ominus] = 0$

Order w.r.t. $[\text{OH}^\ominus] = -1$

S65. The rate law indicate that order of reaction is 2 w.r.t. NO and 1 w.r.t. O_2 . The possible mechanism for given reaction may be.



Overall reaction, (by addition of two steps)



As slowest step of mechanism of reaction determine th rate of reaction,

\therefore
$$\text{rate} = k_2 [\text{NO}_3] [\text{NO}]$$

But
$$[\text{NO}_3] = k_1 [\text{NO}] [\text{O}_2] \quad (\because \text{NO}_3 \text{ is an intermediate species, and its formation is in equilibrium state})$$

\therefore
$$\begin{aligned} \text{rate} &= k_1 k_2 [\text{NO}] [\text{O}_2] [\text{NO}] \\ &= k [\text{NO}]^2 [\text{O}_2] \quad \dots \text{ (where } k \text{ is rate constant and } k = k_1 k_2) \end{aligned}$$

The above expression of rate law derived from proposed mechanism is same as in given data.

S66.
$$-\frac{d[A]}{dt} = k[A]$$

$$-\frac{d[A]}{dt} = 1.85 \times 10^4 \times [A] \quad \dots \text{ (i)}$$

Assuming the reaction to be of second order,

$$-\frac{d[A]}{dt} = k'[A] [B]$$

$$-\frac{d[A]}{dt} = k'[A] [0.1] \quad \dots \text{ (ii)}$$

Dividing Eq. (i) by (ii), we get

$$1 = \frac{1.85 \times 10^4}{k'[0.1]}$$

$$k' = 1.85 \times 10^5 \text{ L mol}^{-1}\text{s}^{-1}.$$

S67. The rate constant k for first order reaction is expressed by relation,

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

or

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

Substitute,

$$t = t_{2/3}, \quad k = 5.4 \times 10^{-14} \text{ s}^{-1}, \quad x = \frac{2a}{3}$$

$$t_{2/3} = \frac{2.303}{5.4 \times 10^{-14} \text{ s}} \log \frac{a}{a - \frac{2}{3}a}$$

$$= \frac{2.303}{5.4} \times 10^{14} (\log 3) \text{ s}$$

$$= 0.4265 \times 0.4771 \times 10^{14} \text{ s} = 2.035 \times 10^{13} \text{ s}$$

Two-third life of given first order reaction is $2.035 \times 10^{13} \text{ s}$.

S68. For a first order reaction, we know that

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

\therefore

$$\begin{aligned} t_{99.9\%} &= \frac{2.303}{k} \log \frac{a}{a - .999a} \\ &= \frac{2.303}{k} \log 10^3 = \frac{3 \times 2.303}{k} \end{aligned} \quad \dots \text{(i)}$$

and

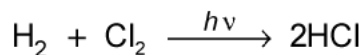
$$\begin{aligned} t_{90\%} &= \frac{3 \times 2.303}{k} \log \frac{a}{a - 0.90a} \\ &= \frac{2.303}{k} \log 10 = \frac{2.303}{k} \end{aligned} \quad \dots \text{(ii)}$$

Now, divided Eq. (i) by Eq. (ii), we get

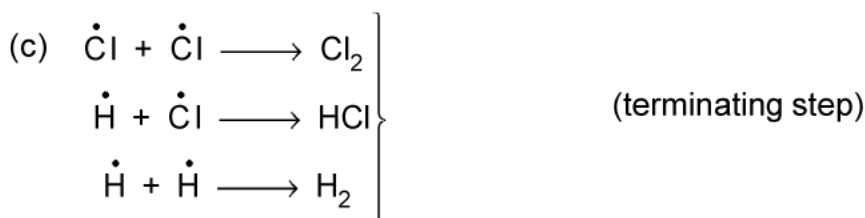
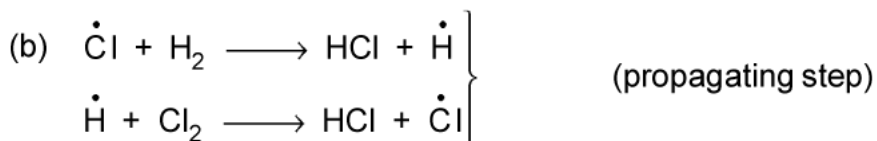
$$\frac{t_{99.9\%}}{t_{90\%}} = \frac{3 \times 2.303}{k} \times \frac{k}{2.303} = \frac{3}{1}$$

$$t_{99.9\%} = 3t_{90\%}.$$

S69. Photochemical reactions are those reactions which take place only when take place only when these are exposed to radiation (or light). These reactions are initiated when one of the reactant molecules absorbs the photon and produces the reactive species. Such reactions follows the course of free radical mechanism.



The above photo chemical reaction follows the course involving 3 steps



S70. Let k_1 and k_2 be the rate constant at 300K and 310K respectively. Then, $k_1 = 6.0 \times 10^{-4} \text{ s}^{-1}$, $k_2 = ?$

Use the relation between energy of activation E_a and two values of rate constants k_1 , k_2 at two different temperatures T_1 and T_2 .

$$\begin{aligned} \log \frac{k_2}{k_1} &= \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \\ &= \frac{305000 \text{ J}}{2.303 \times 8.314} \left(\frac{310 - 300}{300 \times 310} \right) \\ &= \frac{3050}{19.147 \times 93} = 1.7128 \end{aligned}$$

Take antilog of both sides, $\frac{k_2}{k_1} = \text{antilog } 1.7128 = 51.60$

or $k_2 = k_1 \times 51.60 = 6.0 \times 10^{-4} \times 51.60$
 $= 3.096 \times 10^{-2} \text{ s}^{-1}$.

