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- 1. If the instantaneous rate of appearance of $NO_2(g)$ is 0.0400 M/s at some moment in time, what is the rate of disappearance of N_2O_5 (g) in M/s? (a) 0.02 (b) 0.01 (c) 0.04(d) 0.08
- 2. For a chemical reaction $A \longrightarrow$ Products, the rate of disappearance of A is given by : $-\frac{dC_A}{dt} = \frac{K_1C_A}{1+K_2C_A}$ At very low C_A, the reaction is of the order with rate constant..... :

(Assume K_1 , K_2 are lesser than 1) (a) I, K_1/K_2 (b) I, K_1 (c) II, K_1/K_2 (d) II, $K_1/K_1 + K_2$

3. For a gaseous reaction, the rate is expressed in terms of $\frac{dP}{dt}$ in place of $\frac{dC}{dt}$ or $\frac{dn}{dt}$, where C is concentration, n is number of moles

and 'P' is pressure of reactant. The three are related as -

(a)
$$\begin{bmatrix} \frac{dP}{dt} \end{bmatrix} = \frac{RI}{V} \begin{bmatrix} \frac{dn}{dt} \end{bmatrix} = \begin{bmatrix} \frac{dC}{dt} \end{bmatrix}$$

(b) $\frac{1}{RT} \begin{bmatrix} \frac{dP}{dt} \end{bmatrix} = \frac{1}{V} \begin{bmatrix} \frac{dn}{dt} \end{bmatrix} = \begin{bmatrix} \frac{dC}{dt} \end{bmatrix}$
(c) $\begin{bmatrix} \frac{dP}{dt} \end{bmatrix} = \begin{bmatrix} \frac{dn}{dt} \end{bmatrix} = \begin{bmatrix} \frac{dC}{dt} \end{bmatrix}$

(d) None of these

4. For a reaction, $A \longrightarrow B$; if

> $\log_{10} \text{ K} (\text{sec}^{-1}) = 14 - \frac{1.25 \times 10^4}{\text{T}}$ K, the frequency factor and energy of activation for the reaction are -(a) 10^{14} sec⁻¹, 239.34 kJ (b) 14, 57.6 kcal (c) 10^{14} sec⁻¹, 23.93 kJ (d) 10^{14} sec, 5.76 kcal

> > (d) 2

5. For a particular reaction variation of rate constant with temperature is given by

 $\ell n k_t = \ell n k_0 + \left(\frac{\ell n 3}{10}\right) t \quad (t \ge 0^{\circ} C)$ Temp. Coefficient of reaction is -(a) 4 (b) 3 (c) 10

- In the first order reaction, the concentration of the reactants is reduced to 25% in one hour. The half-life period of the reaction is -6. (a) 2 hr (b) 4 hr (c) 1/2 hr (d) 1/4 hr
- 7. The following mechanism has been proposed for the reaction of NO with Br₂ to from NOBr $NO(g) + Br_2(g) \implies NOBr_2(g)$

 $NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$ If the second step is the rate determining step, the order of the reaction with respect to NO(g) is (a) 0 (b) 3 (c) 2 (d) 1

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

log k = constant $-\frac{E_a}{2.303RT}$. When a graph is plotted for log k versus $\frac{1}{T}$ a straight line with a slope -5632 is obtained. The energy of activation for this reaction is -(a) $127.67 \text{ kJ mol}^{-1}$ (b) 107.84 kJ mol⁻¹ (c) 86 kJ mol⁻¹ (d) 246.8 kJ mol⁻¹

9. For reaction $2A + B \longrightarrow D + E$, following mechanism has been proposed mechanism $A + B \longrightarrow C + D \dots$ Slow

(b) r = K[A][B]

 $A + C \longrightarrow E$ fast Rate law for the reaction (a) $r = K[A]^{2}[B]$ (d) $r = K[\underline{A}][C]$ (c) r = K[A]

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- 10. In reaction A ⇒ B, if initial concentration of reactant is changed from 5 M to 10 M, half life of reaction changes from 50 minute to 25 minute. Order of reaction is :

 (a) 2nd
 (b) Zero
 (c) 1st
 (d) None of these
- 11. For a reaction $\frac{dx}{dt} = K[H^+]^n$. If pH of reaction medium changes from two to one the rate becomes 100 times of value at pH = 2, The order of reaction is -

