

MASTER CARD FOR THE TOPIC CHEMICAL KINETICS

1. Define Pseudo unimolecular reaction with example.

Ans. Reaction of higher order under certain condition follow the kinetics of lower order known as pseudo unimolecular reaction.

Ex- (i) $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$

$$\text{Rate} = k[\text{CH}_3\text{COOH}]$$

$$[\text{H}_2\text{O}] = \text{constant}$$

Ex-(ii) Hydrolysis of sugar.

2. Under what condition reaction becomes a pseudo unimolecular reaction.

Ans. When the concentration of water remains constant

3. Write the formula to determine the order from rate constant.

Ans. $k(\text{mol L}^{-1})^{1-n} \text{sec}^{-1}$ for gases reaction

$$k = (\text{atm or bar})^{1-n} \text{sec}^{-1}$$

Where $n=0,1,2,3$, that refers to the order.

4. What is the difference b/w order and molecularity of a reaction?

Ans.

ORDER	MOLECULARITY
1. If the sum of the power of concentration term appeared in the rate law expression.	It is the no. of molecules that take part in a chemical
2. Order is experimentally determined fact	It is the theoretical concept
3. It can be zero	It can never be zero
4. It can be fractional	It can not be fractional

5. What is the difference between rate of reaction and rate constant.

Ans:-

O	Rate constant
1. It is the change in the molar concentration of the reactant per unit time.	It is the proportionality constant of a reaction and is equal to the rate of reaction when the molar concentration of each reactant is unity.
2. Its unit is mol/L/Time	Its unit depends upon the nature of reaction and upon the order of the reaction.
3. Its value depends upon molar concentration of the reactant.	Its value is independent of the molar concentration of the reactant and depends upon temp.

6. Define rate law and activation energy.

Ans:- It is the mathematical expression that gives the true rate of a reaction in terms of molar concentration of the reactant as determined experimentally.

Activation Energy:- The minimum amount of energy supplied to the reactant molecule to make them

able to cross the energy barrier.

7. Give an example of each order.

Ans:- Zero Order $2\text{NH}_3 \xrightarrow{\text{Pt}} \text{N}_2 + 3\text{H}_2$ $r = k[\text{NH}_3]^0$

First Order $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ $r = k[\text{N}_2\text{O}_5]$

Second Order $2\text{HI} \xrightarrow{\text{H}_2 + \text{I}_2} 2\text{H}_2\text{I}$ $r = k[\text{HI}]^2$

Third order reaction $2\text{NO} + \text{O}_2 \xrightarrow{2\text{NO}_2} 2\text{NO}_2$ $r = k[\text{NO}]^2[\text{O}_2]$

Fractional order $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ $r = k[\text{H}_2][\text{Br}_2]^{1/2}$

8. Write mathematical expression for Arrhenius Equation and explain all the terms. OR Write the relation of rate constant with temperature.

Ans:-

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

Where k = Rate constant

A = Pre exponential factor

E_a = Activation energy.

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

T = Temp in K scale.

9. Write mathematical expression for the following.

(i) rate constant for 1st order

(ii) rate constant for zero order

(iii) half life for zero order

(iv) half life for first order

(v) rate constant and activation energy

Ans. ; (i) $k = 2.303/t \log[A]_0/[A]$

$$(ii) k = [A]_0/[A]t$$

$$(iii) t_{1/2} = [A]_0/2k$$

$$(iv) t_{1/2} = 0.693/k$$

$$(v) \log k = \log A - E_a/2.303RT$$

$$\text{Or } \log k_2/k_1 = E_a/2.303R[1/T_1 - 1/T_2]$$

10. (i) Plot a graph between log A VS t for first order.

(ii) Rate and Concentration for first order

(iii) $t_{1/2}$ and Concentration for first order

Ans: Concept of graph is the equation of straight line $y = mx + C$ where C is intercept m = slope.

Similarly for zero order and Arrhenius equation.

11. A reaction is of 2nd order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled

(ii) reduced to half

[CbSE2012]

Ans. Rate = $k[A]^2$

(i) $A = 2A$

$$\text{Rate} = k[2A]^2 = 4k[A]^2$$

i.e. the rate of reaction increases by four times.