S71. Here, $k = 2.2 \times 10^{-5} \text{ sec}^{-1}$; $t = 90 \text{ minutes} = 90 \times 60 = 5,400 \text{ sec}$;

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{5,400} \log \frac{a}{(a-x)}$$

or $\log \frac{a}{(a-x)} = \frac{2.2 \times 10^{-5} \times 5,400}{2.303} = 0.05148$.

On taking antilogarithm, we get:

$$\frac{a}{(a-x)} = 1.126 \quad \text{or} \quad a = 1.126a - 1.126x$$

or $0.126a = 1.126x \quad \text{or} \quad x = \frac{0.126}{1.126} a = 0.1119a$

If $a = 100$, then $x = 0.1119 \times 100 = 11.19$.

Hence, percentage decomposition of $\text{SO}_2\text{Cl}_2 = 11.19$.

S72. (a) 2nd order in NO and 1st order in Cl_2 ;

(b) Rate = $K[\text{NO}]^2[\text{Cl}_2]$

$$0.18 = K[0.10]^2 \times 0.10$$

$$K = 180 \text{ mol}^{-2} \text{ L}^2 \text{ S}^{-1}.$$

S73. (a) Overall reaction is $\frac{1}{2} \text{A}_2 + \text{C} \longrightarrow \text{AC}$

$$K_{eq} \text{ for } 1^{\text{st}} \text{ step} = \frac{k_f}{k_b} = \frac{10^{10}}{10^{10}} = 1$$

(b) Rate law will be

$$\text{Rate} = (K_{eq})^{1/2} k_2 [\text{A}_2]^{1/2} [\text{C}]$$

or $\text{Rate} = k [\text{A}_2]^{1/2} [\text{C}]$

[$\because K_{eq} = 1$]

S74. Initial concentration of Y = 10.0 M. Throughout the reaction its concentration cannot fall below 9.9 M even for complete disappearance of X (0.1 M). Thus, conc. of Y may be assumed constant and the rate expression would be

$$\text{Rate} = 10.0 \times k[\text{A}]$$

Taking $0.6k$ as another constant k , the formula can be applied for 1st order

$$k = \frac{2.303}{t} \log \frac{[\text{A}]_0}{[\text{A}]}$$

$$10.0 \times k = \frac{2.303}{t} \log \frac{[\text{A}]_0}{[\text{A}]}$$

Substitute k , and $[\text{A}]_0$ and calculate $[\text{A}]$.

$$[\text{A}] = 6.7 \times 10^{-4} \text{ mol L}^{-1}.$$

S75. For first order reaction, rate constant (k) is given by:

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

From given data, $a = 0.5 \text{ mol L}^{-1}$, $(a-x) = 0.25 \text{ mol L}^{-1}$ after $t = 5$ minutes.

$$\therefore k = \frac{2.303}{5 \text{ min}} \log \frac{0.5}{0.25}$$

$$= \frac{2.303}{5 \text{ min}} \log 2 = \frac{2.303 \times 0.3010}{5 \text{ min}} = 0.1988 \text{ min}^{-1} \quad \dots (i)$$

During next 5 minutes, total time = 10 min; $a = 0.5 \text{ mol L}^{-1}$ ($a-x$) = 0.125 mol L^{-1} .

$$\begin{aligned} \therefore k &= \frac{2.303}{10 \text{ min}} \log \frac{0.5}{0.125} \\ &= \frac{2.303}{10 \text{ min}} \log 4 = \frac{2.303 \times 0.6020}{10 \text{ min}} = 0.1386 \text{ min}^{-1} \quad \dots \text{(ii)} \end{aligned}$$

S76. The given equation for the variation of rate constant k with temperature is an equation of straight line in the intercept form, i.e., $y = mx + c$ where, slope

$$m = \frac{E_a}{2.303 R}$$

But slope is given to be -6670 K .

\therefore Energy of activation

$$\begin{aligned} E_a &= \frac{2.303 R \times 6670}{1} = \frac{2.303 \times 8.314 \times 6670}{1} \\ &= 127711.44 \text{ J mol}^{-1} = \mathbf{1.28 \times 10^5 \text{ J mol}^{-1}}. \end{aligned}$$

S77. (a) Average rate of reaction between interval of time 30 to 60 second is given by,

$$\begin{aligned} \text{Average rate} &= \frac{\Delta x}{\Delta t} = \frac{C_2 - C_1}{\Delta t} = \frac{0.17 - 0.31}{60 - 30} \\ &= \frac{-0.14}{30} = -0.00467 = -4.67 \times 10^{-3} \text{ Ms}^{-1}. \end{aligned}$$

Minus sign shows that the rate of reaction is decreasing with time as conc. of ester is decreasing with time.

(b) Pseudo first order rate constant k is given as,

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

where a is initial conc. and $a-x$ conc. after time t .