(a) 1 (b) 2 (c) 0 (d) 3

- 12. In the respect of the equation k = Ae^{-Ea/RT} in chemical kinetics, which one of the following statements is correct :
 (a) K is equilibrium constant
 (b) A is adsorption factor
 (c) E_a is energy of activation
 (d) R is Rydberg constant.
- 13. The rate equation for the reaction $2A + B \longrightarrow C$ is found to be: rate = k[A] [B]. The correct statement in relation to this reaction is that the :
 - (a) Unit of k must be \sec^{-1}
 - (b) $t_{1/2}$ is a constant
 - (c) Rate of formation of C is twice the rate of disappearance of A
 - (d) Value of k is independent of initial concentrations of A and B.
- 14. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will be(a) Remain unchanged(b) Tripled
 - (c) Increased by a factor of 4 (d) Doubled
- 15. For a reaction A 2B, rate of disappearance of 'A' related to the rate of appearance of 'B' by the expression.

(a)
$$-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$$
 (b) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$
(c) $-\frac{d[A]}{dt} = 4 \frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$

16. For a first order reaction (a) \Box products the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M is :

(a) 1.73×10 ⁻⁵ M/min	(b) 3.47×10^{-4} M/min
(c) 3.47×10 ⁻⁵ M/min	(d) 1.73×10 ⁻⁴ M/min

17. In the following reaction :

 $xA \longrightarrow Yb$ $log\left[-\frac{d[A]}{dt}\right] = log\left[-\frac{d[B]}{dt}\right] + 0.3 \text{ where } -ve \text{ sign}$ indicates rate of disappearance of the reactant. Thus, x : y is : (a) 1 : 2 (b) 2 : 1 (c) 3 : 1 (d) 3 : 10

- 18. For the reaction, $2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$ the rate expression can be written in the following ways: $\{d[N2]/dt\} = k1[NO][H2]; \{d[H2O]/dt\} = k[NO][H2];$ $\{-d[NO]/dt\} = k1[NO][H2]; \{-d[H2]/dt\} = k 1[NO][H2]$ The relationship between k, k₁, k'₁ and k''₁ is:
 - (a) $k = k_1 = k'_1 = k''_1$ (b) $k = 2k_1 = k'_1 = k''_1$ (c) $k = 2k'_1 = k_1 = k''_1$ (d) $k = k_1 = k'_1 = 2k''_1$
- 19. For the irreversible process, A + B products, the rate is first-order w.r.t. A and second-order w.r.t. B. If 1.0 mol each of A and B introduced into a 1.0 L vessel, and the initial rate was 1.0×10^{-2} mol L⁻¹ s⁻¹, rate when half reactants have been turned into products is :

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$$\begin{array}{ll} \text{(a)} \ 1.25\times 10^{-3} \text{mol } L^{-1} \ \text{s}^{-1} & \text{(b)} \ 1.0\times 10^{-2} \text{mol } L^{-1} \ \text{s}^{-1} \\ \text{(c)} \ 2.50\times 10^{-3} \text{mol } L^{-1} \ \text{s}^{-1} & \text{(d)} \ 2.0\times 10^{-2} \text{mol } L^{-1} \ \text{s}^{-1} \end{array}$$

20. A reaction follows the given concentration (M)-time graph. The rate for this reaction at 20 seconds will be :



(a) 4×10^{-3} M s⁻¹ (b) 8×10^{-2} M s⁻¹ (c) 2×10^{-2} M s⁻¹ (d) 7×10^{-3} M s⁻¹

21. In three different reactions, involving a single reactant in each case, a plot of rate of the reaction on the y \Box axis, versus concentration of the reactant on the x \Box axis, yields three different curves shown below.



What are the possible orders of the reactions (i), (ii), (iii). (a) 1, 2, 3 (b) 2, 1, $\frac{1}{2}$ (c) 0, 1, 2 (d) 0, 1, $\frac{1}{2}$

22. The substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as : $\kappa \rightarrow B$

 $K_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$ and $K_2 = 3.8 \times 10^{-5} \text{ sec}^{-1}$ The percentage distribution of B and C(a) 80% B and 20% C(b) 76.83% B and 23.17% C(c) 90% B and 10% C(d) 60% B and 40% C

23. For a reaction A \otimes B, $E_a = 10 \text{ kJ mol}^{-1}$, DH = 5 kJ mol $^{-1}$. Thus, potential energy profile for this reaction is :



24. The reaction of NO_2 (g) and O_3 (g) is first-order in NO_2 (g) and O_3 (g)

$$2 \operatorname{NO}_{2}(g) + \operatorname{O}_{3}(g) \longrightarrow \operatorname{N}_{2}\operatorname{O}_{5}(g) + \operatorname{O}_{2}(g)$$

