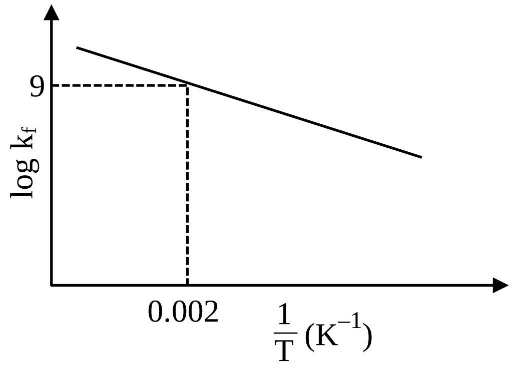
PHYSICAL CHEMISTRY

CHEMICAL KINETICS

1. The plot of log k_f versus $^1\!/_T$ for a reversible reaction A (g) $\rightleftharpoons$ P (g) is shown. **[JEE(Advanced) 2023]**



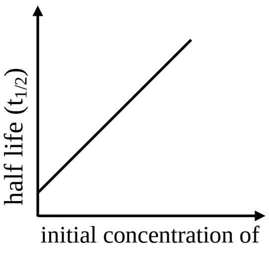
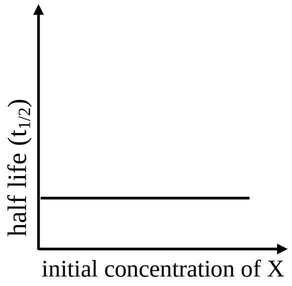
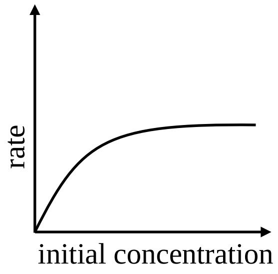
Pre-exponential factors for the forward and backward reactions are 10^{15} s^{-1} and 10^{11} s^{-1}, respectively. If the value of log K for the reaction at 500 K is 6, the value of | log k_b | at 250 K is ______.

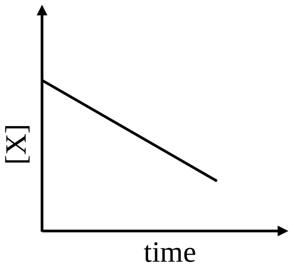
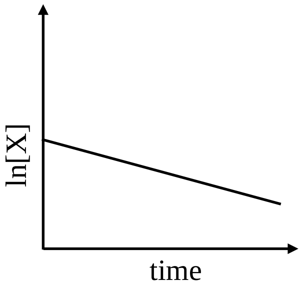
[K = equilibrium constant of the reaction

k_f = rate constant of forward reaction

k_b = rate constant of backward reaction]

2. Match the rate expressions in LIST-I for the decomposition of X with the corresponding profiles provided in LIST-II. X_s and k constants having appropriate units. **JEE(Advanced) 2022]**

LIST-I	LIST-II
(I) rate $= \frac{k[X]}{X_s + [X]}$ under all possible initial concentration of X	(P) 
(II) rate $= \frac{k[X]}{X_s + [X]}$ where initial concentration of X are much less than X_s	(Q) 
(III) rate $= \frac{k[X]}{X_s + [X]}$ where initial concentration of X are much higher than X_s	(R) 

(IV) rate $= \dfrac{k[X]^2}{X_s + [X]}$ where initial concentration of X is much higher than X_s	(S) 
	(T) 

(A) I → P; II → Q; III → S; IV → T

(B) I → R; II → S; III → S; IV → T

(C) I → P; II → Q; III → Q; IV → R

(D) I → R; II → S; III → Q; IV → R

3. For the following reaction **[JEE(Advanced) 2021]**

$$2\mathbf{X} + \mathbf{Y} \xrightarrow{k} \mathbf{P}$$

the rate of reaction is $\dfrac{d[\mathbf{P}]}{dt} = k[\mathbf{X}]$. Two moles of **X** are mixed with one mole of **Y** to make 1.0 L of solution. At 50 s, 0.5 mole of **Y** is left in the reaction mixture. The correct statement(s) about the reaction is(are)

(Use: ln 2 = 0.693)

(A) The rate constant, *k*, of the reaction is $13.86 \times 10^{-4}\ s^{-1}$.

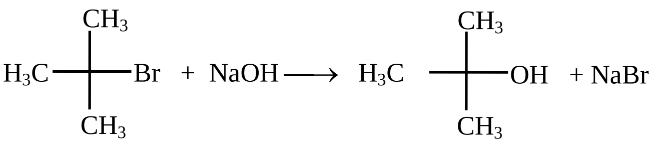
(B) Half–life of **X** is 50s.