Here, $a = 0.55 \text{ M}$. Let us calculate the rate constant k at three different instant of time, 30, 60 and 90 seconds as show below :

time, t (in second)	conc. of ester/M ($a-x$)	$k = \frac{2.303}{t} \log \frac{a}{a-x}$
30	0.31	$k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.91 \times 10^{-2} \text{ s}^{-1}$
60	0.17	$k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.95 \times 10^{-2} \text{ s}^{-1}$
90	0.085	$k_3 = \frac{2.303}{90} \log \frac{0.55}{0.085} = 2.06 \times 10^{-2} \text{ s}^{-1}$

The nearly equal values of k confirms that reactions is of first order.

The actual value of rate constant is the average of three values of k .

∴ rate constant of reaction,

$$k = \frac{k_1 + k_2 + k_3}{3} = \frac{(1.91 + 1.95 + 2.06) \times 10^{-2}}{3} = 1.97 \times 10^{-2} \text{ s}^{-1}.$$

S78. All radioactive decay are first order processes,

∴ decay constant, $\lambda = \frac{2.303}{k} \log 10^2 \times \frac{k}{2.303} \times \frac{1}{\log 10} = \frac{2}{1} = 0.0247 \text{ year}^{-1}$

(a) when $t = 10$ years, $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}$

given, $N_0 = 1$ microgram = 1×10^{-6} g; $N = ?$

After 10 years, the amount of Sr left is given as

$$10 = \frac{2.303}{0.0247} \log \frac{1 \times 10^{-6}}{N}$$

$$\log \frac{1 \times 10^{-6}}{N} = \frac{10 \times 0.0247}{2.303} = 0.172$$

or $\frac{1 \times 10^{-6}}{N} = \text{Antilog } 0.172 = 1.1280$

or $N = \frac{1 \times 10^{-6}}{1.1280} = 0.7842 \mu\text{g}$

(b) At $t = 60$ years, the amount left will be,

$$60 = \frac{2.303}{0.0247} \log \frac{1 \times 10^{-6}}{N}$$

$$\log \frac{1 \times 10^{-6}}{N} = \frac{60 \times 0.0247}{2.303} = 0.6435$$

$$\frac{1 \times 10^{-6}}{N} = \text{Antilog } 0.6453 = 4.400$$

$$N = \frac{1 \times 10^{-6}}{4.400} = 0.227 \mu\text{g}$$

Thus after 10 years and 60 years, 0.7842 mg and 0.227 mg of ^{90}Sr will be left as undecayed.

S79. Rate law for the reaction is given as,

$$\text{Rate} = k[A]^1 [B]^0 = k[A]$$

From experiment 1, we get:

$$2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = k[0.1 \text{ mol L}^{-1}]$$

$$\text{Rate constant, } k = \frac{2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{0.1 \text{ mol L}^{-1}}$$

$$\text{or Rate constant, } k = 0.2 \text{ min}^{-1}$$

(a) In experiment II :

$$\text{rate} = k[A]$$

$$\begin{aligned} \text{or } [A] &= \frac{\text{rate}}{k} \\ &= \frac{4.0 \times 10^{-2} \text{ M min}^{-1}}{0.2 \text{ min}^{-1}} = 0.20 \text{ M} \end{aligned}$$

(b) In experiment III :

$$\begin{aligned} \text{rate} &= k[A] \\ &= 0.2 \text{ min}^{-1} \times 0.4 \text{ M} = 0.08 \text{ M min}^{-1} = 8.0 \times 10^{-2} \text{ M min}^{-1} \end{aligned}$$

(c) In experiment IV :

$$\text{Rate} = k[A]$$

$$[A] = \frac{\text{rate}}{k} = \frac{2.0 \times 10^{-2} \text{ M min}^{-1}}{0.2 \text{ min}^{-1}} = 0.1 \text{ M}$$

Thus the completed table is :

Experiment	[A] mol L ⁻¹	[B] mol L ⁻¹	Initial rate/M min ⁻¹
I	0.1	0.1	2.0×10^{-2}
II	<u>0.2</u>	0.2	4.0×10^{-2}
III	0.4	0.4	<u>8.0×10^{-2}</u>
IV	<u>0.1</u>	0.2	2.0×10^{-2}

S80. Let rate law of reaction be,

$$\text{rate} = k[A]^x [B]^y$$

where x and y order of reaction w.r.t. A and B respectively

From experiments I and IV, we can write,

$$6.0 \times 10^{-3} = k[0.1]^x [0.1]^y \quad \dots \text{ (i)}$$

$$2.4 \times 10^{-2} = k[0.4]^x [0.1]^y \quad \dots \text{ (ii)}$$

Dividing (ii) by (i), we can write,

$$\frac{2.4 \times 10^{-2}}{6.0 \times 10^{-3}} = \left(\frac{0.4}{0.1} \right)^x = 4^x$$

or $4 = 4^x$ or $x = 1$

From experiments (II) and (III), we can write,

$$7.2 \times 10^{-2} = k(0.3)^x (0.2)^y \quad \dots \text{(iii)}$$

$$2.88 \times 10^{-1} = k(0.3)^x (0.4)^y \quad \dots \text{(iv)}$$

Dividing (iv) by (iii), we get

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \left(\frac{0.4}{0.2}\right)^y \quad \text{or} \quad 4 = 2^y \quad \text{or} \quad 2^2 = 2^y$$

$$\therefore y = 2$$

Knowing x and y , rate law can be written as:

$$\text{Rate} = k[A][B]^2 \quad \dots \text{(v)}$$

Order of reaction w.r.t. $A = 1$

Order of reaction w.r.t. $B = 2$

Overall order of reaction = $1 + 2 = 3$

Substituting the values of initial rate of formation of experiment (I) in (equation v) we can write,

$$6.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} = k[0.1 \text{ mol L}^{-1}][0.1 \text{ mol L}^{-1}]^2 \quad (\because 1\text{M} = 1 \text{ mol/l})$$

$$\therefore k = \frac{6.0 \times 10^{-3} \text{ M min}^{-1}}{1 \times 10^{-3} \text{ M}^3} = 6 \text{ M}^{-2} \text{ min}^{-1}$$

