CHEMISTRY

NCERT - NCERT CHEMISTRY(HINGLISH)

CHEMICAL KINETICS

Solved Examples

1. From the concentrations of C_4H_9Cl (butyl chloride) at different times given below, calculate the average rate of the reaction:

$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$

during different intervals of time.

t/s	0	50	100	150	200	300	400
$[C_4H_9Cl]/\text{mol}^{-1}$	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439

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2. The decomposition of N_2O_5 in CCl_4 solution at $318K$ has been studied by monitoring the concentration of N_2O_5 in the solution. Initially, the concentration of N_2O is $2.33M$ and after $184\ \min$, it is reduced to $2.08M$. The reaction takes place according to the equation:

$2N_2O_5 \rightarrow 4NO_2 + O_2$

Calculate the average rate of this reaction in terms of hours, minutes, and seconds. What is the rate of Production of NO_2 during this period?

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3. Calculate the overall order of a reaction which has the rate expresison.

(a) Rate $= k[A]^{\frac{1}{2}}[B]^{\frac{3}{2}}$, (b) Rate $= k[A]^{\frac{3}{2}}[B]^{-1}$

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4. Identify the reaction order from each of the following rate constants.

(i) k $= 2.3 \times 10^{-5} Lmol^{-1}s^{-1}$

(ii) k $= 3 \times 10^{-4} s^{-1}$

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5. The initial concentration of N_2O_5 in the following first order reaction:

$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

was $1.24 \times 10^{-2} molL^{-1}$ at $318K$. The concentration of N_2O_5 after 60 min was $0.20 \times 10^{-2} molL^{-1}$. Calculate the rate constant of the reaction at $318K$.

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6. The following data were obtained during the first thermal decomposition of $N_2O_5(g)$ at constant volume.

$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$

S.No.	Time (s)	Total pressure (atm)
$i.$	0	0.5
$ii.$	100	0.512

Calculate the rate constant.

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7. A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14} s^{-1}$. Find half-life of the reaction.

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8. When reaction is completed 99.9%,$[R]_n = [R]_0 - 0.999[R]_0$

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9. The rate constant of a reaction at $500K$ and $700K$ are $0.02 s^{-1}$, respectively. Calculate the values of E_a and A at $500K$.

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10. The first order rate constant for the decomposition of C_2H_5I by the reaction.

$C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$

at $600Kis1.60 \times 10^{-5}s^{-1}$. Its energy of activation is $209kJmol^{-1}$. Calculate the rate constant at $700K$

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11. In a reaction, $2A \rightarrow$ Products the concentration of A decreases from 0.5 mol $litre^{-1}$ to 0.4 mol $litre^{-1}$ in 10 minutes. Calculate rate during this interval.

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12. For a reaction, $A + B \rightarrow$ Product, the rate law is given by $r = k[A]^{\frac{1}{2}}[B]^2$. What is the order of the reaction ?

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13. The conversion of molecules X to Y follows second order kinetics. If the concenration of X is increased to three times, how will it affect the

rate of formation of Y ?

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14. A first order reaction has a rate constant $1.15 \times 10^{-3} s^{-1}$. How long will $5g$ of this reactant take to reduce to $3g$` ?

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15. Time required to decompose SO_2Cl_2 to half of its intial amount is $60min$. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

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16. What will be effect of temperature on rate constant ?

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17. The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate Ea.

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18. The activation energy for the reaction :

$2HI(g) \rightarrow H_2(g) + I_2(g)$

is $209.5kJmol^{-1}$ at $581K$. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy ?

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19. From the rate expression for the following reactions, determine their order of reaction and dimensions of the rate constants.

$a.\ 3NO(g) \rightarrow N_2O(g),$ Rate $= k[NO]^2$

$b.\ H_2O_2(aq) + 3I^-(aq) + 2H^{\oplus} \rightarrow 2H_2O(l) + I_3^-,$ Rate $= k[H_2O_2]\left[I^-\right]$

c. $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$, Rate $= k[CH_3CHO]^{3/2}$

d. $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$, Rate $k[C_2H_5Cl]$

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20. For the reaction :

$2A + B \rightarrow A_2B$

the rate $= k[A][B]^2$ with $k = 2.0 \times 10^{-6} mol^{-2} L^2 s^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1 mol L^-$, $[B] = 0.2 mol L^{-1}$. Calculate the rate of reaction after $[A]$ is reduced to $0.06 mol L^{-1}$.