The reaction can take place by mechanism :

$$I: NO_2 + O_3 \xrightarrow{Slow} NO_3 + O_2$$

$$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$$

k_a fast

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II :
$$O_3 \xrightarrow{k_b} O_2 + [O]$$

 $NO_2 + O \xrightarrow{Slow} NO_3$
 $NO_3 + NO_2 \xrightarrow{fast} N_2O_5$
Select correct mechanism.
(a) I only (b) II only
(c) Both I and II (d) None of I and II

25. A sample of rock from moon contains equal number of atoms of uranium and lead ($t_{1/2}$ for U = 4.5 × 10⁹ years). The age of the rock would be :

(a) 9.0×10^9 years (b) 4.5×10^9 years (c) 13.5×10^9 years (d) 2.25×10^9 years

26. A graph plotted between log $t_{50\%}$ vs. log concentration is a straight line. What conclusion can you draw from this graph.



28. Inversion of sucrose $(C_{12}H_{22}O_{11})$ is first-order reaction and is studied by measuring angle of rotation at different instant of time $C_{12}H_{22}O_{11}H_2O \xrightarrow{H^+} C_{16}H_{12}O_6 + C_6 + H_{12}O_6$ Sucrose Glu cose Fructose If $(\mathbf{r}_{\infty} - \mathbf{r}_0) = a$ and $(\mathbf{r}_{\infty} - \mathbf{r}_t) = (a - x)$ (where \mathbf{r}_0 , \mathbf{r}_t and \mathbf{r}_{∞} are the angle of rotation at the start, at the time t and at the end of the reaction respectively, then there is 50% inversion when :

(a) $\mathbf{r}_{0} = 2\mathbf{r}_{t} - \mathbf{r}_{\infty}$ (b) $\mathbf{r}_{0} = \mathbf{r}_{t} - \mathbf{r}_{\infty}$ (c) $\mathbf{r}_{0} = \mathbf{r}_{t} - 2\mathbf{r}_{\infty}$ (d) $\mathbf{r}_{0} = \mathbf{r}_{t} + \mathbf{r}_{\infty}$

29. For the following parallel chain reaction



What will be that value of overall half-life of A in minutes? Given that $\frac{[B]_t}{[C]_t} = \frac{16}{9}$

(a) 3.3 (b) 6.3 (c) 3.6 (d) None

30. Consider the following reactions at 300 K.

 $A \rightarrow B$

(uncatalysed reaction)

 $A \xrightarrow{catalyst} B$ (catalyst reaction)

The activation energy is lowered by 8.314 KJ mol⁻¹ for the catalysed reaction. How many times the rate of this catalysed reaction greater than that of uncatalysed reaction ? (Given $e^{3.33} = 28$) (a) 15 times (b) 38 times (c) 22 times (d) 28 times

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$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$
$$\frac{2N_2O_5}{1} = \frac{R_{NO_2}}{2}$$
$$= \frac{.04}{2}$$
$$= 0.02$$

2. (b)

 $-\frac{dC_A}{dt} = \frac{K_1C_A}{1+K_2C_A}$ At very low C_A: 1 >> K₂C_A; (1 + K₂V_A) ≈ 1 \therefore rate = $-\frac{dC_A}{dt} = K_1C_A$; Rate constant = K₁ order = 1

3. (b)

$$Rate = \frac{dC}{dt}$$

$$C = \frac{n}{V} \text{ and } C = \frac{P}{RT}$$

$$\frac{dC}{dt} = \frac{d}{dt} \left(\frac{n}{V}\right) = \frac{1}{V} \times \left(\frac{dn}{dt}\right)$$

$$\frac{d}{dt} \left(\frac{P}{RT}\right) = \frac{1}{RT} \times \left(\frac{dP}{dt}\right)$$

$$\begin{split} & \text{og}_{10} \text{ K}(\text{sec}^{-1}) = 14 - \frac{1.25 \times 10^4}{\text{T}} \\ & \text{log}_{10} \text{ K} = \text{log}_{10} \text{ A} - \frac{\text{E}_a}{2.303 \text{RT}} \\ & \text{log}_{10} \text{ A} = 14 \\ & \text{A} = 10^{14} \text{ sec}^{-1} \text{ and } \frac{\text{E}_a}{2.303 \text{R}} = 1.25 \times 10^4 \text{ ;} \\ & \text{E}_a = 1.25 \times 2.303 \times 10^4 \times 8.314 \text{ J} \\ & \approx 239 \times 10^3 \text{ J} \end{split}$$

5. (b)

