

CHEMISTRY

JEE (MAIN AND ADVANCED) CHEMISTRY

CHEMICAL KINETICS

Problems

1. Formation of water from its elements is spontaneous, but is slow.

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2. Express the rate of the reaction between bromide and bromate ions in acid medium.



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3. $N_2 + 3H_2 \rightarrow 2NH_3$. The rate of disappearance of nitrogen is $0.02 \text{ mol L}^{-1} \text{ s}^{-1}$. What is the rate of appearance of ammonia ?



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4. $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$, $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$.
Which is relatively faster ? Why ?



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5. Decolourisation of acidified permanganate is fast by Mohr's salt ,
but is slow by oxalate . Explain .



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6. At $27^{\circ}C$ and $37^{\circ}C$, the rates of a reaction are given as $1.6 \times 10^{-2} mol L^{-1} s^{-1}$ and $3.2 \times 10^{-2} mol L^{-1} s^{-1}$. Calculate the energy of activation for the given reaction .

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7. The temperature coefficient of a reaction is 2 and the rate of the reaction at $25^{\circ}C$ is $3 mol L^{-1} min^{-1}$. Calculate the rate at $75^{\circ}C$.

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8. Pre -exponential factor for a reaction is $8.4 \times 10^{21} mol L^{-1} s^{-1}$. What will be the specific rate at temperature of one million degree ?

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9. A_2B is an ideal gas, which decomposes according to the equation: $A_2B \rightarrow A_2 + \frac{1}{2}B_2$. At start, the initial pressure is 100 mm Hg and after 5 minutes, the pressure is 120 mm Hg. What is the average rate of decomposition of A_2B ? Assume T and V are constant.



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10. Rate of a chemical reaction depends on concentration of reactant is independent on concentration. Why?



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11. For a reaction $aA \rightarrow \text{Products}$, the units of rate constant are given as $Lmol^{-1}s^{-1}$. Write the rate expression.



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12. Rate expression for two reaction are : (a) $\text{rate}_a = k_a[A]$ and (b) $\text{rate}_b = k_b[B]^2$. When $[A] = [B] = 1 \text{ mol L}^{-1}$, $k_a = k_b \text{ mol L}^{-1}$. If $[A] = [B] = 2 \text{ mol L}^{-1}$, write the relation between rate_a and rate_b .



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13. Units of rate constant is the same for the elementary reactions :

Reaction (1) $A + B + C \rightarrow \text{products}$,

Reaction (2) , $A + 2B \rightarrow \text{products}$,

Reaction (3), $3A \rightarrow \text{products}$. Substantiate.



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14. The decomposition of nitrogen pentoxide is given as

$2N_2O_5 \rightarrow 4NO_2 + O_2$. The rates of reaction are

$$\frac{[N_2O_5]}{\Delta t} = k_1[N_2O_5], \quad \frac{\Delta[NO_2]}{\Delta t} = k_2[N_2O_5] \quad \text{and} \quad \frac{\Delta[O_2]}{\Delta t} = k_3[N_2O_5]$$

Relate the rate constants k_1 , k_2 and k_3 .



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15. An increase in temperature by 10° , can increase the number of collisions only by 2% , but the rate of reaction increases by 100%. Why?



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16. What is the difference between activated complex and unstable intermediate ?



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17. At 25°C the activation energy for a catalysed reaction is 126KJmol^{-1} and for uncatalysed reaction is 350KJmol^{-1} . How many times the rates is increased in the presence of catalyst ?



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18. Energy of activation and orientation of molecule together determine the criteria for effective collision . Explain.



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19. For the reaction $X \rightarrow Y + Z$ if the initial concentration of X was reduced from 2M to 1M in 20 min and from 1M to 0.25M in 40min , find the order .



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20. A first order reaction is 20% complete in 10 min. How long it takes to complete 80% ?



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21. $2NO + H_2 \rightarrow N_2O + H_2O$, The reaction , follows third order kinetics.

Write (a) rate law and (b) units of rate constant.

What happens to the rate if the volume of vessel is reduce to one - half at constnat temperature ?



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22. The initial concentration of ethyl acetane is 0.85 mol L^{-1} . Following the acid catalysed hydrolysis the , concentrations of ester after 30 min and 60 min of the reaction are respectively

0.8 and 0.754 mol L^{-1} . Calculate the rate constant and pseudo rate constant.



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23. At 193°C , the rate law for the reaction $2\text{Cl}_2\text{O} \rightarrow 2\text{Cl}_2 + \text{O}_2$ is $\text{rate} = k[\text{Cl}_2\text{O}]^2$.

(a) How the rate changes if $[\text{Cl}_2\text{O}]$ is raised to threefold of the original?

