PHYSICAL / INORGANIC CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 52

Total Marks : 31

Max. Time : 32 min.

Topic : Chemical Kinetics

Type of Questions		**M.M., Min.**
Single choice Objective ('–1' negative marking) Q.1 to Q.9	**(3 marks 3 min.)**	**[27, 27]**
Subjective Questions ('–1' negative marking) Q.5 to Q.10	**(4 marks 5 min.)**	**[4, 5]**

1. For a certain reaction the variation of the rate constant with temperature is given by the equation

$$\ln k_t = \ln k_0 + 0.0693\, t\, (t \geq 0°C)$$

The value of the temperature coefficient of the reaction rate is, therefore

(A) 0.1 (B) 1.0 (C) 10 (D) 2

2. The activation energies of two reactions are E_a and E_a' with $E_a > E_a$'. If temperature of the reacting systems is increased from T_1 to T_2, predict which of the following alternatives is correct?

(Where k_1' and k_2' are rate constant at higher temperature).

(A) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$ (B) $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$ (C) $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$ (D) $\frac{k_1'}{k_1} < 2\frac{k_2'}{k_2}$

3. Two reactions A $\longrightarrow$ products and B $\longrightarrow$ products have rate constants k_A and k_B at temperature, T and activation energies E_A and E_B respectively. If $k_A > k_B$ and $E_A < E_B$ and assuming that 'A', pre-exponential factor for both the reactions is same, then.

(A) at higher temperatures k_B will be greater than k_A

(B) at lower temperatures k_A and k_B will be close to each other in magnitude

(C) as temperature rises k_A and k_B will be close to each other in magnitude.

(D) at lower temperature $k_B > k_A$

4. On introduction a catalyst at 500 K, the rate of a first order reaction increases by 1.718 times. If the activation energy in the presence of a catalyst is 4.15 kJ mol^{-1}. Then, the E_a in absence of catalyst is (R = 8.3 MKS)

(A) 4.15 kJ (B) 2.08 kJ (C) 2.718 kJ (D) 8.3 kJ.

5. What percentage fraction of the molecule will cross over the energy barrier at 1000 K temperature for 18.424 KJ activation energy (R = 8J mol^{-1} K^{-1})

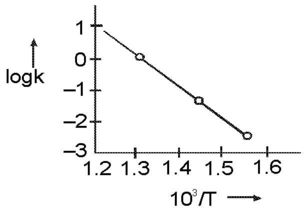
(A) 10% (B) 20% (C) 90% (D) 80%

6. For the decomposition of HI the following logarithmic plot is shown : [R = 1.98 cal/mol-K]

The activation energy of the reaction is about

(A) 45600 cal (B) 13500 cal

(C) 24600 cal (D) 32300 cal



7. Decomposition of A follows first order kinetics by the following equation. $4A(g) \longrightarrow B(g) + 2C(g)$

If initially, total pressure was 800 mm of Hg and after 10 minutes it is found to be 650 mm of Hg. What is half-life of A ? (Assume only A is present initially)

(A) 10 mins (B) 5 mins (C) 7.5 mins (D) 15 mins

8. In a hypothetical reaction, $A(aq) \rightleftharpoons 2B(aq) + C(aq)$ (1st order decomposition)

'A' is optically active (dextro-rototory) while 'B' and 'C' are optically inactive but 'B' takes part in a titration reaction (fast reaction) with H_2O_2. Hence, the progress of reaction can be monitored by measuring rotation of plane polarised light or by measuring volume of H_2O_2 consumed in titration.

In an experiment the optical rotation was found to be $\theta = 40°$ at t = 20 min and $\theta = 10°$ at t = 50 min. from start of the reaction. If the progress would have been monitored by titration method, volume of H_2O_2 consumed at t = 15 min. (from start) is 40 ml then volume of H_2O_2 consumed at t = 60 min will be:

(A) 60 ml (B) 75 ml (C) 52.5 ml (D) 90 ml

9. **S_1 :** The frequency factor has the same unit as the rate constant, k

S_2 : A plot ℓn rate vs ℓn C for the nth order reaction gives a straight line with slope –n and intercept k_n

S_3 : The order of a reaction A → product in which half the reagent is reacted in half an hour, three quarters in one hour and seven - eighth in one and half hours must be 1(unity).

S_4 : The unit of rate constant for a second order reaction will be $M^{-1}s^{-1}$.(M is representing the molarity of solution)

(A) T F T T (B) T T T T (C) F F T T (D) T F F T

10. The activation energy of $H_2 + I_2 \rightarrow 2HI$, in equilibrium, for forward reaction is 167 kJ mol^{-1} where as for the reverse reaction is 180 kJ mol^{-1}. The presence of catalyst lowers the activation energy by 80 $kJmol^{-1}$. Assuming that the reactions are made at 27ºC and the frequency factor for forward and backward reactions are 4×10^{-4} and 2×10^{-3} respectively. Calculate K_C .

Given : $e^{13/8.314\times0.3} = 183$.