(ii) if half
 $[A] = [A]/2$
 $\text{Rate} = 1/4K[A]^2$
 The rate of reaction becomes $1/4$ the initial rate .

12.(a) For a reaction $A+B \rightarrow P$, the rate law is given by $r = K[A]^{1/2}[B]$ What is the order of the reaction.

(b) A first order reaction is found to have a rate constant $K = 5.5 \times 10^{-14} \text{ sec}^{-1}$ find the half life of the reaction. [CBSE2013]

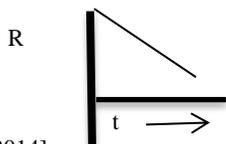
Ans:- (a) $\text{Order} = 1/2 + 2 = 5/2$
 (b) $t_{1/2} = 0.693/K = 0.693/5.5 \times 10^{-14} \text{ sec}^{-1} = 1.26 \times 10^{13} \text{ sec}$

13. The rate of a reaction becomes four times when the temperature changes from 293K to 313K. Calculate the energy of activation of the reaction assuming that it does not change with

temperature. $R = 8.314 \text{ J/k.mol}$. $\log 4 = 0.6021$ (3) [CBSE2013]

Ans:- $\log K_2/K_1 = E_a/2.303R[1/T_1 - 1/T_2]$
 $T_1 = 293 \text{ K}, T_2 = 313 \text{ K}, K_1 = K, K_2 = 4K$
 $\log 4K/K = E_a/2.303 \times 4.314 [1/293 - 1/313]$
 $E_a = 52.863 \text{ KJ/mol}$

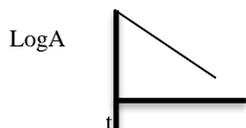
14. For a chemical reaction $R \rightarrow P$ the variation in the concentration R between time (t) plot is given as (2)



[CBSE2014]
 (i) Predict the order of the reaction
 (ii) What is the slope of the curve
 Ans: (i) Zero order reaction
 (ii) slope = $-K$

Hint: $-K = [A]_0/[A]_t/t$
 $[A] = -kt + [A]_0$
 $y = mx + c$

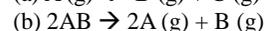
15. Study the curve and answer the questions.



(i) What is order
 (ii) Write expression K for that order
 (iii) Write Unit of rate constant
 (iii) Write expression $t_{1/2}$ for that order
 Ans: (i) 1st order
 (ii) $K = 2.303/t \log [A]_0/[A]$
 (iii) $K = \text{time}^{-1}$
 (iv) $t_{1/2} = 0.693/K$

(i) $Kt/2.303 = \log [A]_0 - \log [A]$
 $\log [A] = -Kt/2.303 + \log [A]_0$

16. Write the expression for rate constant K for following types of 1st order reaction in gaseous phase.



Ans:- (a) $K = 2.303/t * \log P_0/2P_0 - P_t$

(b) $K = 2.303/t * \log P_0/3P_0 - 2P_t$

17. The following data were obtained during the 1st order thermal decomposition of SO_2Cl_2 at constant volume. [CBSE 2014]



Expt.	Time/s ⁻¹	Total pressure /atm
1	0	0.4
2	100	0.7

Calculate the rate constant. Given $\log 4 = 0.6021$ and $\log 2 = 0.3010$

Ans: - use formula

$K = 2.303/t \log P_0/2P_0 - P_t$

At $T = 100 \text{ s}$

$K = 2.303/t \log 0.4/0.8 - 0.7$
 $= 2.303/100 \log 0.4/0.1$
 $= 2.303/100 \log 4 - \log 1$
 $= 2.303/100 * 0.6021 - 0$
 $= 1.39 * 10^{-2} \text{ sec}^{-1}$

18. The rate constant of a first order reaction increases from $2 * 10^{-2}$ to $4 * 10^{-2}$. When the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a) [CBSE 2015]

$\log 2 = 0.3010$ $\log 6 = 0.6021$

Ans: $\log K_2/K_1 = E_a/2.303 [1/T_1 - 1/T_2]$

$\log 4 * 10^{-2} / 2 * 10^{-2} = E_a/2.303 [1/300 - 1/310]$

$\log 2 = E_a/2.303 * 310 - 300/300 * 310$

$0.3010 = E_a/2.303 * 10/300 * 310$

So, $E_a = 0.3010 * 2.303 * 300 * 310/10$

So, $E_a = 53.598 \text{ KJ/mol}$.