We know
$$k_{t_2} = k_{t_1} (\mu) \frac{t_2 - t_1}{10}$$

OR $\ell n \ k_{t_2} = \ell n \ k_{t_1} + \frac{t_2 - t_1}{10} \ \ell n \ \mu$
putting $t_1 = 0$
 $\ell n \ k_{t_2} = \ell n \ k + \frac{t_2}{10} \ \ell n \ \mu$
Comparing with $\ell n \ k_t = \ell n \ k_0 + \frac{\ell n 3}{3} t$
M = 3

6. (c)

 $t_{75\%} = 1 hr, \, t_{50\%} = \frac{1}{2} = 0.5 hr$

7. (d) $r = k [NO]^{1} [NOBr_{2}]^{1}$

order w.r.t (NO) is 1

8. (b)

Slope = $-\frac{E_a}{2.303R}$ = -5632 $\Rightarrow E_a = 5632 \times 2.303 \times 8.314 = 107.8 \text{ kJ/mol}$

9. (b)

 $\begin{aligned} R.D.S &= step ,\\ R &= K[A]'[B]' \end{aligned}$

10. (a)

 $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$

11. (b)

rate = k [H⁺]ⁿ at pH = 2, [H⁺] = 10⁻² at pH = 1, [H⁺] = 10⁻¹ $\frac{r_1}{r_2} = \left[\frac{10^{-2}}{10^{-1}}\right]^n$ $\frac{1}{100} = \left[\frac{1}{10}\right]^n \Rightarrow n = 2$

12. (c)

n Arrhenius equation, $k = Ae^{-Ea/RT}$

k = rate constant, A = frequency factor

T = temperature, R = gas constant, $E_a = energy$ of activation.

This equation can be used for calculation of energy of activation.

13. (d)

 $2 A + B \longrightarrow C$

rate = k [A] [B]

The value of k (velocity constant) is always independent of the concentration of reactant and it is a function of temperature only.

14. (c)

Given rate = $k [CO]^2$

Thus, according to the rate law expression doubling the concentration of CO increases the rate by a factor of 4.

15. (a)

$\frac{1}{2}A\longrightarrow$	2B
$-\frac{1}{1/2}\frac{d(A)}{dt}$	$=\frac{1}{2}\frac{\mathrm{d}(\mathrm{B})}{\mathrm{dt}}$
(A)	1 d(B)
dt	4 dt

16. (b)

$$K = \frac{1}{40} \operatorname{In} \frac{0.1}{0.025} = \frac{1}{40} \operatorname{In} 4 \operatorname{R} = \operatorname{K}[A]^{-1}$$
$$= \frac{1}{40} \operatorname{In} 4(.01) = \frac{2 \operatorname{In} 2}{40} (0.1) = 3.47 \times 10^{-4}$$

17. (b)

$$x A \longrightarrow YB \xrightarrow{-1}{x} \frac{d}{dt} [A] = \frac{1}{y} \frac{d}{dt} [B] \qquad \Rightarrow \frac{-d}{dt} [A] = \frac{x}{y} \frac{d}{dt} [B]$$
$$\log\left(\frac{-d[A]}{dt}\right) = \log\left(\frac{x}{y}\right) \left(\frac{+d[B]}{dt}\right) \quad \log\frac{-d}{dt} [A] = \log\frac{-d}{dt} [B] + \log\left(\frac{x}{y}\right)$$
$$\log\left(\frac{x}{y}\right) = 0.3 \qquad \Rightarrow \frac{x}{y} = \frac{2}{1} \qquad \Rightarrow x:y \quad 2:1$$

18. (b)

$$2NO(g) + 2H_{2}(g) \longrightarrow N_{2}(g) + 2H_{2}O(g) Rate = -\frac{1}{2} \frac{d[NO]}{dt} = -\frac{1}{2} \frac{d[H_{2}]}{dt} = \frac{d[N_{2}]}{dt} = \frac{1}{2} \frac{d[H_{2}O]}{dt} = K_{1}[NO][H_{2}]$$

$$\frac{d[H_{2}O]}{dt} = 2K_{1}[NO][H_{2}] = K[NO][H_{2}] So \qquad k = 2k_{1}$$

$$(2) - \frac{d[NO]}{dt} = 2k_{1}[NO][H_{2}] = K_{1}'[NO][H_{2}]$$

$$(3) - \frac{d[H_{2}]}{dt} = 2k_{1}[NO][H_{2}] = K_{1}''[NO][H_{2}]$$

$$k_{1}'' = 2K_{1}$$

19. (a)

A + B
$$\longrightarrow$$
 product
r = K[A]¹[B]²
r₁ = K [1]¹ [1]² = 1×10⁻² (K=1×10⁻²)
r₁ = K = 1×10⁻² × =1.25×10⁻³





_dC dt C



$$\frac{-\mathrm{d}c}{\mathrm{d}t} = \mathrm{K}[\mathrm{C}]^{\frac{1}{2}}$$
 So reaction is $\left(\frac{1}{2}\right)$ order.

