CHEMICAL KINETICS

1. For the reaction

$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$

the observed rate expression is, rate = $k_f[NO]^2[H_2]$. The rate expression of the reverse reaction is :

(1) $k_b[N_2][H_2O]^2/[NO]$ (2) $k_b[N_2][H_2O]$

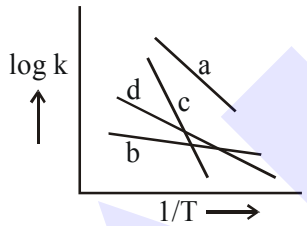
(3) $k_b[N_2][H_2O]^2$ (4) $k_b[N_2][H_2O]^2/[H_2]$

2. The rate of a certain biochemical reaction at physiological temperature (T) occurs 10^6 times faster with enzyme than without. The change in the activation energy upon adding enzyme is :

(1) –6RT (2) +6RT

(3) +6(2.303)RT (4) –6(2.303)RT

3. Consider the following plots of rate constant versus $\frac{1}{T}$ for four different reactions. Which of the following orders is correct for the activation energies of these reactions?



(1) $E_b > E_d > E_c > E_a$

(2) $E_a > E_c > E_d > E_b$

(3) $E_c > E_a > E_d > E_b$

(4) $E_b > E_a > E_d > E_c$

4. For the following reactions

$A \xrightarrow{700\,K} Product$

$A \xrightarrow[catalyst]{500\,K} Product$

it was found that E_a is decreased by 30 kJ/mol in the presence of catalyst.

If the rate remains unchanged, the activation energy for catalysed reaction is (Assume pre exponential factor is same):

(1) 135 kJ/mol (2) 105 kJ/mol

(3) 198 kJ/mol (4) 75 kJ/mol

5. A sample of milk splits after 60 min. at 300 K and after 40 min. at 400 K when the population of *lactobacillus acidophilus* in it doubles. The activa tion energy (in kJ/ mol) for this process is closest to_____.

(Given, R = 8.3 J mol^{-1} K^{-1}, $ln\left(\frac{2}{3}\right) = 0.4$, $e^{-3} = 4.0$)

6. The number of molecules with energy greater than the threshold energy for a reaction increases five fold by a rise of temperature from 27 °C to 42 °C. Its energy of activation in J/mol is _____. (Take ln 5 = 1.6094; R = 8.314 J $mol^{-1}K^{-1}$)

7. If 75% of a first order reaction was completed in 90 minutes, 60% of the same reaction would be completed in approximately (in minutes) _____. (Take : log 2 = 0.30; log 2.5 = 0.40)

8. It is true that :

(1) A zero order reaction is a single step reaction

(2) A second order reaction is always a multistep reaction

(3) A first order reaction is always a single step reaction

(4) A zero order reaction is a multistep reaction

9. For the reaction $2A + 3B + \frac{3}{2}C \rightarrow 3P$, which statement is correct ?

(1) $\frac{dn_A}{dt} = \frac{dn_B}{dt} = \frac{dn_C}{dt}$

(2) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

(3) $\frac{dn_A}{dt} = \frac{3}{2}\frac{dn_B}{dt} = \frac{3}{4}\frac{dn_C}{dt}$

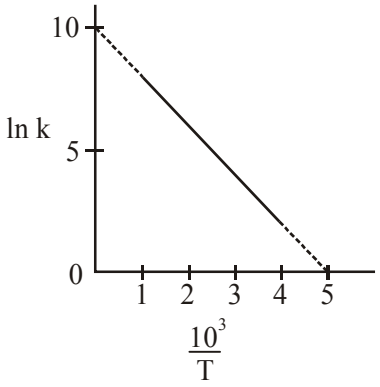
(4) $\frac{dn_A}{dt} = \frac{2}{3}\frac{dn_B}{dt} = \frac{4}{3}\frac{dn_C}{dt}$

10. A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives for A and B are 300 s and 180 s, respectively. If the concentrations of A and B are equal initially, the time required for the concentration of A to be four times that of B(in s) : (Use ln 2 = 0.693)