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

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

Rate $= k[CH_3OCH_3]^{3/2}$

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

Rate $= k[p_{CH_3OCH_3}]^{3/2}$

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

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23. Mention the factors that affect the rate of a chemical reaction.

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

(a) doubled, (b) reduced to $1/2$?

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25. What is the effect of temperature on the rate constant of a reaction ? How can this temperature effect on rate constant be represented quantitatively ?

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

t/s	0	30	60	90
$[\text{Ester}]$	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

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27. A reaction is first order in A secod order in B:

(i) write differential rate equation.

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

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

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28. In a reaction between A and B, the initial rate of reaction was measured for different initial concentration of A and B as given below:

A/M	0.20	0.20	0.40
B/M	0.30	0.10	0.05
r_0/Ms^{-1}	5.07×10^{-5}	5.07×10^{-5}	7.6×10^{-5}

Calculate the order of reaction w.rt. A and B.

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29. The following rate data were obtained at $303K$ for the following reaction:

$2A + B \rightarrow C + D$

$2A + B \longrightarrow C + D$

Exp	[A] (mol L^{-1})	[B] (mol L^{-1})	Initial rate of formation of D
I	0.1	0.1	6.0×10^{-3} mol L^{-1} min^{-1}
II	0.3	0.2	7.2×10^{-2} mol L^{-1} min^{-1}
III	0.3	0.4	2.88×10^{-1} mol L^{-1} min^{-1}
IV	0.4	0.1	2.4×10^{-2} mol L^{-1} min^{-1}

What is the rate law? What is the order with respect to each reactant and the overall order? Also calculate the rate constant and write its units.

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30. 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/ mol L^{-1}	B/ mol L^{-1}	Initial rate/mol L^{-1} 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}

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

$a.\ 200s^{-1}, b.\ 2min^{-1}, c.4years^{-1}$

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32. The half life for radioactive decay of $.^{14}C$ is 5730 years. An archaeological artifact containing wood had only $80\ \%$ of the $.^{14}C$ found in a living tree. Estimate the age of the sample.

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

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

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35. For a first order reaction, show that the time required for 99% completion is twice the time required for the completion of 90% of reaction.

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

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37. For the decomposition of azoisopropane to hexane and nitrogen at 54 K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rare constant.

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38. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.5
2	100	0.6

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

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39. The rate constant for the decomposition of N_2O_5 at various temperatures

is given below:

$T/°C$	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 $50^\circ C$.

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

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

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42. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2} = 3.00hr$. What fraction of sample of sucrose remains after $8hr$?

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43. The decomposition of hydrocarbon follows the equation $k = \left(4.5 \times 10^{11} s^{-1}\right) e^{-28000K/T}$

Calculate E_a.

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

$$\log k\left(s^{-1}\right) = 14.34 - \frac{1.25 \times 10^4 K}{T}$$

(a) What is the energy of activation for the reaction?

(b) At what temperature will its half-life period be 256 min ?

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45. The decomposition of A into product has value of k as $4.5 \times 10^3 s^{-1}$ at $10^\circ C$ and energy of activation of $60kJmol^{-1}$. At what temperature would k be $1.5 \times 10^4 s^{-1}$?

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46. The time required for $10\,\%$ completion of a first order reaction at $298K$ is equal to that required for its $25\,\%$ completion at $308K$. If the value of A is $4 \times 10^{10} s^{-1}$, calculate k at $318K$ and E_a.

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

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Exercise

1. The concentration of a reactant changes form $0.03M$ to $0.02M$ in $25\ \text{min}$. Calculate the average rate of reaction uisng of time both in minutes and seconds.

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Solved Example

1. The experimental data for decomposition of N_2O_5

$[2N_2O_5 \rightarrow 4NO_2 + O_2]$

in gas phase at 318K are given below:

$t(s)$	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5]\,\text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot $[N_2O_5]$ against t.

(ii) Find the half-life period for the reaction.

(iii) Draw a graph between $\log[N_2O_5]$ and t.

(iv) What is the rate law ?

(v) Calculate the rate constant.

(vi) Calculate the half-life period from k and compare it with (ii).

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