(C) At 50 s, $-\dfrac{d[\mathbf{X}]}{dt} = 13.86 \times 10^{-3}$ mol L^{-1} s^{-1}.

(D) At 100 s, $-\dfrac{d[\mathbf{Y}]}{dt} = 3.46 \times 10^{-3}$ mol L^{-1} s^{-1}.

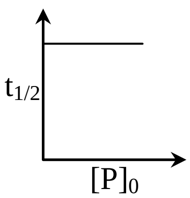
4. Which of the following plots is(are) correct for the given reaction? **[JEE(Advanced) 2020]**

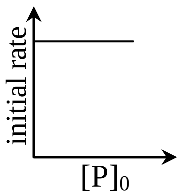
($[P]_0$ is the initial concentration of **P**)

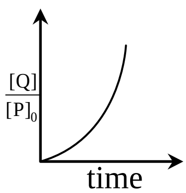


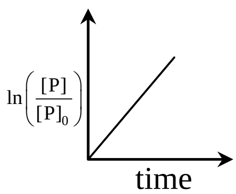
$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br + NaOH \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH + NaBr$$

P **Q**

(A) 

(B) 

(C) 

(D) 

5. In the decay sequence : **[JEE(Advanced) 2019]**

$$^{238}_{92}U \xrightarrow{-x_1} {}^{234}_{90}Th \xrightarrow{-x_2} {}^{234}_{91}Pa \xrightarrow{-x_3} {}^{234}Z \xrightarrow{-x_4} {}^{230}_{90}Th$$

x_1, x_2, x_3 and x_4 are particles/ radiation emitted by the respective isotopes. The correct option(s) is/are-

(A) Z is an isotope of uranium

(B) x_2 is β^-

(C) x_1 will deflect towards negatively charged plate

(D) x_3 is γ-ray

6. Consider the kinetic data given in the following table for the reaction A + B + C → Product.

Experiment No.	[A] (mol dm^{-3})	[B] (mol dm^{-3})	[C] (mol dm^{-3})	Rate of reaction (mol dm^{-3} s^{-1})
1	0.2	0.1	0.1	6.0×10^{-5}
2	0.2	0.2	0.1	6.0×10^{-5}
3	0.2	0.1	0.2	1.2×10^{-4}
4	0.3	0.1	0.1	9.0×10^{-5}

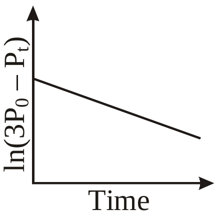
The rate of the reaction for [A] = 0.15 mol dm^{-3}, [B] = 0.25 mol dm^{-3} and [C] = 0.15 mol dm^{-3} is found to be **Y** × 10^{-5} mol dm^{-3} s^{-1}. The value of **Y** is ________. **[JEE(Advanced) 2019]**

7. The decomposition reaction $2N_2O_5(g) \xrightarrow{\Delta} 2N_2O_4(g) + O_2(g)$ is started in a closed cylinder under isothermal isochoric condition at an initial pressure of 1 atm. After Y × 10^3 s, the pressure inside the cylinder is found to be 1.45 atm. If the rate constant of the reaction is 5×10^{-4} s^{-1}, assuming ideal gas behavior, the value of Y is ______. **[JEE(Advanced) 2019]**

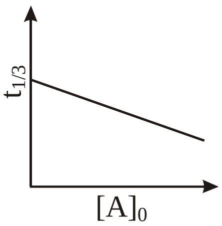
8. For a first order reaction $A(g) \rightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning (t = 0) and at time t are P_0 and P_t, respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach 1/3rd of its initial value. The correct option(s) is (are) :-

(Assume that all these gases behave as ideal gases) **[JEE(Advanced) 2018]**

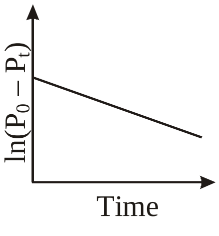
(A)



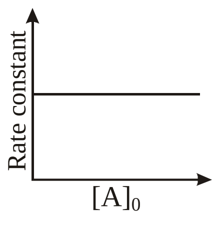
(B)



(C)



(D)



9. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are): **[JEE(Advanced) 2017]**

(A) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(B) The activation energy of the reaction is unaffected by the value of the steric factor

(C) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used.

(D) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation.

