CHEMICAL KINETICS [JEE ADVANCED PREVIOUS YEAR SOLVED PAPERS]

JEE ADVANCED

Single Correct Answers Type

1. The rate constant of a reaction depends on
- **a.** temperature
- **b.** initial concentration of the reactants
- **c.** time of reaction
- **d.** extent of reaction **(IIT-JEE 1981)**

2. The specific rate constant of a first-order reaction depends on the
- **a.** concentration of the reactant
- **b.** concentration of the product
- **c.** time
- **d.** temperature **(IIT-JEE 1983)**

3. A catalyst is a substance which
- **a.** increases the equilibrium concentration of the product
- **b.** changes the equilibrium constant of the reaction
- **c.** shortens the time to reach equilibrium
- **d.** supplies energy to the reaction **(IIT-JEE 1983)**

4. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3.0×10^{-4} s^{-1}, 104.4 kJ mol^{-1} and 6.0×10^{14} s^{-1} respectively. The value of the rate constant as $T \rightarrow \infty$ is
- **a.** $2.0 \times 10^{18}\ s^{-1}$
- **b.** $6.0 \times 10^{14}\ s^{-1}$
- **c.** infinity
- **d.** $3.6 \times 10^{30}\ s^{-1}$

(IIT-JEE 1996)

5. The rate constant for the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, is $3.0 \times 10^{-5}\ sec^{-1}$. If the rate is 2.40×10^{-5} mol $litre^{-1}\ sec^{-1}$, then the concentration of N_2O_5 (in mol $litre^{-1}$) is
- **a.** 1.4
- **b.** 1.2
- **c.** 0.04
- **d.** 0.8

(IIT-JEE 2000)

6. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process, $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to
- **a.** C
- **b.** I
- **c.** I^2
- **d.** C.I

(IIT-JEE 2001)

7. Consider the chemical reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions.
- **a.** Rate $= -d(N_2)/dt = -1/3\ d[H_2]/dt = 1/2d\ [NH_3]/dt$
- **b.** Rate $= -d(N_2)/dt = -3\ d[H_2]/dt = 2d\ [NH_3]/dt$
- **c.** Rate $= d(N_2)/dt = 1/3\ d[H_2]/dt = 1/2d\ [NH_3]/dt$
- **d.** Rate $= -d(N_2)/dt = -d[H_2]/dt = d\ [NH_3]/dt$

(IIT-JEE 2002)

8. In a first-order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is
- **a.** 2×10^4
- **b.** 3.45×10^{-5}
- **c.** 1.386×10^{-4}
- **d.** 2×10^{-4}

(IIT-JEE 2003)

9. The reaction, A → Product, follows first order kinetics. In 40 minutes the concentration of A changes from 0.1 to 0.025 M. The rate of reaction, when concentration of A is 0.01 M is
- **a.** 1.73×10^{-4} M min^{-1}
- **b.** 3.47×10^{-5} M min^{-1}
- **c.** 3.47×10^{-4} M min^{-1}
- **d.** 1.73×10^{-5} M min^{-1}

(IIT-JEE 2004)

10. Which one of the following statements for order of reaction is not correct?
- **a.** Order can be determined experimentally
- **b.** Order of reaction is equal to sum of the powers of concentration terms in differential rate law.

c. It is not affected with the stoichometric coefficient of the reactants

d. Order cannot be fractional. **(IIT-JEE 2005)**

11. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+; k_1 = 6.8 \times 10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+; k_2 = 1.6 \times 10^{-3}$

then the formation constant of $[Ag(NH_3)_2]^+$ is

a. 6.8×10^{-6} **b.** 1.08×10^{-5}

c. 1.08×10^{-6} **d.** 6.8×10^{-5}

(IIT-JEE 2006)

12. Consider a reaction aG + bH → Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

a. 0 **b.** 1 **c.** 2 **d.** 3

(IIT-JEE 2007)

13. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero-order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reaction is

a. 0.5 mol^{-1} dm^3 **b.** 1.0 mol dm^{-3}

c. 1.5 mol dm^{-3} **d.** 2.0 mol^{-1} dm^3

(IIT-JEE 2008)

14. For a first-order reaction A→P, the temperature (*T*) and dependent rate constant (*k*), was found to follow the equation $\log k = -(2000)\dfrac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are

a. 1.0×10^6 s^{-1} and 9.2 kJ mol^{-1}

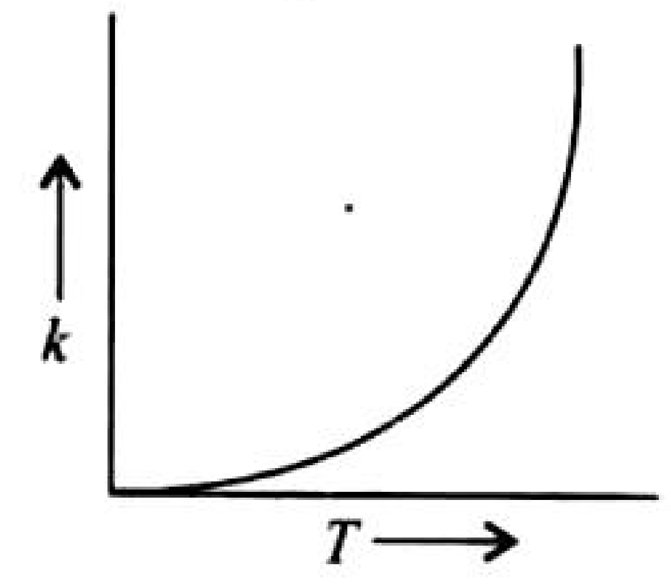
b. 6.0 s^{-1} and 16.6 kJ mol^{-1}

c. 1.0×10^6 s^{-1} and 16.6 kJ mol^{-1}

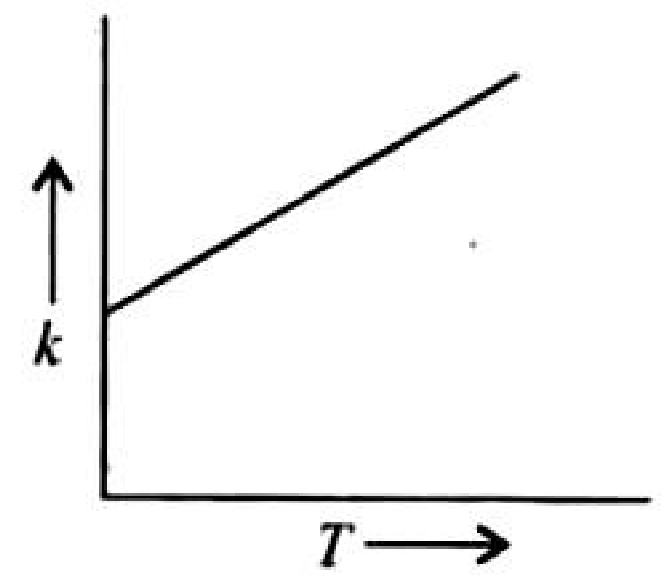
d. 1.0×10^6 s^{-1} and 38.3 kJ mol^{-1} **(IIT-JEE 2009)**

15. Plots showing the variation of the rate constant (*k*) with temperature (*T*) are given below. The plot that follows Arrhenius equation is