S81. Suppose initial pressure of SO_2Cl_2 is p_i and its pressure decrease by x atm after time t

then,



Initial pressure (at $t = 0$) 0.5 atm 0 0

Pressure (at time = t) 0.5 - x x x

$$P_{\text{Total}} \text{ at time } t = 0.5 - x + x + x = 0.5 + x \text{ atm}$$

i.e., $0.6 = 0.5 + x$ or $x = 0.6 - 0.5 = 0.1 \text{ atm}$

Now, $p_i = 0.5 \text{ atm}$ and p (at time 100 sec)

$$= 0.5 - x = 0.5 - 0.1 = 0.4 \text{ atm}$$

(a) Evaluation of k

$$\begin{aligned} k_{100} &= \frac{2.303}{t} \log \frac{\text{Initial Pressure}}{\text{Pressure at time } t} \\ &= \frac{2.303}{100} \log \frac{0.5}{0.4} = \frac{2.303}{100} \log 1.25 \\ &= \frac{2.303}{100} \times 0.0969 = 2.23 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

(b) Rate at $P_T = 0.65$ atm

$p_{\text{SO}_2\text{Cl}_2}$ at total pressure of 0.65 atm

$$= 0.5 - 0.15$$

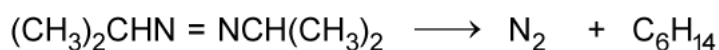
$$= 0.35 \text{ atm}$$

$$\text{Rate} = k (p_{\text{SO}_2\text{Cl}_2})$$

$$= 2.23 \times 10^{-3} \times 0.35$$

$$= 7.8 \times 10^{-4} \text{ atm s}^{-1}$$

S82. Suppose p_i is the initial pressure at $t = 0$. After time t say x moles of zoisopropane decompose and the pressure is p .



Initial pressure (at $t = 0$) p_i 0 0

Pressure at time = t $pi - x$ x x

The rate constant at 360 sec,

$$k_{360} = \frac{2.303}{t} \log \frac{[p_i]}{[p]}$$

$$p_i = 35.0 \text{ mm};$$

At time t , $p = p_i - x + x + x = p_i + x$

or $x = p - p_i = 54 - 35 = 19.0 \text{ mm}$

Now p at time 360 sec = $35 - 19.0 = 16 \text{ mm}$

Hence,

$$k_{360} = \frac{2.303}{360} \log \frac{35}{16} = \frac{2.303}{360} \times 0.3399$$
$$= 2.17 \times 10^{-3} \text{ s}^{-1}$$

Similarly,

$$k_{720} = \frac{2.303}{720} \log \frac{35}{7} = \frac{2.303}{720} \times 0.699$$
$$= 2.235 \times 10^{-3} \times \text{s}^{-1}$$
$$k = \frac{K_{360} + K_{720}}{2} = \frac{(2.17 + 2.235) \times 10^{-3}}{2}$$
$$= 2.2025 \times 10^{-3} \text{ s}^{-1}$$

S83. (a) On comparing Arrhenius equation, $k = A \cdot e^{-E_a/RT}$ with the given value of k .

$$\frac{E_a}{2.303 R} = 1.25 \times 10^4$$

or

$$E_a = 1.25 \times 10^4 \times 2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$= 239,339 \text{ J mol}^{-1} = 239.34 \text{ kJ mol}^{-1}.$$

(b) For a first order reaction, $k = \frac{0.693}{t_{1/2}}$

or $k = -\frac{0.693}{256 \times 60} = 4.51 \times 10^{-5} \text{ s}^{-1}$

Given, $\log k = 14.34 - 1.25 \times 10^4 \text{ K/T}$

or $\log (4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$

$$-4.35 = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

or $14.34 + 4.35 = \frac{1.25 \times 10^4 \text{ K}}{T}$

or $T = \frac{1.25 \times 10^4 \text{ K}}{18.69} = 668.8 \text{ K}$

S84. Given, $k = 2.0 \times 10^{-2} \text{ s}^{-1}$

At $t_1 = 0$ $[A]_1 = 1.0 \text{ M}$

At $t_1 = 100 \text{ s}$ $[A]_2 = ?$

For a first order reaction

$$k = \frac{1}{t_1 - t_2} \ln \frac{[A]_1}{[A]_2}$$

$$2.0 \times 10^{-2} = \frac{1}{(100 - 0)} \ln \frac{1.0}{[A]_2}$$

$$(2.0 \times 10^{-2}) \times 100 = \ln \frac{1.0}{[A]_2}$$

or $2.0 = \ln \frac{1}{[A]_2}$ or $\frac{1}{[A]_2} = e^2$

or $7.389 = \frac{1}{[A]_2}$

$$[A]_2 = \frac{1}{7.389} = 0.135 \text{ M.}$$

S85. Let the order of reaction w.r.t. A is x and w.r.t. B is y . Then rate of reaction can be written as