10. According to the Arrhenius equation, **[JEE(Advanced) 2016]**

(A) A high activation energy usually implies a fast reaction

(B) Rate constant increase with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy

(C) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant

(D) The pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

11. 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

[JEE(Advanced) 2014]

(A) 4 (B) 3 (C) 2 (D) 1

SOLUTIONS

1. **Ans. (5)**

Sol. For reaction $A(g) \rightleftharpoons P(g)$

$\log k_f = \dfrac{-E_f}{2.303RT} + \log A_f$ [Arrhenius equation for forward reaction]

From plot when, $\dfrac{1}{T} = 0.002$, $\log k_f = 9$

$$\Rightarrow \quad 9 = \frac{-E_f}{2.303R}(0.002) + \log(A_f)$$

Given : $A_f = 10^{15}\ s^{-1}$

$$\Rightarrow \quad 9 = \frac{-E_f}{2.303R}(0.002) + 15$$

$$\Rightarrow \quad \frac{E_f}{2.303R} = \frac{6}{0.002} = 3000$$

Now, $K = \dfrac{k_f}{k_b} = \dfrac{A_f}{A_b} e^{-(E_f - E_b)/RT}$

$$\log K = -\frac{1}{2.303}\frac{(E_f - E_b)}{RT} + \log\left(\frac{10^{15}}{10^{11}}\right)$$

At 500 K

$$\Rightarrow \quad 6 = \frac{-(E_f - E_b)}{500R\ (2.303)} + 4$$

$\Rightarrow \quad (1000\ R)\ (2.303) = E_b - E_f$

$\Rightarrow \quad (1000\ R)\ (2.303) = E_b - 3000\ (2.303\ R)$

$\Rightarrow \quad E_b = 4000\ R\ (2.303)$ ....(1)

Now $k_b = A_b e^{-E_b/RT}$

$$\Rightarrow \log k_b = \frac{-E_b}{2.303RT} + \log A_b$$

At 250 K

$\Rightarrow \quad \log k_b = -\dfrac{4000}{250} + \log(10^{11})$ [From equation (1)]

$= -16 + 11 = -5$

$|\log k_b| = 5$

2. **Ans. (A)**

Sol. (I) $\text{rate} = \dfrac{k[x]}{x_s + [x]} = \dfrac{k}{\dfrac{x_s}{[x]} + 1}$

If $[x] \rightarrow \infty \Rightarrow \text{rate} \rightarrow k \Rightarrow \text{order} = 0$

$\Rightarrow$ (I) – (R), (P)

(II) $[x] << x_s \Rightarrow \text{rate} = \dfrac{k[x]}{x_s} \Rightarrow \text{order} = 1$

$\Rightarrow$ (II) – (Q), (T)

(III) $[x] >> x_s \Rightarrow \text{rate} = k \Rightarrow \text{order} = 0$

$\Rightarrow$ (III) – (P), (S)

(IV) $\text{rate} = \dfrac{k[x]^2}{x_s + [x]}$

$[x] >> x_s \Rightarrow \text{rate} = k[x]$

$\Rightarrow$ (IV) – (Q), (T)

3. **Ans. (B, C, D)**

Sol. $\dfrac{dp}{dt} = k[x]^1$

	$2x$	$+$	y	$\rightarrow$	p
$t = 0$	2		1		
$t = 50$ s	(2–1)		(1–0.5)		0.5

$$-\frac{1}{2}\frac{dx}{dt} = \frac{dp}{dt} = k[x]^1$$

$$-\frac{dx}{dt} = 2k[x]^1$$

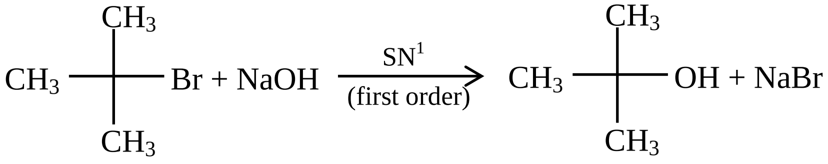
$$2k = \frac{\ln 2}{50} \quad \Rightarrow \quad k = \frac{\ln 2}{100}$$

At 50 sec $\dfrac{-dx}{dt} = 2k \times (1)^1 = \dfrac{\ln 2}{50}$

At 100 sec $-\dfrac{1}{2}\dfrac{dx}{dt} = \dfrac{-dy}{dt} \Rightarrow -\dfrac{dy}{dt} = \dfrac{\ln 2}{100} \times \dfrac{1}{2}$ $\left\{\dfrac{-dy}{dt} = k[x]^1\right\}$

4. **Ans. (A)**

Sol.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + NaOH \xrightarrow[\text{(first order)}]{SN^1} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + NaBr$$