(1) 180 (2) 120

(3) 300 (4) 900

11. The rate constant (k) of a reaction is measured at different temperatures (T), and the data are plotted in the given figure. The activation energy of the reaction in kJ mol^{-1} is :
(R is gas constant)



(1) 2R (2) R
(3) 1/R (4) 2/R

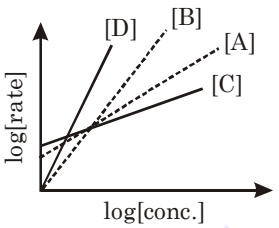
12. The results given in the below table were obtained during kinetic studies of the following reaction:

$2A + B \longrightarrow C + D$

Experiment	[A]/molL^{-1}	[B]/molL^{-1}	Initial rate/molL^{-1} min^{-1}
I	0.1	0.1	6.00×10^{-3}
II	0.1	0.2	2.40×10^{-2}
III	0.2	0.1	1.20×10^{-2}
IV	X	0.2	7.20×10^{-2}
V	0.3	Y	2.88×10^{-1}

X and Y in the given table are respectively :
(1) 0.3, 0.4
(2) 0.4, 0.3
(3) 0.4, 0.4
(4) 0.3, 0.3

13. Consider the following reactions :
$A \rightarrow P1$; $B \rightarrow P2$; $C \rightarrow P3$; $D \rightarrow P4$
The order of the above reactions are a, b, c, and d, respectively. The following graph is obtained when log [rate] vs. log[conc] are plotted:



Among the following , the correct sequence for the order of the reactions is:
(1) a > b > c > d (2) c > a > b > d
(3) d > b > a > c (4) d > a > b > c

14. The rate of a reaction decreased by 3.555 times when the temperature was changed from 40°C to 30°C. The activation energy (in kJ mol^{-1}) of the reaction is_ _ _ _ _.
Take; R=8.314 J mol^{-1} K^{-1} In 3.555 = 1.268

SOLUTION

1. NTA Ans. (4)

Sol. $K_{eq} = \frac{k_f}{k_b} = \frac{[N_2][H_2O]^2}{[H_2]^2[NO]^2}$

At equilibrium $r_f = r_b$

$$\underset{[\text{Given}]}{k_f}[H_2][NO]^2 = k_b \frac{[N_2][H_2O]^2}{[H_2]}$$

Hence, rate expression for reverse reaction.

$$= k_b \frac{[N_2][H_2O]^2}{[H_2]}$$

2. NTA Ans. (4)

Sol. $K = Ae^{\frac{-E_a}{RT}}$

$K' = Ae^{\frac{-E_a'}{RT}} = 10^6 K$

$Ae^{\frac{-E'}{RT}} = 10^6 \times Ae^{\frac{-E_a}{RT}}$

$\frac{-E_a'}{RT} = \frac{-E_a}{RT} + \ln 10^6$

$E_a' = E_a - RT \ln 10^6$

$E_a' - E_a = -RT \ln 10^6 = -6RT \times 2.303$

3. NTA Ans. (3)

Sol. $\log K = \frac{-Ea}{2.303RT} + \log A$

Acrroding to Arrhenius equation plot of 'log K' Vs. $\frac{1}{T}$ is linear with.

Slope = $\frac{-Ea}{2.303R}$

From plot we conclude :

$\underset{(\text{magnitude})}{|\text{slope}|}$: c > a > d > b

$\therefore\ E_c > E_a > E_d > E_b$

4. NTA Ans. (4)

Sol. $K_1 = Ae^{-\frac{Ea}{R\times 700}}$

$K_2 = A \times e^{-\frac{(Ea-30)}{R\times 500}}$

For same rate

$K_1 = K_2$

$e^{-\frac{Ea}{700R}} = e^{-\frac{(Ea-30)}{R\times 500}}$

$\frac{Ea}{700R} = \frac{Ea-30}{R\times 500}$

$5Ea = 7Ea - 210$

$210 = 2Ea$

$E_a = 105$ kJ/mole

$E_a - 30 = 75$

5. NTA Ans. (3.98 to 4.00 or –3.98 to –4.00)

Sol. $\ln\left(\frac{t_1}{t_2}\right) = \frac{-Ea}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$