$$\text{rate} = k[A]^x [B]^y$$

From run 1 and 2, we can write

$$5.07 \times 10^{-5} = k[0.20]^x [0.30]^y \quad \dots (i)$$

$$5.07 \times 10^{-5} = k[0.20]^x [0.10]^y \quad \dots (ii)$$

Dividing (ii) by (i), we get

$$\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k[0.20]^x [0.10]^y}{k[0.20]^x [0.30]^y}$$

or $1 = \left(\frac{0.10}{0.30}\right)^y$ or $y = 0$

From run 2 and 3 we can write

$$5.07 \times 10^{-5} = k[0.20]^x [0.10]^y$$
$$= k[0.20]^x \times 1 \quad [\because y = 0] \quad \dots (iii)$$

$$7.06 \times 10^{-5} = k[0.40]^x [0.05]^y = k[0.40]^x \times 1 \quad \dots (iv)$$

Divide (iv) by (iii) we get,

$$\frac{7.60 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k[0.40]^x}{k[0.20]^x} = \left[\frac{0.4}{0.2}\right]^x = (2)^x$$

$$(2)^x = \frac{3}{2} = 1.5 \text{ on solving } x = 0.5$$

Thus the order of reaction w.r.t. A is $\frac{1}{2}$ and w.r.t. B is zero.

S86. Let the reaction, $A \longrightarrow B$ be a 2nd order reaction w.r.t. A and conc. of A is a mol L^{-1} then rate of reaction can be written as

$$\frac{dx}{dt} = k[A]^2 = ka^2 \quad \dots (i)$$

(a) When conc. of $[A]$ is doubled i.e., $[A] = 2a$ and mol L^{-1} then new rate of reaction,

$$\frac{d'(x)}{dt} = k[2a]^2 = 4ka^2 = 4 \frac{dx}{dt}$$

Thus, rate of reaction will become four times when conc. is doubled.

(b) Similarly, when conc. of A is reduced to $\frac{1}{2}$ i.e., $[A]$ is $\frac{a}{2}$ then new rate of reaction,

$$\frac{d'(x)}{dt} = \left[\frac{a}{2}\right]^2 = \frac{1}{4}ka^2 = \frac{1}{4} \frac{dx}{dt}$$

The rate of reaction will become one-fourth of the initial rate of reaction.

$$\mathbf{S87.} \quad k_{298} = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{100}{90} \quad \dots (i)$$

$$\text{Similarly,} \quad k_{308} = \frac{2.303}{t} \log \frac{100}{75} \quad \dots (ii)$$

Dividing eq. (ii) by Eq. (i), we get

$$\frac{k_{308}}{k_{298}} = \frac{\frac{2.303}{t} \log \frac{100}{75}}{\frac{2.303}{t} \log \frac{100}{90}}$$

As time required for 10% completion = time required for 25% completion

$$\therefore \frac{k_{308}}{k_{298}} = \frac{\log 100/75}{\log 100/90} = \frac{0.1249}{0.0457} = 2.733$$

According to Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\therefore \log 2.733 = \frac{Ea}{2.303 \times 8.314} \left[\frac{308 - 298}{308 \times 298} \right]$$

$$\text{or} \quad Ea = \frac{0.436 \times 2.303 \times 8.314}{1.089 \times 10^{-4}} = \frac{8.36}{1.089 \times 10^{-4}}$$

$$= 76658 \text{ J mol}^{-1}$$

$$\text{Now,} \quad k_{308} = A \cdot e^{-Ea/RT}$$

$$\text{or} \quad \log k_{308} = \log 4 \times 10^{10} - \frac{Ea}{2.303R} \times \frac{1}{308}$$

$$= 10.602 - \frac{76658}{2.303 \times 8.314 \times 308}$$

$$= 10.602 - 12.998 = -2.396$$

$$\text{or} \quad k_{308} = \text{antilog } -2.396 = 4.02 \times 10^{-3} \text{ s}^{-1}$$

$$\mathbf{S88.} \quad \text{We know that,} \quad \log \frac{k_2}{k_1} = \frac{Ea}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60,000}{2.303 \times 8.314} \left[\frac{T_2 - 283}{283 T_2} \right]$$

$$0.5228 = 3133.62 \left[\frac{T_2 - 283}{283 T_2} \right]$$

or
$$\frac{0.5228}{3133.62} = \frac{T_2 - 283}{283T_2}$$

$$1.67 \times 10^{-4} \times 283 = \frac{T_2 - 283}{T_2}$$

$$0.0472 T_2 = T_2 - 283$$

$$T_2 - 0.0472 T_2 = T_2 - 283$$

$$0.9528 T_2 = 283$$

Hence,
$$T_2 = \frac{283}{0.9528} = 297 \text{ K}$$

S89. (a) When $\frac{dx}{dt} = k[A]$, order w.r.t. $A = 1$ and order w.r.t. $B = 0$

(b) When $\left(\frac{dx}{dt}\right) = k[B]^2$

Order w.r.t. $A = 0$, w.r.t. $B = 2$

(c) Rate $(r_1) = k[A]^\alpha [B]^\beta$

Case (a) $2r_1 = k[2A]^\alpha [B]^\beta \dots$ (i)