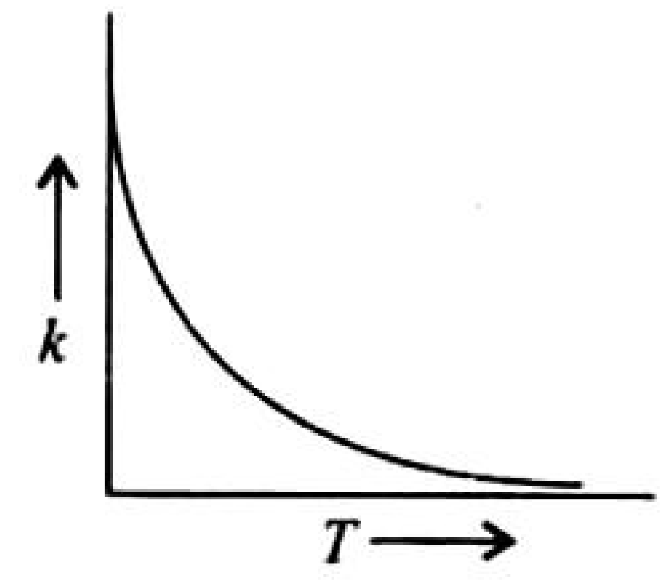
a.



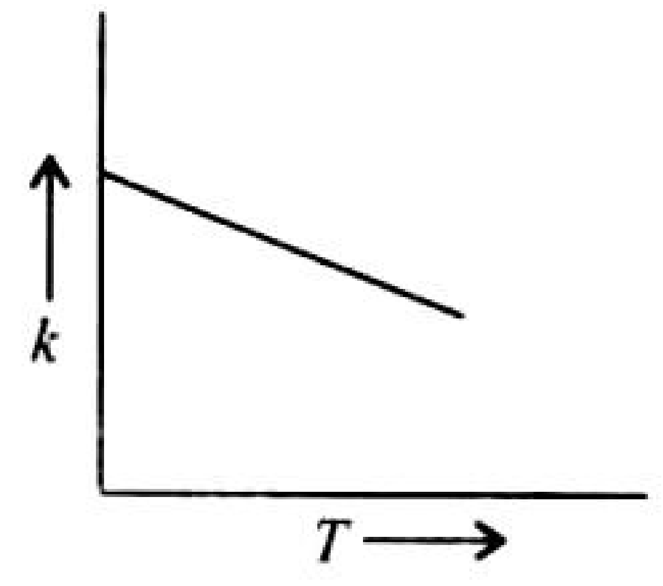
b.



c.



d.

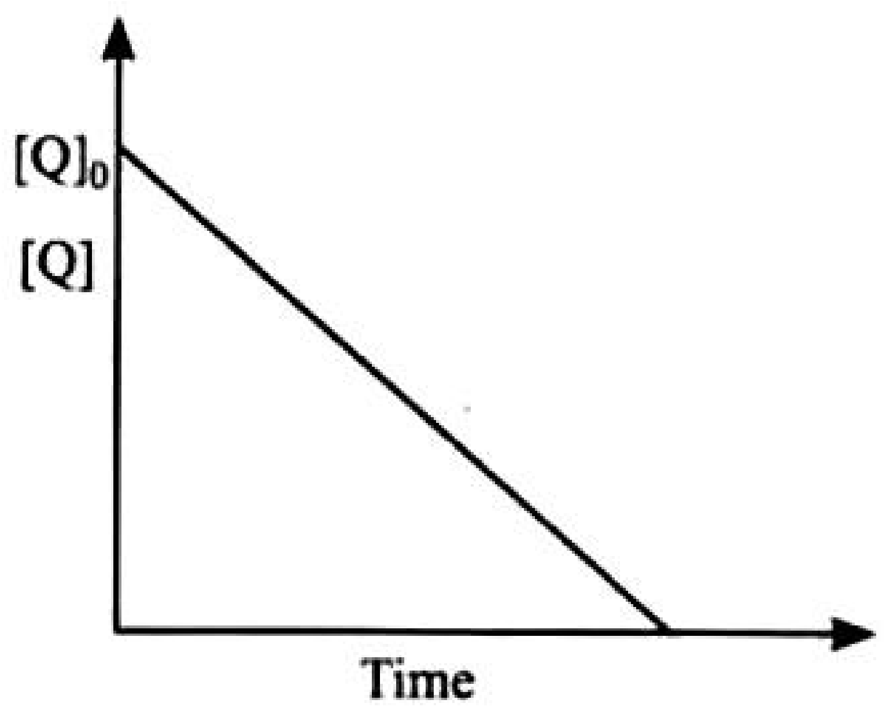


(IIT-JEE 2010)

16. In the reaction,

$$P + Q \rightarrow R + S$$

The time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is



a. 2 **b.** 3 **c.** 0 **d.** 1

(JEE Advanced 2013)

17. For the elementary reaction M → N, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is

a. 4 **b.** 3 **c.** 2 **d.** 1

(JEE Advanced 2014)

Multiple Correct Answers Type

1. A catalyst:

a. increases the average kinetic energy of reacting molecules

b. decreases the activation energy

c. alters the reaction mechanism

d. increases the frequency of collisions of reacting species

(IIT-JEE 1984)

2. The rate of law for the reaction:

RCl + NaOH (aq) → ROH + NaCl

is given by Rate = k_1 [RCl]. The rate of the reaction will be

a. doubled on doubling the concentration of sodium hydroxide

b. halved on reducing the concentration of alkyl halide to one half

c. increased on increasing the temperature of the reaction

d. unaffected by increasing the temperature of the reaction **(IIT-JEE 1988)**

3. For a first-order reaction,

a. the degree of dissociation is equal to $(1 - e^{-kt})$

b. a plot of reciprocal concentration of the reactant vs time gives a straight line

c. the time taken for the completion of 75% reaction is thrice the $t_{1/2}$ of the reaction

d. the pre-exponential factor in the Arrhenius equation has the dimension of time. s^{-1} **(IIT-JEE 1998)**

4. The following statement(s) is(are) correct:

a. A plot of log K_p versus 1/*T* is linear

b. A plot of log [X]versus time is linear for a first-order reaction, $X \rightarrow P$

c. A plot of P versus $1/T$ is linear at constant volume

d. A plot of P versus $1/V$ is linear at constant **(IIT-JEE 1999)**

5. For the first-order reaction

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

a. The concentration of the reactant decreases exponentially with time

b. the half-life of the reaction decreases with increasing temperature

c. the half-life of the reaction depends on the initial concentration of the reactant

d. the reaction proceeds to 99.6% completion in eight half-life duration **(IIT-JEE 2011)**

Integer Answer Type

1. The concentration of R in the reaction R → P was measured as a function of time and the following data is obtained:

[*R*] (molar)	1.0	0.75	0.40	0.10
***t*(min)**	0.0	0.05	0.12	0.18

The order of reaction is **(IIT-JEE 2010)**

2. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\left[\frac{t_{1/8}}{t_{1/10}}\right] \times 10$? ($\log_{10}2 = 0.3$)

$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$ **(IIT-JEE 2012)**

3. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is **(JEE Advanced 2015)**

Assertion-Reasoning Type

Read the following assertion and statement and answer as per the options given below:

a. If both assertion and statement are correct and statement is an explanation of assertion.

b. If assertion is correct and statement is wrong, statement is not an explanation of assertion.

c. If assertion is wrong and statement is correct, statement is not an explanation of assertion.

d. If both assertion and statement are wrong and statement is not an explanation of assertion.