Answer Key

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1.	(D)	**2.**	(B)	**3.**	(C)	**4.**	(D)	**5.**	(A)
6.	(A)	**7.**	(B)	**8.**	(B)	**9.**	(A)	**10.**	$K_c = 36.6$

Hints & Solutions

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1. $\frac{k_t}{k_0} = (TC)^{t-0/10}$

Taking log gives $\log_e k_t - \log_e k_0 = \frac{t}{10} \log_e (TC)$ $\Rightarrow$ $\ln k_t = \ln k_0 + \left(\frac{\ln (TC)}{10}\right) t$

Comparison indicates $\frac{\ln (TC)}{10} = 0.0693$ $\Rightarrow$ $\ln (TC) = 0.693 \Rightarrow$ $TC = 2$

2. $k_1 = Ae^{-Ea/RT_1}$ & $k_2 = Ae^{-Ea'/RT_1}$

$k'_1 = Ae^{-Ea/RT_2}$ & $k'_2 = Ae^{-Ea'/RT_2}$

$\Rightarrow$ $\frac{k'_1}{k_1} = e^{\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$ & $\frac{k'_2}{k_2} = e^{\frac{E'a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$

Since Ea > E'a $\Rightarrow$ $\frac{k'_1}{k_1} > \frac{k'_2}{k_2}$

3. As temperature increases, K_A & K_B tends to A.
So, they are equal in magnitude.

4. According to Arrhenius equation

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

At temp., T the equation will be

$k' = A \, . \, e^{-E_{a'}/RT}$

Given $E_a{}' = 4.15$ kJ mol^{-1}

.... in the presence of a catalyst

$\therefore$ $\frac{k'}{k} = e^{(E_a - E_a{}')/RT}$

Given $k' = (1 + 1.718)\,k = 2.718k = ek$

Hence $e = e^{(E_a - E_a')/RT}$

or $\quad E_a - E_a' = RT$

or $\quad Ea = E_a' + RT \quad = 4.15 + 8.3 \times 500 \times 10^{-3} \quad$ **= 8.3 kJ mol^{-1}.**

5. Fraction of molecules which cross over the barrier

$$= e^{-\frac{Ea}{RT}} = e^{-\frac{18428}{8 \times 1000}} = e^{-2.303} = e^{-\ln 10} = \frac{1}{10}$$

6. $\log k = -\dfrac{E_a}{2.303\,R}\ \dfrac{1}{T}$ + constant

$$= -\frac{E_a}{2.303\,R} \times 10^{-3} \times \frac{10^3}{T} + \text{constant}$$

thus, slope of graph will be $-\dfrac{E_a \times 10^{-3}}{2.303\,R} = -\dfrac{4}{0.4}$

$\Rightarrow \quad E_a = 2.303 \times 1.98 \times 10^4 = 45600$ cal

7.

	$4A(g)$	$\longrightarrow$	$B(g)$	+	$2C(g)$
t = 0	800		–		–
t = 10 minutes,	800 – 4p		p		2p
	800 – p = 650		∴ p = 150		Pressure of A = 200, so

∴ $\quad 2 \times t_{1/2} = 10$ minutes $\quad \Rightarrow \quad t_{1/2} = 5$ minutes

8. As only A is optically active. So conc. of A at t = 20 min $\propto 40°$
While concentration of A at t = 50 min $\propto 10°$
so $t_{1/2} = 15$ min.
So volume consumed of H_2O_2 at t = 15 min = $t_{1/2}$, is according to 50% production of B.
at t = 60 min. production of B = 94.75% (four half lives)

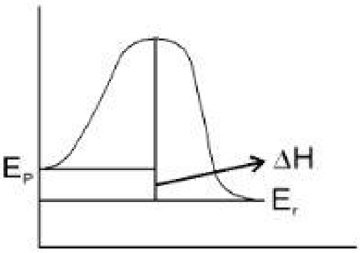
So volume consumed = $(40\text{ ml}) + \left(\dfrac{40}{2}\right)\text{ml} + \left(\dfrac{40}{4}\right)\text{ml} + \left(\dfrac{40}{8}\right)\text{ml} = 75$ ml ans.

9. S_1 $k = Ae^{-Ea/RT}$
S_2 rate = $k_n[C]^n \Rightarrow \quad \ln \text{rate} = \ln k_n + n \ln C$
S_3 $A \to$ product

$$a \xrightarrow{\frac{1}{2}\text{hr}} \frac{a}{2} \xrightarrow{\frac{1}{2}\text{hr}} \frac{a}{4} \xrightarrow{\frac{1}{2}\text{hr}} \frac{a}{8} \quad \Rightarrow \text{I}^{\text{st}} \text{ order reaction.}$$

10. $K_f = A_f\, e^{-Ea_f/RT}$; $\qquad K_b = A_b\, e^{-Ea_b/RT}$.

$$K_c = \frac{K_f}{K_b} = \frac{A_f}{A_b}\ e^{-(Ea_f - Ea_b)/RT}.$$



$$K_C = \frac{4 \times 10^{-4}}{2 \times 10^{-3}}\ e^{-(167000 - 180000)/8.314 \times 300.}$$

$K_C = 2 \times 10^{-1} \times 183 = 36.6.$