Case (b) $8r_1 = k[2A]^\alpha [2B]^\beta \dots$ (ii)

From Eqn (i) and (ii) we get

$$\alpha = 1, \beta = 2$$

\therefore Order w.r.t. $A = 1$

Order w.r.t. $B = 2$

S90. (a) Rate = $k[A]^2 [B]^1 [C]^0$ (Since C is in excess)

(b) Unit of rate = $\text{mol L}^{-1} \text{time}^{-1}$

Unit of rate constant for third order = $\text{L}^2 \text{mol}^{-2} \text{time}^{-1}$

(c) Let initial concentration of A, B, and C be a, b, and c, respectively.

$$\therefore r_1 = k(a)^2 (b)^1 (c)^0 \dots$$
 (i)

Now, $[A] = 2a; [B] = 3b$

$$\therefore r_2 = K(2a)^2 (3b)^1 (c)^0 \dots$$
 (ii)

By Eqs. (i) and (ii), we get

$$\frac{r_1}{r_2} = \frac{1}{12}$$

$$\therefore r_2 = 12r_1$$

S91. The rate of the reaction is expressed as

$$\text{rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = +\frac{1}{4} \frac{d[\text{NO}_2]}{dt} = +\frac{d[\text{O}_2]}{dt}$$

And given that $+\frac{d[\text{NO}_2]}{dt} = 0.0072 \text{ mole/L/s}$.

(a) Rate of appearance of $\text{O}_2 = \frac{1}{4} \times$ rate of appearance of NO_2

$$\begin{aligned} \frac{d[\text{O}_2]}{dt} &= \frac{1}{4} \times \frac{d[\text{NO}_2]}{dt} \\ &= \frac{1}{4} \times 0.0072 = 0.0018 \text{ mole/L/s.} \end{aligned}$$

(b) Rate of disappearance of $\text{N}_2\text{O}_5 = \frac{1}{2} \times$ rate of appearance of NO_2

$$\begin{aligned} -\frac{d[\text{N}_2\text{O}_5]}{dt} &= \frac{1}{2} \times \frac{d[\text{NO}_2]}{dt} \\ \frac{d[\text{N}_2\text{O}_5]}{dt} &= -\frac{1}{2} \times 0.0072 = -0.0036 \text{ mole/L/s.} \end{aligned}$$

(c) Rate of reaction = $\frac{1}{4} \times \frac{d[\text{NO}_2]}{dt}$
 $= \frac{1}{4} \times 0.0072 = 0.0018 \text{ mole/L/s.}$

S92. (a) Specific rate constant, k for first order reaction is given by,

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{a}{a-x} \\ &= \frac{2.303}{15} \log \frac{100}{100-20} = \frac{2.303}{15} \times 0.0969 \text{ min}^{-1} \\ &= 0.0148 \text{ min}^{-1} = 1.48 \times 10^{-2} \text{ min}^{-1} \end{aligned}$$

(b) When 10% of original reactant remains unreacted, 90% of reaction is complete. We are required to calculate $t_{90\%}$ of reaction.

$$\begin{aligned} t_{90\%} &= \frac{2.303}{k} \log \frac{100}{100-90} = \frac{2.303}{0.0148} \times \log 10 \\ &= 155.6 \text{ minutes.} \end{aligned}$$

(c) After first 15 minutes, 80% of reactant is left unreacted.

$$\begin{aligned}\therefore a &= 80 \quad a - x = 80 - 20\% \text{ of } 80 \\ &= 80 - \frac{20}{100} \times 80 = 80 - 16\end{aligned}$$

Time for next 20% of reactant left to react is given by.

$$\begin{aligned}t &= \frac{2.303}{k} \log \frac{80}{80 - 16} \\ &= \frac{2.303}{0.0148} \times \log \frac{80}{64} = \frac{2.303}{0.0148} \times 0.0969 \\ &= \mathbf{15.07 \text{ minutes.}}\end{aligned}$$

S93. Let initial conc. of reactant be 'a', then conc. after 10 minutes will be, $a - x = a - 20\% \text{ of } a = 80\% \text{ of } a$

$$a - x = \frac{80}{100} \times a = \frac{4a}{5} = 0.8a$$

For the first order reaction, rate constant k can be expressed as,

$$\begin{aligned}k &= \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{10} \log \frac{a}{0.8a} \\ &= \frac{2.303}{10} \log \frac{5}{4} = \frac{2.303}{10} (\log 5 - \log 4)\end{aligned}$$

$$\frac{2.303}{10} (0.6990 - 0.6021) = 0.02232 \text{ min}^{-1}.$$

Knowing the rate constant, k we can find time for 75% completion of reaction again by using the relation.

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

$$a - x = a - 75\% \text{ of } a = \frac{a}{4} \quad \text{and} \quad t = t_{75\%}$$

$$\begin{aligned}t_{75\%} &= \frac{2.303}{0.02232} \times \log \frac{a}{a/4} = \frac{2.303}{0.02232} \times \log 4 \\ &= \frac{2.303}{0.02232} \times \frac{0.6021}{1} = \mathbf{62.125 \text{ min.}}\end{aligned}$$

S94. For first order reaction, rate constant is given by,

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

Here, $a = 22.8$ ml, $(a - x) = 13.8$ and 8.2 ml at $t = 600$ and $1,200$ s respectively.