1. Assertion: For each ten degree rise of temperature the specific rate constant is nearly doubled.
Statement: Energy-wise distribution of molecules in a gas is an experimental function of temperature. **(IIT-JEE 1989)**

Fill in the Blanks Type

1. The rate of chemical change is directly proportional to ______. **(IIT-JEE 1985)**

2. The hydrolysis of ethyl acetate in ______ medium is a ______ order reaction. **(IIT-JEE 1986)**

3. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg h^{-1}. The rate of conversion of H_2 under the same condition is ______ kg h^{-1}. **(IIT-JEE 1994)**

4. In the Arrhenius equation, $k = A \exp(-E_a/RT)$, A may be termed as the rate constant at ______ **(IIT-JEE 1997)**

True / False Type

1. For a first-order reaction, the rate of the reaction doubles as the concentration of the reactant(s) doubles. **(IIT-JEE 1986)**

2. Catalyst makes a reaction more exothermic. **(IIT-JEE 1987)**

3. Catalyst does not affect the energy of activation in a chemical reaction. **(IIT-JEE 1989)**

4. The rate of an exothermic reaction increases with increasing temperature. **(IIT-JEE 1990)**

Subjective Type

1. Rate of a reaction A + B → products, is given below as a function of different initial concentrations of A and B:

[A] (mol/l)	[B] (mol/l)	Initial rate (mol/l)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and with respect to B. what is the half-life of A in the reaction? **(IIT-JEE 1982)**

2. A first-order reaction is 20% complete in 10 minutes. Calculate (i) the specific rate constant of the reaction, and (ii) the time taken for the reaction to go to 75% completion. **(IIT-JEE 1984)**

3. While studying the decomposition of gaseous N_2O_5 it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parameter can be obtained from this observation? **(IIT-JEE 1985)**

4. A first-order reaction has $K = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed in the product? What is the half life of this reaction? **(IIT-JEE 1987)**

5. A first-order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the reaction rate constant at 27°C and the energy of activation of the reaction in kJ/mole. **(IIT-JEE 1988)**

6. In the Arrhenius equation for a certain reaction, the values of A and E_a (activation energy) are 4×10^{13} $\sec^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period to be 10 minutes? **(IIT-JEE 1990)**

7. The decomposition of N_2O_5 according to the equation:

$$2N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g)$$

Is a first-order reaction. After 30 min from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction. **(IIT-JEE 1991)**

8. Two reactions (I) A → products, (II) B → products, follow first-order kinetics. The rate of the reaction: (I) is doubled when the temperature is raised from 300 K to 310 K. The half life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction, (II) is half that of reaction (I), calculate the rate constant of the reaction (II) at 300 K. **(IIT-JEE 1992)**

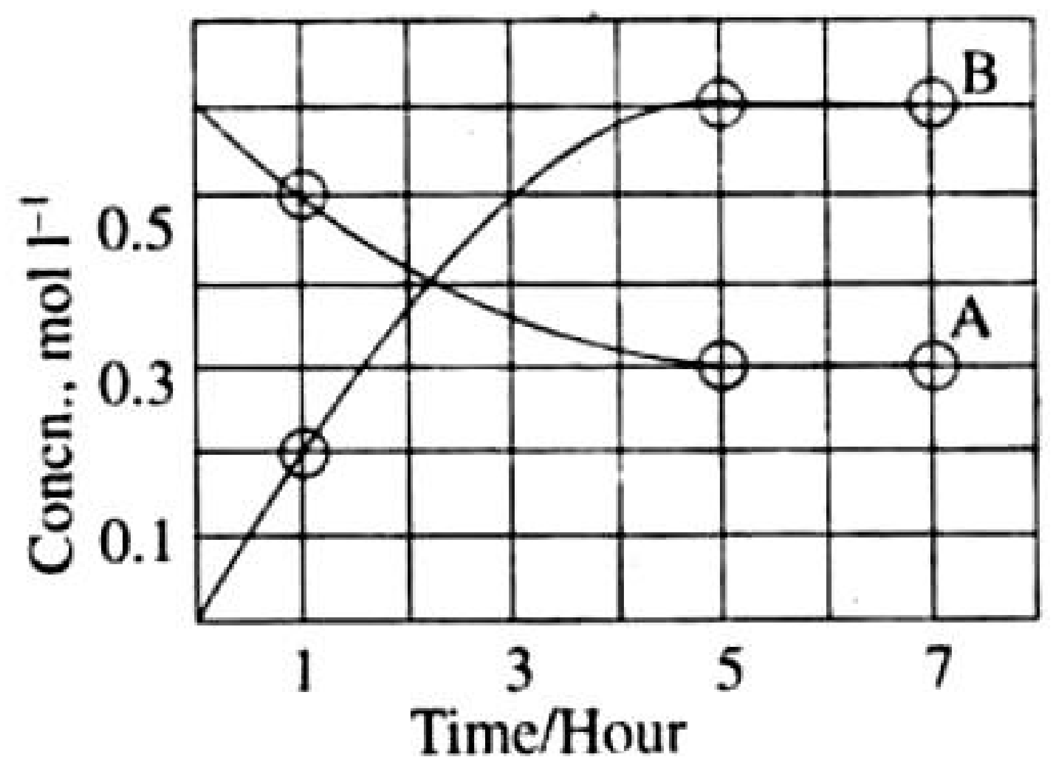
9. A first-order reaction A → B, requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percentage decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. **(IIT-JEE 1993)**

10. The gas phase decomposition of dimethyl ether follows first-order kinetics.

$$CH_3 - O - CH_{3(g)} \rightarrow CH_{4(g)} + H_{2(g)} + Co_{(g)}$$

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially, only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour. **(IIT-JEE 1993)**

11. The progress of the reaction. $A \rightleftharpoons nB$, with time, is presented in figure given below. Determine



i. The value of n,

ii. The equilibrium constant K, and

iii. The initial rate of conversion of A. **(IIT-JEE 1994)**

12. From the following data for the reaction between A and B.

	[A], mol l^{-1}	[B], mol l^{-1}	Initial rate mole l^{-1} s^{-1} at	
			300 K	320 K
(I)	2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
(II)	5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
(III)	1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	–

Calculate

i. The order of the reaction with respect to A and with respect to B,

ii. The rate constant at 300 K,

iii. The energy of activation, and

iv. The pre-exponential factor. **(IIT-JEE 1994)**

13. At 380°C, the half-life period for the first-order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C. **(IIT-JEE 1995)**

14. 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 pre-exponential factor for the reaction is 3.56×10^9 s^{-1}, calculate its rate constant at 318 K and also the energy of activation. **(IIT-JEE 1997)**

15. The rate constant for the first-order decomposition of a certain reaction is described by the equation

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

i. What is the energy of activation for this reaction?

ii. At what temperature will its half-life period be 256 min? **(IIT-JEE 1997)**

16. The rate constant of a reaction is 1.5×10^7 s^{-1} at 50°C and 4.5×10^7 s^{-1} at 100°C. Evaluate the Arrhenius parameters A and E_a. **(IIT-JEE 1998)**

17. The rate constant for an isomerisation reaction, A → B is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1 M, calculate the rate of the reaction after 1hr. **(IIT-JEE 1999)**