(b) How should $[\text{Cl}_2\text{O}]$ be changed in order to double the rate?



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24. The rate of a reaction is given as, $\text{rate} = k[\text{X}]^{3/2}[\text{Y}]^{-1/2}$

What is the order of the reaction? If Y is taken large in excess, write the rate equation.



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25. A and B are two radioactive substance with half lives 20 min and 30 min respectively. Starting from equal number of moles A and B, after 1hr, what is the (a) ratio of moles of A and B and (b) ratio of activity of A and B ?



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26. Half-life of ^{210}Pb is 22 years. 2gram of lead is allowed decay for 11 years. (a) How much lead is left ?and (b) What is the percentage decay ?



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1. Mention different types of reaction based on their speeds . Give examples .



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2. What are average rate and instant rate ? How is rate determined graphically ?



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3. How nature and concentration of reactants influence the rate of a reaction .



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4. Discuss the effect of temperature on the rate of a reaction.



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5. What is catalyst ? How does it influences the rate ?



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6. Define rates with respect to substance and rate of the reaction for Haber's process. $N_2 + 3H_2 \rightarrow 2NH_3$.



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



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8. For the reaction $R \rightarrow P$, the concentration of a reaction changes from 0.03 M to 0.02 M in 25 minutes . Calculate the average rate of reaction .

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9. The first order rate constant for the decomposition of ethyl iodide by the reaction.

$C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$ at 600 K is $1.60 \times 10^{-5} s^{-1}$. It's energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700 K.

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1. Define rate law . How is it related to the stoichiometric equation and experimental result ?



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2. What are (a) rate constant and (b) specific rate ? Write the units of rate constant.



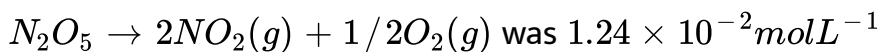
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3. Write four main difference between reaction rate and reaction rate constant.



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



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5. Write the rate law units of rate constant for the following elementary reactions.

(a) $A + B \rightarrow \text{Products}$. (b) $2A \rightarrow \text{Products}$, (c) $2A + B \rightarrow \text{Products}$ and (d) $A + 2B \rightarrow \text{Products}$.



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6. For the decomposition of azoisopropane to hexane and nitrogen at 543 K , the following data are obtained .

t(sec) P(mm of Hg)

0 35.0

360 54.0

720 63.0



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Exercise 3 1 3

1. What is activated complex ? Discuss its formation and transformation .



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2. Write the main points of collision theory of reaction rates .



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3. Distinguish between a proper and an improper collision .



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4. How is the reaction rate influenced by energy of activation ?



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



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6. The activation energy for the reaction $2HI(g) \rightarrow H_2 + I_2(g)$ is 209.5 KJmol^{-1} at 581 K. Calculate the fraction of molecules of

reactants having energy equal to or greater than activation energy

?



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Exercise 3 2

1. Discuss on the kinetic spontaneity of a chemical reaction. Is a slow reaction spontaneous? Why?



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2. Why the reactions involving covalent substances are slow? How they can be made rapid?



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3. How are rate and rate constant related to a free radical reaction?



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4. Write on the concept of reaction rate with respect to reactant and with respect to product. Equate them.



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5. What are reaction rate and specific rate? Write their units.



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6. What is the role played by catalyst to alter the rate of reaction? Explain diagrammatically.



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7. Time requires for 99% completion of a first order reaction is twice to that required for 90% completion of the same reaction. Explain.



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8. Acid hydrolysis of ester is more rapid in heavy water than in water. Why?



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9. A collision that attains threshold energy level need not be successful. Explain.



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10. Decomposition of ozone to oxygen proceeds in two steps : Step 1 (fast) $O_3 \rightleftharpoons O_2 + (O)$ and Step 2 (slow) , $O_3 + (O) \rightleftharpoons 2O_2$. The rate law is , rate $=K[O_3]^2[O_2]^{-1}$. Explain.



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11. $A \rightarrow$ products. The concentration of A changes from 0.2 to 0.15 mol L^{-1} in 10 min. Calculate the average rate.



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12. $Cl_2 + 2I^- \rightarrow 2ClI^- + I_2$, was carried out in water . Initial concentration of iodide ion was $0.25 mol L^{-1}$. Calculate the rate of appearance of iodine.



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13. Bond energy and orientation play a role in the determination of effectiveness of the collision. Comment.



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14. What is activated complex? How is it formed and transformed into product?



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15. Discuss the energy barrier diagram for reaction rates. When the reaction becomes exothermic Discuss and when it will be endothermic?