19. For the reaction $A+B \rightarrow$ products, the following initial rates were obtained at various given initial concentrations. [CBSE 2011]

Sr No.	[A]	[B]	Rate ($\text{mol l}^{-1} \text{ sec}^{-1}$)
I	0.1	0.1	0.05
II	0.2	0.1	0.10
III	0.1	0.2	0.05

Write rate law and rate constant for the above reaction.

Ans: $-r = K [A]^x [B]^y$

$0.05 = K (0.1)^x (0.1)^y$ --- i

$0.10 = K (0.2)^x (0.1)^y$ --- ii

$0.05 = K (0.1)^x (0.2)^y$ --- iii

Dividing ii by i

$0.10/0.05 = K (0.2)^x (0.1)^y / K (0.1)^x (0.1)^y$

$2^1 = 2^x$

So, $X=1$

Dividing iii by i

$0.05/0.05 = K (0.1)^x (0.2)^y / K (0.1)^x (0.1)^y$

$2^0 = 1 = 2^y$

$Y=0$

$r = K [A]^1 [B]^0$

$K = \text{rate} / [A]^1 [B]^0$

$= 0.05/0.10$

$= 1/2 = 0.05 \text{ ans.}$

20. Fill in the blanks in the following table which treats are reactions of a compound A with a compound B that is the first order w.r.t. A and zero order w.r.t. B.

Expt.	[A]	[B]	Initial rate
I	0.1	0.1	$2.0 * 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$
II	_____	0.2	$4.0 * 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$
III	0.4	0.4	_____
IV	_____	0.2	$2.0 * 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$

Ans: $-r = K [A]^1 [B]^0$

$2.0 * 10^{-2} = K(0.1) (0.1)^0$

So, $K = 2.0 * 10^{-1} \text{ min}^{-1}$

From Expt. II

$4.0 * 10^{-2} = r = K [A]^1 [0.2]^0$

$4.0 * 10^{-2} = 2.0 * 10^{-1} * [A]$

$[A] = 2.0 * 10^{-1}$

$[A] = 0.2 \text{ mol L}^{-1}$

Expt. III

Rate = $K [A]^1 [B]^0$

$= 2.0 * 10^{-1} * 0.4$

$= 0.08 \text{ mol L}^{-1}$

Expt. IV

Rate = $K [A]^1 [B]^0$

$2.0 * 10^{-2} = 2.0 * [A]$

$[A] = 0.1 \text{ mol L}^{-1}$

21. For a first order reaction show that the time required for 99% completion of a 1st order reaction is twice the time required for the completion of 90%

Ans: $-K = 2.303/t \log [A]_t/[A]$

T for 99%

$T_{99} = 2.303 / K \log 100/100-99 = 2.303/K \log 10^2$

$= 2.303/K * 2 * \log 10$

$= 2.303/K * 2$ -----I

T for 90%

$T_{90} = 2.303/k \log 100/10$

$T_{90} = 2.303/K \log 10$

$= 2.303/k * 1$ ---- II

Dividing I by II

$T_{99}/T_{90} = 2 * 2.303/K / 2.303/K$

$T_{99} = 2 * T_{90}$

22. What are the factors that affect the rate of reaction?

- (i) Nature of reactant
- (ii) Concentration of reactant
- (iii) Temperature
- (iv) Presence of catalyst
- (v) Surface area of reactant
- (vi) Presence of light

23. Write the average rate for the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, the change of concentration of NO_2 is from 2.06 to 1.04 in 60s. K is $1.62 * 10^{-4} \text{ s}^{-1}$.

Ans. Average rate = $-1/2 \Delta[\text{N}_2\text{O}_5] / \Delta t = + 1/4 \Delta[\text{NO}_2] / \Delta t = + \Delta[\text{O}_2] / \Delta t$

Put the value and solve

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