18. A hydrogenation reaction is carried out at 500 K. If same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1}. **(IIT-JEE 2000)**

19. The rate of a first-order reaction is 0.04 mol $litre^{-1}$ s^{-1} at 10 min and 0.03 mol $litre^{-1}$ s^{-1} at 20 min after initiation. Find the half-life of the reaction. **(IIT-JEE 2001)**

20. The vapour pressure of the two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 moles of (A) is mixed with 12 moles of (B). However, as soon as (B) is added, (A) starts polymerizing into a completely insoluble solid. The polymerization follows first-order kinetics. After 100 min, 0.525 mole of a solute is dissolved which arrests the polymerization completely. The final vapour pressure of the solution is 400 mm of

Hg. Estimate the rate of constant of the polymerization completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate of constant of the polymerization reaction. Assume negligible volume change on mixing and polymerization and ideal behaviour for the final solution. **(IIT-JEE 2001)**

21. For the given reactions, A + B → Products, following data were obtained.

	$[A_0]$	$[B_0]$	$R_0(\text{mol L}^{-1}\text{ s}^{-1})$
1.	0.1	0.2	0.05
2.	0.2	0.2	0.10
3.	0.1	0.1	0.05

a. Write the rate law expression

b. Find the rate constant **(IIT-JEE 2004)**

22. At constant temperature and volume, X decomposes as $2X(g) \rightarrow 3Y(g) + 2Z(g)$; P_x is the partial pressure of X.

Observation No.	Time (in minute)	P_x (in mm of Hg)
1	0	800
2	100	400
3	200	200

i. What is the order of reaction with respect to X?

ii. Find the rate constant.

iii. Find the time for 75% completion of the reaction.

iv. Find the total pressure when pressure of X is 700 mm of Hg. **(IIT-JEE 2005)**

Answer Key

JEE Advanced

Single Correct Answer Type

1. a. **2.** d. **3.** c. **4.** b. **5.** d.
6. b. **7.** a. **8.** c. **9.** c. **10.** d.
11. b. **12.** d. **13.** a. **14.** d. **15.** a.
16. d. **17.** b.

Multiple Correct Answers Type

1. b., c. **2.** b., c. **3.** a., d. **4.** a., b., d.
5. a., b., d.

Integer Answer Type

1. (0) **2.** (9) **3.** (8)

Assertion–Reasoning Type

1. c.

Fill in the Blanks Type

1. Product of active masses of reactant at that time
2. Acidic, first (or basic, second)
3. 1.765×10^{-4} kg/hr
4. Very high temperature

True/False Type

1. True **2.** False **3.** False **4.** True

Hints and Solutions

JEE ADVANCED

Single Correct Answers Type

1. a. It is a constant of a particular reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

2. d. It is characteristic constant of a particle reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

3. c. A catalyst decreases the activation energy of the reactants and thus shortens time of reaction.

4. b. The Arrhenius equation is: $k = A \exp(-E_a/RT)$ As $T \to \infty$, $\exp(-E_a/RT) \to 1$. Hence, $k = A$ where A, the Arrhenius parameter, is $6.0 \times 10^{14}\ \text{s}^{-1}$.

'A' is also known as frequency factor.

5. d. Find the order of reaction and then use appropriate equation.

As unit of K is sec^{-1}, reaction is of first order,

$$r = k[\text{N}_2\text{O}_5];\ \therefore [\text{N}_2\text{O}_5] = \frac{2.4 \times 10^{-5}}{3 \times 10^{-5}} = 0.8\ \text{mol/L}$$

6. b. The rate of photochemical process varies with the intensity of absorption.

Since greater is the intensity of absorbed light more photons will fall at a point, and further each photon causes one molecular to undergo reaction.

7. a. The given reaction is

$\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$

$$r = \frac{d[\text{N}_2]}{dt} = -\frac{1}{3}\frac{d[\text{H}_2]}{dt} = \frac{1}{2}\frac{d[\text{NH}_3]}{dt}$$

$\therefore$ Correct relationship amongst the rate expression is shown in (a)

8. c. $K = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$

$$\therefore \quad k = \frac{2.303}{2 \times 10^4}\log\frac{800}{50} = 1.386 \times 10^{-4}\ \text{s}^{-1}$$

9. c. As it is first-order reaction where $t_{1/2}$ doesn't depend on initial conc. of reactant. So all half lives are same

$$r = k[A]^1$$

$$r = \frac{0.693}{20} \times 0.01$$

$$r = 0.03465 \times 0.01$$

$$r = 0.0003465$$

$$r = 346.5 \times 10^{-6}$$

$$r = 3.47 \times 10^{-4}\ \text{M min}^{-1}$$

10. d. Order of a reaction can be fractional. Rest of all are true.

11. b. The required reaction is

$\text{Ag}^+ + 2\,\text{NH}_3 \rightleftharpoons [\text{Ag(NH}_3)_2]^+;\ \text{K} = ?$

From the given equations, we have

$$k_1 = \frac{[\text{Ag(NH}_3)]^+}{[\text{Ag}^+][\text{NH}_3]};\ k_2 = \frac{[\text{Ag(NH}_3)_2]^+}{[\text{Ag(NH}_3)]^+[\text{NH3}]}$$

If equations are added, their rate constants are multiplied.

$\therefore$ The value of K is given by

$$K = k_1 \times k_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 1.08 \times 10^{-5}$$

12. d. $r_1 = k[\text{G}]^x[\text{H}]^y$ (1)

If G becomes 2G and H becomes 2H, then $r_2 = 8r_1$

$8r_1 = k[2\text{G}]^x[2\text{H}]^y$ (2)

If G becomes 2G and H becomes H, then $r_3 = 2r_1$

$2r_1 = k[2\text{G}]^x[\text{H}]^y$ (3)

Divide equation (3) with equation (1), we get

$2 = 2^x$

$\Rightarrow \quad x = 1$

Divide equation (2) with equation (3), we get

$4 = 2^y$

$2^2 = 2^y$

$\Rightarrow \quad y = 2$

$\Rightarrow$ Order w.r.t. G = 1

Order w.r.t. H = 2

So overall order = 3

13. a. The values of rate constants k_0, k_1 for zero order and first-order reaction, respectively, are given by the following equation:

$k_o = \dfrac{A_0}{2 \times t_{1/2}}$ [where A_0 = initial concentration, and $t_{1/2}$ = half-life period]

and $\quad k_1 = \dfrac{0.693}{t_{1/2}}$

Substantiating various given values, we get

$$k_0 = \frac{1.386\ \text{mol litre}^{-1}}{2 \times 20\ \text{sec}} \qquad \text{(i)}$$

$$\text{and} \quad k_1 = \frac{0.693}{40\ \text{sec}} \qquad \text{(ii)}$$

Dividing (ii) by (i), we get

$$\frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{2 \times 20}{1.386}\ \text{mol}^{-1}\ \text{litre}$$

$$= \frac{0.693}{1.386}\ \text{mol}^{-1}\ \text{litre}$$

$$= 0.5\ \text{mol}^{-1}\ \text{litre}$$

$$= 0.5\ \text{mol}^{-1}\text{dm}^3 \qquad [1\ \text{litre} = 1\ \text{dm}^3]$$

Thus the correct answer is (a).