$\ln\left(\frac{60}{40}\right) = \frac{-Ea}{8.3}\left[\frac{1}{400} - \frac{1}{300}\right]$

$E = 0.4 \times 1200 \times 8.3$

$= 3.984$ kJ/mole

6. Official Ans. by NTA (84297)
Official Ans. by ALLEN
(84297.47 or 84297.48)

Sol. $T_1 = 300K \qquad T_2 = 315K$

As per question $K_{T_2} = 5K_{T_1}$ as molecules activated are increased five times so k will increases 5 times

Now

$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln 5 = \frac{Ea}{R}\left(\frac{15}{300\times 315}\right)$

So $Ea = \frac{1.6094\times 8.314\times 300\times 315}{15}$

Ea = 84297.47 Joules/mole

7. Official Ans. by NTA (60)

Sol. $t_{0.75} = 2\times\frac{\ln 2}{k} = 90$

$k = \frac{\ln 2}{45}\text{min}^{-1}$

$kt = \ln\frac{1}{1-0.6} = \ln 2.5$

$\frac{\ln 2}{45}\times t = \ln 2.5$

$$t = 45 \times \frac{\log 2.5}{\log 2} = 45 \times \frac{0.4}{0.3} = 60\,\text{min}$$

8. Official Ans. by NTA (4)

Sol. Zero order reaction is multiple step reaction.

9. Official Ans. by NTA (4)

Sol. For $aA + bB \rightarrow cC$;

$$\frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt}$$

$$\therefore \quad \frac{-1}{2}\frac{d[A]}{dt} = \frac{-1}{3}\frac{d[B]}{dt} = \frac{-2}{3}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[P]}{dt}$$

10. Official Ans. by NTA (4)

Sol. $[A]_t = 4[B]_t$

$$[A]_0\ e^{-(\ln^2/300)t} = 4[B]_0 e^{(-\ln 2/180)t}$$

$$e^{\left(\frac{\ln^2}{180} - \frac{\ln^2}{300}\right)} = 4$$

$$\left(\frac{\ln^2}{180} - \frac{\ln^2}{300}\right)t = \ln 4$$

$$\left(\frac{1}{180} - \frac{1}{300}\right)t = 2 \Rightarrow t = \frac{2 \times 180 \times 300}{120} = 900\,\text{sec.}$$

11. Official Ans. by NTA (1)

Sol. Slope = $-\frac{E_a}{R}$

$$-\frac{10}{5} = -\frac{E_a}{R}$$

$E_a = 2R$

12. Official Ans. by NTA (1)

Sol. From rate law

$$r = -\frac{1}{2}\frac{d[A]}{dt} = \frac{-d[B]}{dt}$$

$= K[A]^x\ [B]^y$

$6 \times 10^{-3} = K(0.1)^x\ (0.1)^y$ .....(1)

$2.4 \times 10^{-2} = K(0.1)^x\ (0.2)^y$ .....(2)

$1.2 \times 10^{-2} = K(0.2)^x\ (0.1)^y$ .....(3)

(3) ÷ (1) $\Rightarrow$ x = 1

(2) ÷ (3) $\Rightarrow$ x = 2

So, order with respect to A = 1

Order with respect to B = 2

(4) ÷ (3)

$$\left(\frac{x}{0.2}\right) \times \left(\frac{0.2}{0.1}\right)^2 = \frac{7.2 \times 10^{-2}}{1.2 \times 10^{-2}}$$

$$x = \frac{6 \times 0.2}{4}$$

x = 0.3 M

(5) ÷ (4)

$$\left(\frac{y}{0.2}\right)^2 = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}}$$

$y^2 = 4 \times 0.2^2$

y = 0.4 M

13. Official Ans. by NTA (3)

14. Official Ans. by NTA (100.00)

Official Ans. by ALLEN (99.98)

Sol. $\ell n\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$T_1 = 303\ K\ ;\ T_2 = 313\ K$

$$\frac{K_{T_2}}{K_{T_1}} = 3.555$$

$$\ell n(3.555) = \frac{E_a}{8.314}\left[\frac{1}{303} - \frac{1}{313}\right]$$

$E_a = 99980.715$

$E_a = 99.98\ \frac{kJ}{mole}$