22. (b)

% of
$$B = \frac{k_1 \times 100}{k_1 + k_2} = \frac{1.26 \times 10^{-4} \times 100}{12.6 \times 10^{-5} + 3.8 \times 10^{-5}} = 76.83\%.$$

% of $C = \frac{k_2 \times 100}{k_1 + k_2} = \frac{3.8 \times 10^{-5} \times 100}{12.6 \times 10^{-5} + 3.8 \times 10^{-5}} = 23.17\%$

23. (b)

For reaction A \longrightarrow B. $E_a = 10 \text{ kJ/mole}$, $\Delta H = 5 \text{ kJ/mole Rxn}$ endothermic because $\Delta H (+) \Delta H = E_a - E_b$ $5 = 10 - E_b$ $E_{ab} = 10 - 5 = 5 \text{ kJ/mole.Then [B].}$

24. (c)

For Rxn rate determining step is slowest step Then in 1st Rxn Rate = k [NO₂][O₃].....(i) But 2nd Rxn $O_3 \xrightarrow{k_a \text{ fast}} O_2 + [O]....(a)$ $NO_2 + O \xrightarrow{\text{slow}} NO_3....(b)$ $NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5$ (c) Then for Rxn (a) $\frac{k_a}{k_b} = \frac{[O_2][O]}{[O_3]} = k_{eq}$(d) by Rxn (b) Rate = k [NO₂][O](ii) put value of [O] from (d) to (ii) Rate = k $\frac{k_{eq}[O_3]}{[O_2]} \times [NO_2]$ Rate = $\frac{k_1[NO_2][O_3]}{[O_2]}$

25. (b)
$$T = \frac{2.303}{\lambda} \log_{10} \left[\frac{n+n}{n} \right]$$

$$t = \frac{2.303}{0.693} \times 4.5 \times 10^9 \log_{10}[2] = 4.5 \times 10^9 \text{ years}$$

26. (c)

As $t_{50\%}$ is constant. Hence order of reaction is 1.

$$t_{50\%} = \frac{0.693}{K}$$

n = 1, $t_{1/2} = \frac{0.693}{K}$

27. (c)

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

$$\log\left(\frac{dx}{dt}\right) = \log k + 2\log[A]$$



Slope = 2
Intercept=
$$\log k$$
.

28. (a)

Given $(r_{\infty} - r_{0}) = a$, $(r_{\infty} - r_{t}) = (a - x)$ At 50% Inversion

$$\frac{a}{2} = (a - x)$$

$$\frac{(r_{\infty} - r_0)}{2} = (r_{\infty} - r_0)$$

$$(r_{\infty} - r_0) = 2r_{\infty} - 2rt$$

$$r_0 = 2r_t - r_{\infty}$$

29. (a)

We have, $\frac{\begin{bmatrix} B \end{bmatrix}_{t}}{\begin{bmatrix} C \end{bmatrix}_{t}} = \frac{4k_{1}}{3k_{2}} = \frac{16}{9}$ so, $\frac{k_{1}}{k_{2}} = \frac{4}{3}$

Now,

$$k = k_{1} + k_{2} = [2 \times 10^{-3} + \frac{3}{4} \times 2 \times 10^{-3}] \sec^{-1}$$
$$= \frac{7}{2} \times 10^{-3} \sec^{-1} = \frac{7 \times 10^{-3} \times 60}{2} \text{ min}^{-1}$$
$$\text{so, } T_{1/2} = \frac{\ell n 2}{7 \times 30 \times 10^{-3}} \text{ min} = \frac{693}{7 \times 30} = 3.3 \text{ min}.$$

30. (d) $A \rightarrow B$ (uncatalysed reaction) $A \rightarrow B$ $A \xrightarrow{\text{catalyst}} B$ (catalyst reaction) $K = A e^{-Ea/RT}$ $K_{cat} = A e^{-Ea(cat)/RT}$

 $\frac{K_{cat}}{K} = e^{(E_a - E_a) \approx \frac{1}{RT}} \frac{K_{cat}}{K} = e^{\frac{8.314 \times 10^3}{8.314 \times 300}} = e^{3.33} = 28 \text{ times}$