14. d. $\log k = \log A - \dfrac{E_a}{2.303RT}$ (1)

Also given $\log k = 6.0 - (2000)\dfrac{1}{T}$ (2)

On comparing equations (1) and (2),

$\text{Log}\ A = 6.0 \Rightarrow A = 10^6\ \text{s}^{-1}$

and $\quad \dfrac{E_a}{2.303R} = 2000$

$\Rightarrow \quad E_a = 2000 \times 2.303 \times 8.314 = 38.29\ \text{kJ mol}^{-1}$

15. a. As per Arrhenius equation ($k = Ae^{-E_a/RT}$), the rate constant increases exponentially with temperature.

16. d. Overall order of reaction can be decided by the data given $t_{75\%} = 2t_{50\%}$

$\therefore$ It is a first-order reaction with respect to P.

From graph [Q] is linearly decreasing with time, i.e., order of reaction with respect to Q is zero and the rate expression is $r = k[\text{P}]^1[\text{Q}]^0$.

Hence (d) is correct.

17. b. $r \propto [M]^x$

$$r_1 = k[M]^x$$

If M → 2M, $r_2 = 8r_1$

$$8r_1 = k[2M]^x$$
$$8r_1 = 2^x k[M]^x$$
$$8r_1 = 2^x r_1 \Rightarrow 2^3 = 2^x \Rightarrow x = 3$$

Multiple Correct Answers Type

1. b., c.

A catalyst provides a new path of lower activation energy. The catalyst reacts with the reactants to form an intermediate of low activation energy. The intermediate then decomposes to from the products along with regeneration of catalyst. Thus the reaction mechanism changes completely.

2. b., c.

As rate = k [RCl], so it is first-order reaction. On decreasing the concentration of RCl to half, the rate will also be halved. Rate will also increase with temperature.

3. a., d.

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$\frac{kt}{2.303} = \log\frac{[A_0]}{[A]}$$

or $$kt = ln\frac{A_0}{A} = ln\frac{1}{1-a}$$

If a is the degree of dissociation,

$$e^{kt} = \frac{1}{1-a} \text{ or } 1-a = e^{-kt}$$

or $$a = 1 - e^{-kt}$$

$\therefore\ k = Ae^{-E_a/RT}$ (Arrhenius equation)

Pre-exponential factor has the same dimensions as the rate constant, and for a first-order reaction that is (t^{-1}).

4. a., b., d.

The relevant expressions are as follows.

a. $k_p = A\,e^{-\Delta H/RT}$

$$\ln k_p = \ln A \frac{-\Delta H}{RT}$$

$$\log k_p = \log A - \frac{\Delta H}{2.303R} \times \frac{1}{T}$$

$$\log k_p = \frac{-\Delta H}{2.303R}\frac{1}{T} + \log A$$

$$y = m\,x + c$$

b. $k = \dfrac{2.303}{t}\log\dfrac{[x_0]}{[x]}$

$$\log\frac{[x_0]}{[x]} = \frac{kt}{2.303}$$

$$\log\frac{[x]}{[x_0]} = \frac{-kt}{2.303}$$

d. $p \propto \dfrac{1}{v}$

$$p = k \times \frac{1}{v}$$

$$y = mx$$

5. a., b., d.

For first-order reaction

$$[A] = [A]_0 e^{-kt}$$

Hence concentration of $[NO_2]$ decreases exponentially.

Also, $t^{1/2} = \dfrac{0.693}{K}$, which is independent of concentration and $t_{1/2}$ decreases with the increase of temperature.

$$t_{99.6} = \frac{2.303}{K}\log\left(\frac{100}{0.4}\right)$$

$$t_{99.6} = \frac{2.303}{K}(2.4) = 8 \times \frac{0.693}{K} = 8t_{1/2}$$

Integer Answer Type

1. (0) The integrated form of a zero-order reaction is

$$[A_0] - [A_t] = k_0 t$$
$$1.0 - 0.75 = k_0 \times 0.05,\ k_0 = 5$$

Again, $1.0 - 0.4 = k_0 \times 0.12,\ k_0 = 5$

As value of k is coming out to be same, this means it is zero-order reaction.

2. (9) $t_{1/8} \Rightarrow$ Let $[A_0] = 1$

$$[A] = \frac{1}{8} \times 1$$

$$t_{1/8} = \frac{2.303}{k}\log\frac{1}{1/8}$$

$$t_{1/8} = \frac{2.303}{k}\log 8$$

$$t_{1/8} = \frac{2.303}{k}\log 2^3$$

$$t_{1/8} = 3 \times \frac{2.303}{k}\log 2 \qquad (1)$$

$$t_{1/10} \Rightarrow [A_0] = 1$$

$$[A] = \frac{1}{10} \times 1 = \frac{1}{10}$$

$$t_{1/10} = \frac{2.303}{k}\log\frac{1}{1/10}$$

$$t_{1/10} = \frac{2.303}{k}\log 10$$

$$\left[\frac{t_{1/8}}{t_{1/10}}\right] \times 10 = \frac{\left(\dfrac{2.303 \times 3\log 2}{k}\right)}{\left(\dfrac{2.303}{k}\right)} \times 10 = 9$$

3. (8) $8H^+ = 5[Fe(H_2O)_2(OX)_2]^{2-} + MnO_4^- \rightarrow Mn^{2+}$

$$+ 5[Fe(H_2O)_2(OX)_2]^- + 4H_2O$$

$$\text{Rate} = \frac{1}{8}\frac{d[H^+]}{dt} = \frac{d[MnO_4^-]}{dt}$$

Hence, $\dfrac{\text{rate of } [H^+] \text{decay}}{\text{rate of } [MnO_4^-] \text{decay}} = 8.$

Assertion - Reasoning Type

1. c. Assertion is correct as for every 10°C raise in temperature, the specific rate constant, K nearly doubles.

Fill in the Blanks Type

1. Product of active masses of reactants at that time

2. Acidic, first (or basic, second)

3. 1.765×10^{-4} kg/hr;

$N_2(g) + 3H_2(g) \rightarrow 2NH_3\,(g)$

Here rate of reaction = $\frac{1}{3}$[Rate of disappearance of H_2]= $\frac{1}{2}$ [Rate of appearance of NH_3]

$$\text{or}\quad \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt} \Rightarrow \frac{d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt}$$

$$\frac{d[NH_3]}{dt} = 0.01 \text{ kg/hr} = \frac{0.001}{17} \times 1000 = \frac{1}{17}\text{ mole/hr}$$

$$\therefore\quad \frac{d[H_2]}{dt} = \frac{1}{17} \times \frac{3}{2} = \frac{3}{34}\text{ mole/hr} = \frac{3}{34} \times \frac{2}{1000}\text{ kg/hr}$$

$$= 1.765 \times 10^{-4}\text{ kg/hr}$$

4. Very high temperature ($T = \infty$) or zero activation energy and $K = A$.

True / False Type

1. **True**:
   The rate of reaction of first order is directly proportional to the concentration of reacting substance.
2. **False**:
   Catalyst does not make a reaction more exothermic, but decreases the activation energy and hence increases the rate of reaction forward as well as backward.
3. **False**:
   Catalysts lower the energy of activation and therefore influence the rate as well as rate constant of the reaction.
4. **True**:
   The rate of reaction increases with increase in temperature because at higher temperature more number of molecules attain the activation energy. But rate constant k of exothermic reaction decreases with increase in temperature.