When $t = 600$ seconds, rate constant k is,

$$\begin{aligned} k &= \frac{2.303}{600 \text{ s}} \log \frac{22.8}{13.8} \\ &= \frac{2.303}{600 \text{ s}} [\log 22.8 - \log 13.8] \\ &= \frac{2.303}{600 \text{ s}} [1.3579 - 1.1399] \\ &= \frac{2.303}{600 \text{ s}} [0.2180] = 8.37 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

When $t = 1,200$ s, rate constant value again can be calculated as:

$$\begin{aligned} k &= \frac{2.303}{1,200 \text{ s}} \log \frac{22.8}{8.2} \\ &= \frac{2.303}{1,200 \text{ s}} [\log 22.8 - \log 8.2] \\ &= \frac{2.303}{1,200 \text{ s}} [1.3579 - 0.9138] \\ &= \frac{2.303}{1,200 \text{ s}} [0.4441] = 8.52 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

The average value of rate constant:

$$\begin{aligned} k &= \frac{1}{2} [8.37 \times 10^{-4} + 8.52 \times 10^{-4}] \text{ s}^{-1} \\ &= 8.445 \times 10^{-4} \text{ s}^{-1} \end{aligned}$$

S95. Given, $T_1 = 295$ K, $T_2 = 305$, $k_2 = 2k_1$

Expression for energy of activation, E_a is given by:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$E_a = \frac{2.303 R \times T_1 T_2}{T_2 - T_1} \log \frac{k_2}{k_1}$$

$$= \frac{2.303 \times 8.314 \times 295 \times 305}{10} \times \log 2$$

$$= \frac{172276.4 \times 0.3010}{1} \text{ J mol}^{-1}$$

$$= 51855.2 \text{ J mol}^{-1} = 51.86 \text{ kJ mol}^{-1}$$

S96. Use the following relation to calculate k , rate constant of first order reaction.

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

Here, $t = 20$ minutes, $a = 100$, $x = 15$ (for completion of 15% of reaction)

$$20 = \frac{2.303}{k} \log \frac{100}{100-15}$$

$$\begin{aligned} \therefore \text{Rate constant, } k &= \frac{2.303}{20} \log \frac{100}{85} \\ &= \frac{2.303}{20} \times \frac{0.0706}{1} \\ &= 0.00813 \text{ min}^{-1}. \end{aligned}$$

Again use the relation for completion of 60% of reaction:

$$t_{60\%} = \frac{2.303}{k} \log \frac{a}{a-x}$$

Now, $a = 100$, $a - x = 100 - 60$

$$= \frac{2.303}{0.00813} \log \frac{100}{100-60}$$

$$= \frac{2.303}{0.00813} \log \frac{100}{40}$$

$$= \frac{2.303}{0.00813} \times \frac{(0.3979)}{1}$$

$$= \mathbf{112.7 \text{ minutes.}}$$

The 60% completion of reaction will take 112.7 minutes.

S97. Let k_1 and k_2 be the rate constants at 300 K and 350 K respectively.

$$t_{1/2} = \frac{0.693}{k}$$

we can write

$$k_1 = \frac{0.693}{20} \text{ min}^{-1} \quad \text{and} \quad k_2 = \frac{0.693}{5} \text{ min}^{-1}$$

E_a is given by,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \left[\frac{0.693}{5} \times \frac{20}{0.693} \right] = \frac{E_a}{2.303 \times 8.314} \left(\frac{350 - 300}{300 \times 350} \right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \frac{50}{300 \times 350}$$

$$E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 300 \times 350}{50}$$

$$= 24210 \text{ J mol}^{-1} = \mathbf{24.21 \text{ kJ mol}^{-1}}$$

S98. (a) From the given data, the rate law comes out to be

$$R = k_1[A]^2[B]$$

\therefore Order w.r.t. A = 2
Order w.r.t. B = 1

(b) Now,

$$k_1 = \frac{\text{Rate}}{[A]^2[B]}$$

$$= \frac{5.0 \times 10^{-4}}{(2.5 \times 10^{-4})^2 (3 \times 10^{-5})}$$

$$= \mathbf{2.67 \times 10^8 \text{ L}^{-2} \text{ mol}^{-2} \text{ s}^{-1}}$$

(c)

$$k_2 = \frac{2.0 \times 10^{-3}}{(2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})}$$

$$= \mathbf{1.07 \times 10^9 \text{ L}^{-2} \text{ mol}^{-2} \text{ s}^{-1}}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times 8.314} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

or $\log \frac{1.07 \times 10^9}{2.69 \times 10^8} = \frac{E_a}{2.303 \times 8.314} \left[\frac{320 - 300}{320 \times 300} \right]$

or $E_a = 5.53 \times 10^4 \text{ J}$

or $E = \mathbf{55.3 \text{ kJ}}$

(d) Calculation of A:

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

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

$$\log A = \log (2.67 \times 10^8) + \frac{5.53 \times 10^4}{2.303 \times 8.314 \times 300}$$

$$= 18.0565$$

or $A = \mathbf{1.145 \times 10^{18}}$

S99. To draw the plot of log K versus 1/T, we can rewrite the given data as follows:

$T(K)$	273	293	313	333	353
$1/T$	0.003663	0.003413	0.003195	0.003003	0.002833
$\log k$	-6.1040	-4.7696	-3.5900	-2.7496	-1.6996

Draw the graph as shown in the given figure. From graph, we find,

$$\text{Slope} = \frac{-2.4}{0.00047} / \frac{-E_a}{2.303 R}$$

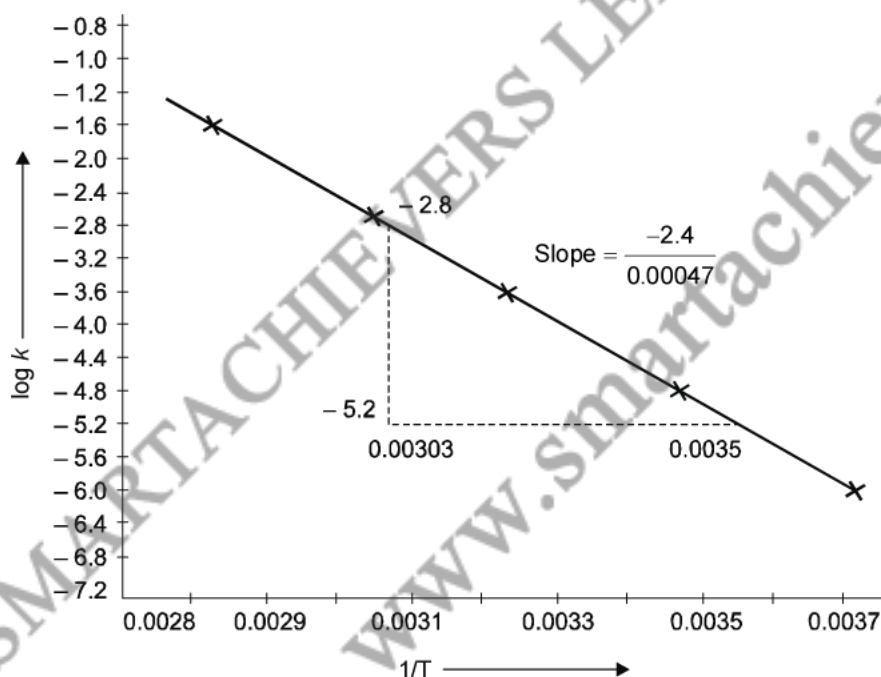
$$\begin{aligned} \therefore \text{Activation energy, } E_a &= \frac{2.4 \times 2.303 \times R}{0.00047} \\ &= \frac{2.4 \times 2.303 \times 8.314 \text{ J mol}^{-1}}{0.00047} \\ &= 17.689 \text{ kJ mol}^{-1} \end{aligned}$$

We know that $\log k = \log A - \frac{E_a}{2.303 RT}$

or $\log A = \left(\frac{E_a}{2.303 RT} \right) \frac{1}{T} + \log k$

(compare it with $y = mx + c$ which is equation of line in intercept form)

$$\begin{aligned} \therefore \log A &= \text{value of intercept on } y\text{-axis } i.e., \text{ on } \log k = \text{ axis} \\ &= (-1 + 7.2) = 6.2 \quad [y_2 - y_1 = -1 - (-7.2)] \end{aligned}$$



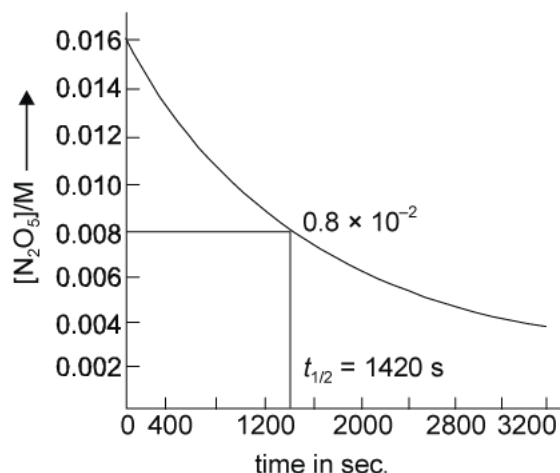
Graph of $\log k$ vs. $1/T$

Frequency factor, $A = \text{antilog } 6.2 = 1585000$
 $= 1.585 \times 10^6 \text{ collisions s}^{-1}$

The values of rate constant k can be found from graph as follows:

T	$1/T$	value of $\log k$ (from graph)	value of k
303	0.003300	- 4.2	$6.31 \times 10^{-5} \text{ s}^{-1}$
323	0.003096	- 2.8	$1.585 \times 10^{-3} \text{ s}^{-1}$

S100(a) Given below figure show the plot of $[\text{N}_2\text{O}_5]$ against time, t in seconds.



Plot of $[\text{N}_2\text{O}_5]$ vs. time

- (b) Half life period, $t_{1/2}$ for the given reaction is the time during which initial conc. of $[\text{N}_2\text{O}_5]$ changes from $1.63 \times 10^{-2} \text{ M}$ to half this value i.e., to $0.815 \times 10^{-2} \text{ M}$ and in the graph it has been shown to be 1420 seconds.

(In graph locate the time against the conc. 0.0081)

(c) Half-time, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.850 \times 10^{-4} \text{ s}^{-1}} = 1428 \text{ s}$

(The two values are almost same within limits of possible error)