SOLUTION TEST-A

1. For zero order reaction, [R} = $[R]_o$ –kt

   The graph between [R] and t will be a straight line with negative slope (slope = –k) and y-intercept equals to $[R]_o$.

   The correct answer is (ii)

2. $\log k = 10.00 - \frac{100\,K}{T}$

   $\log k = \log A - \frac{E_a}{2.303RT}$

   Comparing these two equations gives, $\log A = 10.00$ and A = 10^{10} s^{-1}

   $\frac{E_a}{2.303R} = 100$ $\therefore E_a = 2.303 \times 8.314 \times 100$

   E_a = 1914.71 J mol^{-1}

   E_a = 1.914 kJ mol^{-1}

   The correct answer is (iv)

3. **The incorrect statement is given in answer (iv).**

   The catalyst does not change the $\Delta rH°$.

4. Reason is incorrect. Order is an experimental concept whereas molecularity is a theoretical concept.

   The answer is (iii)

5. $[R] = [R]_o e^{-kt}$

   The concentration of the reactant decreases exponentially with time for all nuclear disintegration reactions since they follows first order kinetics.

   The answer is (i)

6. Rate is defined as the change in concentration of the reactant or product with time, each divided by its stoichiometric coefficient. It has a units of (conc) $time^{-1}$.

   Rate constant is defined as the rate of chemical reaction when the concentration of each reactant appearing in the experimentally derived rate equation is taken as unity. It has a units of $(conc)^{1-n}$ $time^{-1}$.

   where n = order of reaction.

7. $r = k[R]^x$ ...(i)

   $27r = k[3R]^x$ ...(ii)

   as volume is reduced to $\frac{1}{3}$rd, the concentration is increased to 3 times

   eqn, (ii) ÷ eqn (i)

   $27 = 3^x$ and $\boxed{x = 3}$

   order of the reaction = 3.

8. $t_{1/2} = 40\,\text{min}$

$$k = \frac{0.693}{40}\ \text{min}^{-1}$$

$$t = \frac{2.303}{k}\log\frac{[R]_o}{[R]} \qquad t = \frac{2.303\times 40}{0.693}\log\frac{100}{20}$$

$$t = \frac{40}{0.301}\times[\log 5]$$

$$t = \frac{40}{0.301}\times 0.699 \qquad t = 92.89\ \text{min}$$

9. $$\log k = \log A - \frac{Ea}{2.303k} - \frac{1}{T}$$

$$-\frac{Ea}{2.303R} = -3.0\times10^{+3}$$

$$E_a = 3.0\times10^3\times2.303\times8.314$$

$$E_a = 57441.426\ \text{J/mol}$$

10. Rate $= -\frac{1}{2}d\frac{[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k[NH_3]^o = k$

$$\frac{d[N_2]}{dt} = k = 1.25\times10^{-3}\ \text{mol}\,L^{-1}\,\text{min}^{-1}$$

$$\frac{d[H_2]}{dt} = 3k = 3\times1.25\times10^{-3} = 3.75\times10^{-3}\ \text{mol}\,L^{-1}\ \text{min}^{-1}$$

11. $$(CH_3)_2CHN = NCH(CH_3)_2 \longrightarrow (CH_3)_2CHCH(CH_3)_2 + N_2$$

t = 0	35 mm Hg	0	0
t = 360 s	(35– x) mm Hg	x	x

But 35 – x + x + x = p_{total} = 54

x = 54 – 35 = 19 mm Hg

$$k_{360} = \frac{2.303}{360}\log\frac{35}{16} = \frac{2.303}{360}\times0.3399$$

= $2.17 \times 10^{-3}\ s^{-1}$

at t = 720 s

total pressure = 63 = 35 – x + x + x

x = 28 mm Hg and

$$k_{120} = \frac{2.303}{720}\log\frac{35}{(35-28)}$$

$$= \frac{2.303}{720}\times0.699 = 2.23\times10^{-3}\ s^{-1}$$

value of k $= \frac{2.17\times10^{-3}\times2.23\times10^{-3}}{2} = 2.2\times10^{-3}\,s^{-1}$

12. (i) More than three molecules cannot collide simultaneously to bring about an effective collision to cross the energy of activation barrier.

(ii) Slow: $NO_2 + Cl_2 \rightarrow NO_2Cl + Cl$

Fast: $NO_2 + Cl \rightarrow NO_2Cl$

13. (i) $k = \frac{2.303}{t}\log\frac{[R]_o}{[R]}$

at $t = t_{1/2}$, we have $t_{1/2} = \frac{2.303}{k}\log\frac{[R]_o}{[R]_o/2}$

$$t_{1/2} = \frac{2.303}{k}\times\log 2$$

$$t_{1/2} = \frac{2.303\times0.301}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$

As this equation does not include concentration, it means that the half-life of a first order reaction is independent of the initial concentration of the reactant.

(ii) Comparing units L $mol^{-1}\,s^{-1}$ with $(mol\,L^{-1})^{1-n}\,s^{-1}$ gives $-1 = 1 - n$, $n = 2$

The order of reaction - 2.

14. (i) Rate $= -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{d[D]}{dt} = k[A][B]^2$

(ii) $r = k[A][B]^2$ ...(i)

$r' = k[2A][2B]^2$ ...(ii)

eqn (ii) ÷ eqn (i) given $\frac{r'}{r} = 8$

$r' = 8r$

Rate increases eight times.

(iii) $r = k[A][B]^2$ ...(i)

$r' = k[½A][2B]^2$ ...(ii)

eqn (ii) ÷ (i) gives $r' = 2r$

The rate increases two times

15. (a)

	Order		Molecularity
(i)	It is the sum of the exponents to which each concentration term is raised in the experimental derived rate equation	(i)	It is the number of reactant molecules which can collides simultaneously in the elementary step to bring about a chemical reaction.
(ii)	It is an experimental equantity	(ii)	It is a theoretical concept
(iii)	It can be zero or fractional or can have integral values	(iii)	It has only values possible 1, 2, 3
(iv)	It does not explain the mechanism of reaction.	(iv)	It does explain the mechanism of reaction

(b) 0.24 M → 0.12 M

t = 20 s → half-complete

0.24 M → 0.06 M

t = 40 s → three fourth complete

Since, $t_{3/4} = 2\, t_{1/2}$, it means that it is a first order reaction.

∴ half-life, $t_{1/2} = 20\text{s}$

and $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20}$

$k = 0.03465\ s^{-1}$.