Subjective Type

1. $r = k\,[A]^x\,[B]^y$

$0.005 = k\,[0.01]^x\,[0.01]^y$ (i)

$0.010 = k\,[0.02]^x\,[0.01]^y$ (ii)

$0.005 = k\,[0.01]^x\,[0.02]^y$ (iii)

Divide equation (ii) by equation (i), we get

$2 = 2^x$

$\Rightarrow\quad x = 1$

Divide equation (iii) by equation (i), we get,

$1 = 2^y$

$2^0 = 2^y$

$\Rightarrow\quad y = 0$

Rate r = $k\,[A]^1\,[B]^0$

$r = k\,[A]$

$$\therefore\quad k = \frac{r}{[A]} = \frac{0.005}{0.01} = 0.5\text{ min}^{-1}$$

[$\because r = 0.005$ mol/l m and $[A] = 0.01$ mol/l]

We know that $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5}$ [$\because k = 0.5\text{ min}^{-1}$]

$= 1.386$ min

2. i. For-first order reaction; $k = \frac{2.303}{t}\log\frac{a}{a-x}$

Calculation of specific rate constant

Let the initial concentration = 100

$\therefore a = 100, x = 20$, when $t = 10$ min

Substituting these values in the first-order rate equation

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{10}\log\frac{100}{100-20}$$

$$= \frac{2.303}{10} \times 0.0969 = 0.02231\text{ min}^{-1}$$

ii. Suppose the time when 75% of the given first order reaction is completed = t minute

Here $a = 100, x = 75$ at time t

Substituting these values again in the first-order rate equation, we get

$$0.02231 = \frac{2.303}{t}\log\frac{100}{100-75} \quad [\because k = 0.02231\text{ min}^{-1}]$$

$$0.02231 = \frac{2.303}{t} \times 0.6021 \quad [\because \log 4 = 0.6021]$$

$$\therefore\ t = \frac{2.303 \times 0.6021}{0.02231} = 62.07\text{ min}$$

3. Assuming that the decomposition of N_2O_5 is a first-order reaction, then

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{t}\log\frac{P_0}{P}$$

$$\text{or}\quad \log P = \frac{-kt}{2.303} + \log P_0$$

Thus $\log P$ vs time graph is linear with slope = $\frac{-k}{2.303}$, if the given reaction is of first order which is in accordance with the given statement. Thus the reaction obeys first-order reaction.

4. For a first-order reaction we know that

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

Here, $t = 10 \times 60 \times 60$ sec and let $a = 1$, then substituting the values, we get

$$1.5 \times 10^{-6} = \frac{2.303}{10 \times 3600}\log\frac{1}{(1-x)}$$

$$0.0234 = \log\frac{1}{(1-x)}$$

Taking antilog, $1.055 = \frac{1}{(1-x)}$

or $\quad 1.055 - 1.055\,x = 1$

$$x = \frac{(1.055-1)}{1.055} = 0.052$$

Thus, 5.2% of the initial concentration has changed into product.

Again we know that

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-6}} = 462000\text{ sec} = 128.33\text{ h}$$

5. $k = \frac{0.693}{t_{1/2}};\ \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]$

Substituting the value at the two given conditions

$$k_1 = k_{300} = \frac{0.693}{30} = 0.0231\text{ min}^{-1}$$

$$k_2 = k_{320} = \frac{0.693}{10} = 0.0693\text{ min}^{-1}$$

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

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

$$= \frac{2.303 \times 8.314 \times 10^{-3} \times 300 \times 320}{320 - 300} \times \log \frac{0.0693}{0.0231}$$

$$= 43.848 \text{ kJ mol}^{-1}$$

6. According to Arrhenius equation

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

We know that $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \times 60}$ $(t_{1/2} = 10 \times 60 \text{ sec})$

$$= 1.555 \times 10^{-3}$$

Substituting the various values in the above equation, we get

$$\log 1.155 \times 10^{-3} = \log 4 \times 10^{13} - \frac{98.6}{2.303 \times 8.314 \times 10^{-3} \times T}$$

On usual calculations, $T = 311.35$ K

7. $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

2 mol of gaseous nitrogen pentoxide on complete decomposition gives 5 mol of gaseous products.

Therefore, initial pressure of $N_2O_5 = 584.5 \times \frac{2}{5} = 233.8$ mm Hg.

Let x be the amount of N_2O_2 decomposed after 30 min. Therefore, after 30 min,

Pressure due to $N_2O_2 = 233.8 - x$

Pressure due to $NO_2 = 2x$

and pressure due to $O_2 = \frac{x}{2}$

Total pressure after 30 min

$$= 284.5 \text{ mm Hg} = 233.8 - x + 2x + \frac{x}{2}$$

or $$233.8 + \frac{3x}{2} = 284.5$$

or $$x = 33.8 \text{ mm Hg}$$

Hence pressure of N_2O_2 after 30 min

$$= 233.8 - 33.8 = 200 \text{ mm Hg}$$

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{30} \log \frac{233.8}{200}$$

$$k = \frac{2.303}{30} \times 0.0679 = 5.2 \times 10^{-3} \text{ min}^{-1}$$

8. For reaction (I),

A → Products

$T_1 = 300$ K, $T_2 = 310$ K,

$(K_1)_A$ is at 300 K and $(K_2)_A$ is at 310 K

Given:

$$\left(\frac{k_{2(310\text{K})}}{k_{1(300\text{K})}}\right)_A = 2 \qquad \text{(i)}$$

According to Arrhenius equation, $k = Ae^{-E_a/RT}$

(For reaction (I))

or $$\log\left(\frac{k_{2(310\text{K})}}{k_{1(300\text{K})}}\right)_A = \frac{E_{a(A)}}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad \text{(ii)}$$

$$\log 2 = \frac{E_{a(A)}}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad \text{(iii)}$$

For reaction (II),

$B \rightarrow$ Products

Since at 310 K, B decomposes twice as fast as A.

$\therefore$ $[K_{2(310\text{ K})}]_A = 0.0231 \text{ min}^{-1}$

$\therefore$ $[K_{2(310\text{ K})}]_B = 2 \times 0.0231 \text{ min}^{-1}$

$= 0.0462 \text{ min}^{-1}$

We have to calculate $[K_{1(300\text{K})}]_B$

According to Arrhenius equation, $k = Ae^{-E_a/RT}$

(For reaction (II))

$$\log\left(\frac{k_{2(310\text{K})}}{k_{1(300\text{K})}}\right)_B = \frac{E_{a(B)}}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad \text{(iv)}$$

Given, $$(E_a)_B = \frac{1}{2}(E_a)_A \qquad \text{(v)}$$

Subsititute the value of equation (v) in equation (iv),

$$\log\left(\frac{k_{2(310\text{K})}}{k_{1(300\text{K})}}\right)_B = \frac{1}{2} \times \frac{E_{a(A)}}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad \text{(vi)}$$

Compairing equations (iii) and (vi), we get

$$\log\left(\frac{k_{2(310\text{K})}}{k_{1(300\text{K})}}\right)_B = \frac{1}{2} \times \log 2$$

$$\therefore \quad \frac{0.0462}{[k_{1(300\text{k})}]_B} = (2)^{1/2} = \sqrt{2} = 1.414 \qquad \text{(vii)}$$

$$\therefore \quad [k_{1(300\text{K})}]_B = \frac{0.0462}{1.414} = 0.03267 \text{ min}^{-1}$$