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16. The rate of a reaction triples when temperature changes from 20°C to 50°C . Calculate the energy of activation.



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17. The rate constant at 0°C is $7.87 \times 10^{-7}\text{s}^{-1}$ for a reaction whose energy of activation is 103kJmol^{-1} . Calculate the rate constant at 20°C .



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18. Decomposition of X and Y obey first order with half lives 54 and 18 min, respectively. Starting with $[X]/[Y] = 1$, calculate the time required for the ratio 4:1.



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19. In the chemical reaction, $3A + B \rightarrow 2C + 3D$, the rate of appearance of C is reported as $1\text{molL}^{-1}\text{s}^{-1}$. What is the rate of disappearance of A?



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20. Decay constant of a nuclear reaction is temperature independent. Why?



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21. At 380°C , the half life of decomposition of hydrogen peroxide is 6 hr and activation energy is 200KJmol^{-1} . Calculate the times required for 50% and 75% decomposition at 450°C .



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22. The rate constant of a first order reaction at 500 K is $2.35 \times 10^{-5} \text{ s}^{-1}$. At what temperature, the half-life of the reaction is 256 min?



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23. With 100 kJ mol⁻¹ activation energy for an uncatalysed reaction at 20°C, the catalyst lowers the energy of activation by 75%. What will be the effective rate if other conditions are same?



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24. Write the rate equation, integral rate constant and half life dependence with initial concentration for zero order and second order reactions.



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25. When rate is plotted vs $(a - x^n)$, a straight line is obtained with positive slope, passing through origin. Draw the graphs and discuss.



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26. What is a pseudo - order reaction ? Why is it so called ?



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27. If a second order reaction is 75% complete in 1 hr , calculate the rate constant .



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28. For a reaction , the reactant concentration decreases 20% in 1 hr and 40% in 2hr. What are the units of rate constant ?



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29. The rate of a first order reaction is $0.04 \text{ mol L}^{-1} \text{ s}^{-1}$ after 10 s, and $0.03 \text{ mol L}^{-1} \text{ s}^{-1}$ after 20 s of starting the reaction . Calculate the half- life of the reaction .



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30. A reaction proceeds 5 times more at 60° C , as it does at 30° C . Calculate the energy of activation.



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31. Rate constant of a reaction is 10^{-3} s^{-1} . Calculate the percentage completion of the reaction in .



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32. For a reaction $A + 2B \rightarrow 2C$, the kinetic data is given below:

[A] mol L^{-1}	[B] mol L^{-1}	Initial reaction rate $\text{mol L}^{-1}\text{min}^{-1}$
1.0	1.0	0.15
1.0	2.0	0.15
2.0	1.0	0.30
3.0	2.0	0.45

Determine the order of the reaction and write the rate law.



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33. Time required for 50% completion of the first order reaction in one hr. What is the time required for 99% completion of the same

reaction ?



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34. A first order reaction is 50% complete in min at $27^{\circ}C$? and 10 min at $47^{\circ}C$. Calculate the rate constant and activation energy at $27^{\circ}C$.



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35. The concentrations of N_2O_5 decomposing in first order kinetics after 800 s is 1.45molL^{-1} and after 1600 s is 0.88molL^{-1} . Calculate the rate constant.



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36. $CH_3OCH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$. The decomposition follows first order kinetics at $500^\circ C$ and has half - life 14.5 min. Initially only dimethyl ether is present at a pressure of 0.4 atm. Calculate the pressure of the mixture after 12 min.



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37. For the catalytic decomposition of a substance , half - lives are given below .

Pressure (pascal)	6667	13333	26666
Half life (Hours)	3.52	1.92	1.0

Calculate the order of reaction.



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38. A drop of solution (0.05 mL) contains 2×10^6 mol of H^+ . How long it takes for this H^+ to disappear, if the rate constant is 10^7 mol $L^{-1} s^{-1}$?



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39. Half-life period of ^{14}C is 5770 years. If an old wooden toy has 0.25% of activity of ^{14}C . Calculate the age of toy. Fresh wood has 2% activity of ^{14}C .



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40. Ten gram atoms of an alpha active element disintegrated in a sealed container in one hour. If the gas collected is 11.2 cc at STP, calculate the half-life of the radioactive element.



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41. During nuclear explosion , one of the products is ^{90}Sr with half - life of 28.1 years. 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 ^{14}C found in a living tree. Estimate the age of the sample.



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42. 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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43. Acid catalysed hydrolysis of ethylacetate can be considered as an example of pseudo first order reaction. Explain.



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44. Rate of decomposition of a substance increases by a factor 2.25 for 1.5 times increase in concentration at constant temperature . Calculate the order of reaction.



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



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