$t = 0$	P_0	0
t	P	$P_0 - P$

rate = k[] $\qquad \ln \dfrac{P_0}{P} = kt$

$t_{1/2} = \dfrac{0.693}{k} \qquad \ln \dfrac{P}{P_0} = -kt$

$$\frac{[Q]}{[P]_0} = \frac{[P_0]-[P]}{[P_0]} = 1 - \frac{[P]}{[P_0]} = 1 - e^{-kt}$$

5. Ans. (A, B, C)

Sol.

$$
\begin{array}{l}
{}_{92}U^{238} \longrightarrow {}_{90}Th^{234} + {}_{2}He^{4}(\text{or } \alpha) \text{ or } x_1 \\
\qquad\qquad\quad \downarrow \\
\qquad\qquad\quad {}_{91}Pa^{234} + \beta^{-}(\text{or } {}_{-1}e^{\circ}) \text{ or } x_2 \\
\qquad\qquad\quad \downarrow \\
\qquad\qquad\quad {}_{92}Z^{234} + \beta^{-}(\text{or } {}_{-1}e^{\circ}) \text{ or } x_3 \\
\qquad\qquad\quad \downarrow \\
\qquad\qquad\quad {}_{90}Th^{230} + {}_{2}He^{4}(\text{or } \alpha) \text{ or } x_4
\end{array}
$$

U and Z are isotopes

6. Ans. (6.70 to 6.80)

Sol. $r = K[A]^{n_1} [B]^{n_2} [C]^{n_3}$

From table

$n_1 = 1$

$n_2 = 0$

$n_3 = 1$

$r = K[A] [C]$

From Exp-1

$6 \times 10^{-5} = K \times 0.2 \times 0.1$

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

$r = (3 \times 10^{-3}) \times 0.15 \times 0.15$

$= 6.75 \times 10^{-5} = Y \times 10^{-5}$

$Y = 6.75$

7. Ans. (2.30 to 2.31)

Sol. $2N_2O_5(g) \xrightarrow{\Delta} 2N_2O_4(g) + O_2(g)$ at constant V, T

t = 0	1		
$t = y \times 10^3$ sec	$(1 - 2P)$	$2P$	P

$P_T = (1 + P) = 1.45$

$P = 0.45$ atm

$$(2K)t = 2.303 \log\left(\frac{1}{1-2P}\right)$$

$$(2 \times 5 \times 10^{-4}) \times y \times 10^3 = 2.303 \log \frac{1}{0.1}$$

$y = 2.303 = 2.30$

8. **Ans. (A, D)**

Sol. $A \longrightarrow 2B + C$

$t = 0 \quad P_0 \quad - \quad -$

$t = t \quad P_0 - P \quad 2P \quad P$

$P_0 + 2P = P_t$

$$K = \frac{1}{t}\ln\frac{P_0}{P_0 - P} = \frac{1}{t}\ln\frac{P_0}{P_0 - \frac{(P_t - P_0)}{2}}$$

$$K = \frac{1}{t}\ln\frac{2P_0}{3P_0 - P_t} \Rightarrow -Kt + \ln 2P_0 = \ln(3P_0 - P_t)$$

and $t_{1/3} = \frac{1}{K}\ln\frac{P_0}{P_0/3} = \frac{1}{K}\ln 3 = \text{constant}$

Rate constant does not depends on concentration

9. **Ans. (B, D)**

Sol. $K = P.A.\ e^{-Ea/RT}$

(A) If $P < 1$ $\quad A_{arr.} > A_{expt}$

(D) If $P > 1$ $\quad A_{arr.} < A_{expt}$

(C) If P is very small, then catalyst is required to carry out the reaction at measurable rate.

10. **Ans. (B, C, D)**

Sol. (A) $k = Ae^{-E_a/RT}$

High E_a means less k, hence slower rate.

(B) $e^{-Ea/RT}$ = fraction of molecules having kinetic energy greater than activation energy which increase as temperature increases.

(C) $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ i.e., $\ln\frac{k_2}{k_1} \propto E_a$

(D) Rate of reaction $\propto$ Total number of collisions × Fraction of collisions which can form product

Rate of reaction $\propto Z_{AB} \times (P \times e^{-Ea/RT})$

$\propto A\, e^{-Ea/RT}$

11. **Ans. (B)**

Sol. $r = k\,[M]^n$; n = order

$$\frac{r_2}{r_1} = \left(\frac{[M]_2}{[M]_1}\right)^n$$

$8 = (2)^n \qquad \Rightarrow n = 3$