9. According to Arrhenius equation

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

Calculation of k at 25°C (298 K), i.e. k_1

Here $a = 100$, $a - x = 100 - 25$, $t = 20$ min

Thus $k_1 = \frac{2.303}{20} \log \frac{100}{75} = 0.014386 \text{ min}^{-1}$

Calculation of k at 40°C (313 K) i.e., k_2

Substituting various values, we get

$$\log \frac{k_2}{0.014386} = \frac{70 \times 10^3}{2.303 \times 8.314} \times \left(\frac{1}{298} - \frac{1}{313}\right)$$

$$= \frac{70 \times 10^3 \times 15}{2.303 \times 8.314 \times 298 \times 313} = 0.587$$

$$\log k_2 = 0.014386 \times 0.587$$

$$k_2 = 0.05570 \text{ min}^{-1}$$

Calculation of % decomposition at 40°C

Thus here $a = 100$, $a - x = 100 - x$, $t = 20$ min $K_2 = 0.05570$

Substituting the values in the first-order reaction equation:

$$k_2 = 0.05570 = \frac{2.303}{20} \log \frac{100}{100 - x}$$

On usual calculations, $x = 67.169 = 67.17\%$

10.

	CH_3—O—CH_3 →	CH_4 +	CO +	H_2	Total conc.
Initial state	a	0	0	0	a
After 12 min	$a - x$	x	x	x	$a + 2x$

Calculation of initial concentration (a) of CH_3OCH_3

$$PV = nRT$$

or $$\frac{n}{V} = \frac{P}{RT}$$

$$a = \frac{P}{RT} = \frac{0.4}{0.082 \times 773} = 6.31 \times 10^{-3} \text{ moles l}^{-1}$$

Calculation of k

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5} = 4.78 \times 10^{-2}\ \text{min}^{-1}$$

Substituting the values in the first-order equation, we get

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

$$4.78 \times 10^{-2} = \frac{2.303}{12}\log\frac{a}{a-x}$$

$$\frac{a}{a-x} = 1.77446$$

$$a - x = \frac{6.31 \times 10^{-3}}{1.77446}\ \text{moles}\ l^{-1} = 3.556 \times 10^{-3}\ \text{moles l}^{-1}$$

$\therefore$ $x = (6.310 - 3.556) \times 10^{-3}$ moles/l $= 2.754 \times 10^{-3}$ moles/l

$\therefore$ After 12 min.

Total no. of moles l^{-1}

$$= a + 2x = 6.31 \times 10^{-3} + 2 \times 2.754 \times 10^{-3} = 11.818 \times 10^{-3}$$

$$\therefore \quad P = \frac{n}{V}RT = 11.818 \times 10^{-3} \times 0.082 \times 773 = 0.749\ \text{atm}$$

11. **i.** According to the figure, in the given time of 4 hours (1 to 5) concentration of A falls from 0.5 to 0.3 M, while in the same time concentration of B increases from 0.2 M to 0.6 M.

Decrease in concentration of A in 4 hours

$$= 0.5 - 0.3 = 0.2\ \text{M}$$

Increase in concentration of B in 4 hours

$$= 0.6 - 0.2 = 0.4\ \text{M}$$

Thus increase in concentration of B in a given time is twice than the decrease in concentration of A. Thus $n = 2$.

ii. $$K = \frac{[B^2]_{\text{eq.}}}{[A]_{\text{eq.}}} = \frac{(0.6)^2}{0.3} = 1.2\ \text{M}$$

iii. Initial rate of conversion of A

= Charge in conc. of A during 1 h

$$= \frac{0.6 - 0.5}{1} = 0.1\ \text{mole l}^{-1}\ \text{hr}^{-1}$$

12. Let the order with respect to A is x and the order with respect to B is y

Then, Rate $= k\,[A]^x\,[B]^y$

$$5.0 \times 10^{-4} = k\,[2.5 \times 10^{-4}]^x\,[3.0 \times 10^{-5}]^y \quad \text{(i)}$$

$$4.0 \times 10^{-3} = k\,[5.0 \times 10^{-4}]^x\,[6.0 \times 10^{-5}]^y \quad \text{(ii)}$$

$$1.6 \times 10^{-2} = k\,[1.0 \times 10^{-3}]^x\,[6.0 \times 10^{-5}]^y \quad \text{(iii)}$$

From (ii) and (iii), we get $2^x = 4$; $x = 2$

From (i) and (ii), we get $2^{x+y} = 8$; $x + y = 3$; $y = 1$

Therefore, the rate of equation for the reaction is

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

i. Thus order of reaction with respect to $A = 2$ and order of reaction with respect to $B = 1$.

ii. Rate constant (k_1) at 300 K

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

$$= \frac{5.0 \times 10^{-4}\ \text{mol l}^{-1}\text{s}^{-1}}{(2.5 \times 10^{-4}\ \text{mol l}^{-1})^2(3.0 \times 10^{-5}\ \text{mol l}^{-1})}$$

$$= 2.66 \times 10^{8}\ \text{mol}^{-2}\ \text{l}^2\text{s}^{-1}$$

iii. Determination of energy of activation:

Rate constant (k_2) at 320 K

$$k_2 = \frac{\text{Rate}}{[A]^2[B]}$$

$$k_2 = \frac{2.0 \times 10^{-3}\ \text{mol l}^{-1}\ \text{s}^{-1}}{(2.5 \times 10^{-4}\ \text{mol l}^{-1})^2(3.0 \times 10^{-5}\ \text{mol l}^{-1})}$$

$$= 1.066 \times 10^{9}\ \text{mol}^{-2}\ \text{l}^2\ \text{s}^{-1}$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_1 - T_2}{T_2T_1}\right]$$

or $$E_a = 2.303R\left[\log\frac{k_2}{k_1}\right]\left[\frac{T_1T_2}{T_2 - T_1}\right]$$

$$= 2.303 \times 8.314\left[\log\frac{1.066 \times 10^{9}}{2.66 \times 10^{8}}\right]\left[\frac{320 \times 300}{20}\right]$$

$$= 5.54 \times 10^{4}\ \text{J}$$

iv. Determination of the pre-exponential factor

$$\log k = -\frac{E_a}{2.303R} \times \frac{1}{T} + \log A$$

$$\log 2.66 \times 10^{8} = \log A - \frac{5.54 \times 10^{4}}{2.303 \times 8.314} \times \frac{1}{300}$$

$$\therefore \quad A = 1.25 \times 10^{18}\ \text{l}^2\ \text{mol}^{-2}\ \text{sec}$$

13. $$k_{653\text{K}} = \frac{0.693}{360} = 1.925 \times 10^{-3}\ \text{min}^{-1}$$

Calculation of $k_{723\text{ K}}$

$E_a = 200$ kJ $\text{mol}^{-1} = 200 \times 10^3$ J mol^{-1}

$T_2 = 723$ K, $T_1 = 653$ K

$K_{653\text{ K}} = 1.925 \times 10^{-3}$ min^{-1}

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

$$\log\frac{k_{723}}{1.925 \times 10^{-3}} = \frac{200 \times 10^3}{2.303 \times 8.314}\left(\frac{1}{653} - \frac{1}{723}\right)$$

On solving,

$$k_{723\text{ K}} = 6.81 \times 10^{-2}\ \text{min}^{-1}$$

Calculation of time for 75% decomposition at 723 K.

Let the initial amount of H_2O_2, $a = 1$

$\therefore$ Amount at the required time, $(a - x) = 0.25$

Substituting the values in the given relation,

$$t = \frac{2.303}{k_{723\text{K}}}\log\frac{a}{a-x} = \frac{2.303}{6.81 \times 10^{-2}}\log\frac{1}{0.25} = 20.34\ \text{min}$$

14. Let the initial concentration (A) = 100

Final concentration at 298 K = 100 − 10 = 90

Final concentration at 308 K = 100 − 25 = 75

Substituting the values in the first-order rate reaction

$$t = \frac{2.303}{k_{298}}\log\frac{100}{90} \quad \text{(i)}$$

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

From (i) and (ii) $\dfrac{k_{308}}{k_{298}} = 2.73$

Substituting the value in the following relation

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

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

$$= \frac{2.303 \times 8.314 \times 298 \times 308}{308 - 298}\log 2.73$$

$$E_a = 76.6227 \text{ kJ mol}^{-1} = 18.33 \text{ kcal mol}^{-1}$$

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

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

$$K = 3.56 \times 10^{9} \times 2.59 \times 10^{-13} = 9.22 \times 10^{-4}\ \text{s}^{-1}$$

15. **i.** The Arrhenius equation is

$$k = A\exp(-E_a/RT)$$

Taking natural logarithm, we get

$\ln k = \ln A - E_a/RT$

Thus $\log k = \log A - \frac{Ea}{2.303R}\cdot\frac{1}{T}$

Comparing this expression with the given one, we get

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

Hence, $E_a = (1.25 \times 10^{4}\ \text{K})\,(2.303)\,(8.314\ \text{JK}^{-1}\ \text{mol}^{-1})$

$$= 2.39 \times 10^{5}\ \text{J mol}^{-1} = 239\ \text{kJ mol}^{-1}$$

ii. The reaction is first order as the unit of rate constant is s^{-1}.

For a first-order reaction,

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

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

Substituting this in the given expression, we get

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

or $$-4.346 = 14.34 - \frac{1.25 \times 10^{-4}\ \text{K}}{T}$$

or $$T = \frac{1.25 \times 10^{-4}\ \text{K}}{18.686} = 669\ \text{K}$$

16. $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$\therefore$ $$\log\frac{4.5 \times 10^{7}}{1.5 \times 10^{7}} = \frac{E_a}{8.314 \times 2.303}\left[\frac{373 - 323}{373 \times 323}\right]$$

$\therefore$ $E_a = 2.2 \times 10^{4}\ \text{J mol}^{-1}$

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

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

On solving $\log(4.5 \times 10^{7}) = \log A - \frac{2.2 \times 10^{4}}{2.303 \times 8.314} \times \frac{1}{323}$

$\therefore$ $A = 5.42 \times 10^{10}\ \text{s}^{-1}$

17. A → B; $k = 4.5 \times 10^{-3}\ \text{min}^{-1}$; $[A]_0 = 1$ M

For first-order reaction, $k = \frac{2.303}{t}\log\frac{a}{(a - x)}$

Find $(a - x)$ at $t = 60$ min.

$$4.5 \times 10^{-3} = \frac{2.303}{60}\log\frac{1}{(a - x)}$$

$\therefore$ $(a - x) = 0.7634$

Thus rate after 60 minute $= k\,(a - x) = 4.5 \times 10^{-3} \times 0.7634$

$= 3.4354 \times 10^{-3}\ \text{M min}^{-1}$

18. According to Arrhenius equation $k = Ae^{-E_a/RT}$.

Let E_a of the reaction in absence of catalyst = x kJ mol^{-1}.

Therefore, E_a of the reaction in presence of catalyst = $x - 20$ kJ mol^{-1}.

The Arrhenius equations in the two conditions can thus be written as

$$k = Ae^{-\frac{x}{R \times 500}} \qquad \text{(i)}$$

$$k = Ae^{-\frac{x-20}{R \times 400}} \qquad \text{(ii)}$$

Dividing equation (i) by equation (ii), we get

$$e^{-\frac{x}{500R}} = e^{-\frac{x-20}{400R}} \Rightarrow \frac{x}{500} = \frac{x - 20}{400} \text{ or } x = 100 \text{ kJ mol}^{-1}$$

19. $r_2 = k_1c_1$ and $r_2 = k_2c_2$

Since rate of first-order reaction is directly proportional to the concentration of its reactant,

$\therefore$ $$\frac{r_1}{r_2} = \frac{c_1}{c_2} = \frac{0.04}{0.03}$$

According to first-order reaction

$$k = \frac{2.303}{t_{20} - t_{10}}\log\frac{c_1}{c_2}$$

On substituting the various values

$k = 0.0287\ \text{min}^{-1}$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287} = 24.14\ \text{min}$$

20. Let the number of moles of A left after 100 min = x.

Total number of moles after 100 min = $x + 12 + 0.525$

$$P_{\text{mix}} = p_A + p_B$$

$$= \left(\frac{x}{12 + x} \times 300\right) + \left(\frac{12}{12 + x} \times 500\right)$$

$$= \frac{6000 + 300x}{12 + x}$$

According to Raoult's law

$$\frac{\left(\frac{6000 + 300x}{12 + x}\right) - 400}{\frac{6000 + 300x}{12 + x}} = \frac{0.525}{x + 12 + 0.525}$$

On solving, we get $x = 9.9$

Now according to first-order kinetics,

$$k = \frac{2.303}{100}\log\frac{10}{9.9} = 1.005 \times 10^{-4}\ \text{min}^{-1}$$

21. **a.** $r_1 = k\,[A_0]^x\,[B_0]^y$

Equation (1) $0.05 = k\,[0.1]^x\,[0.2]^y$

Equation (2) $0.10 = k\,[0.2]^x\,[0.2]^y$

Equation (3) $0.05 = k\,[0.1]^x\,[0.1]^y$

Divide equation (2) by equation (1), we get

$$2 = 2^x$$

$\Rightarrow$ $x = 1$

Divide equation (1) by equation (3), we get

$$1 = 2^y$$

$$\Rightarrow \quad 2^o = 2^y$$

$$\Rightarrow \quad y = 0$$

$$\Rightarrow \quad n = k\,[A_0]^1\,[B_0]^0$$

b. $k = \dfrac{R_0}{[A_0]} = \dfrac{0.05}{0.10} = 0.5\ \text{s}^{-1}$

22. **i.** From the given data, it is evident that the $t_{1/2}$ (half-life period) for the decomposition of X (g) is constant (100 min) therefore the order of reaction is one.

ii. Rate constant, $k = \dfrac{0.693}{t_{1/2}}$

$$= \frac{0.693}{100} \doteq 6.93 \times 10^{-3}\ \text{min}^{-1}$$

iii. Time taken for 75% completion of reaction($t_{75\%} = 2t_{1/2}$, only for first-order reaction).

$$= 2t_{1/2} = 2 \times 100 = 200\ \text{min}$$

iv.

	$2X$	$\rightarrow$ $3Y$	+ $2Z$
Initial pressure	800	0	0
After time t	(800 – 2P)	3P	2P

When the pressure of X is 700 mm of Hg then,

$$800 - 2\,P = 700$$

2P = 100; P = 50 mm of Hg

Total pressure = 800 – 2P + 3P + 2P = 800 + 150

= 950 mm of Hg