

EXAM
DRILL

Chemical Kinetics

ANSWERS

$$1. \text{ (i) (a) : } k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$= \frac{2.303}{20} \log \left(\frac{0.5}{0.005} \right) = 0.2303 \text{ min}^{-1}$$

$$\text{(ii) (c) : } t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$$= \frac{2.303}{2.303 \times 10^{-2} \text{ s}^{-1}} \log \left(\frac{100}{25} \right) = 60.21 \text{ s}$$

$$\text{(iii) (d) : } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{450 \text{ s}^{-1}} = 1.54 \times 10^{-3} \text{ s}$$

2. (d) : 1 hour = 4 half-lives

$$\text{Amount left} = \frac{a}{2^n} = \frac{a}{2^4} = \frac{1}{16} \text{ of } a.$$

3. (c) : When [A] is kept constant [B] is doubled; rate is doubled, Hence rate $\propto [B]$.

When [B] is kept constant, [A] is doubled, rate becomes 4 times. Hence rate $\propto [A]^2$

$$\text{Rate} = k[A]^2[B]$$

$$k = \frac{\text{Rate}}{[A]^2[B]} = \frac{1.15 \times 10^{-4}}{(0.5)^2(0.02)} = 2.30 \times 10^{-2}$$

4. (b) : Rate of zero order reaction is independent of the concentration of the reactant.

5. (a) : $E_f \neq E_r$

6. (b) : $3A \rightarrow 2B$

$$\text{Rate} = \frac{-1}{3} \frac{d[A]}{dt} = \frac{+1}{2} \frac{d[B]}{dt}$$

$$\text{Hence, } \frac{+d[B]}{dt} = \frac{-2}{3} \frac{d[A]}{dt}$$

7. (a)

8. (b)

9. (b)

10. (c) : Plot of $\log A_t$ vs. t gives slope of $\frac{-k}{2.303}$

11. (a)

12. For $3/4$ th life, put $x = \frac{3}{4}a$

$$t_{3/4} = \frac{2.303}{k} \log \left(\frac{a}{a - \frac{3}{4}a} \right) = \frac{2.303}{k} \log 4$$

OR

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$$

$$\frac{kt}{2.303} = \log a - \log(a-x)$$

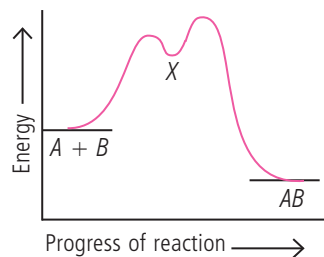
$$\log(a-x) = \log a - \frac{kt}{2.303}$$

A plot of $\log(a-x)$ versus t gives a straight line with a slope

$$= \frac{-k}{2.303}$$

Hence, a negative slope is $\frac{k}{2.303}$

13. As it is an exothermic reaction ΔH is $-ve$; $H_r > H_p$. As the reaction occurs in two steps, it has two activation energy peaks. The first step, being fast, needs less activation energy. The second step, being slow, needs more activation energy.



Therefore, second peak will be higher than the first peak.

$$14. \quad r = k[A]^n \quad \dots(i)$$

$$4r = k[2A]^n \quad \dots(ii)$$

On dividing (ii) by (i), $4 = 2^n \Rightarrow n = 2$.

OR

6.4×10^{-3} . For every 10° rise, the velocity constant becomes nearly double.

15. Rate depends upon slowest step.

Hence from equation (i), $r = k[O][O_3]$

$$\text{From equation (ii), } K_{eq} = \frac{[O_2][O]}{[O_3]}$$

$$\Rightarrow [O] = \frac{K_{eq}[O_3]}{[O_2]}$$

$$\text{Hence, } r = kK_{eq} \frac{[O_3][O_3]}{[O_2]} = k'[O_3]^2[O_2]^{-1}$$

where $k' = k K_{eq}$.

16. For every 10° rise, rate constant is doubled. Hence, for 20°C rise rate constant will become 4 times.

i.e., $k_1 = 4k_2$ or $k_2 = 0.25 k_1$.

17. The two-third life of a first order reaction is the time in which the concentration of the reactant is reduced to one third of its initial concentration.

$$\text{Let } [A]_0 = 1 \text{ mol L}^{-1}; [A]_{t=2/3} = [A]_0 - \frac{2}{3}[A]_0 = \frac{1}{3}[A]_0 \text{ mol L}^{-1}$$

$$\begin{aligned} t_{\frac{2}{3}} &= \frac{2.303}{k} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{5.4 \times 10^{-14} \text{ s}^{-1}} \log \frac{1}{1/3} \\ &= \frac{2.303}{5.4 \times 10^{-14} \text{ s}^{-1}} \log 3 = 2.034 \times 10^{13} \text{ s} \end{aligned}$$

18. For a second order reaction, Rate = $k[A]^2$

$$\begin{aligned} k &= \frac{\text{Rate}}{[A]^2} = \frac{8.4 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.02)^2 \text{ mol}^2 \text{ L}^{-2}} \\ &= 2.1 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1} \end{aligned}$$

19. Average rate : The average rate of a chemical reaction is defined as the change in the concentration of a reactant (or product) in a particular time interval. It is simply the average rate during the time interval Δt . It is obtained by dividing the change in reactant concentration by the time interval *i.e.*, $\Delta[A]/\Delta t$.

Instantaneous rate : The instantaneous rate of a chemical reaction is the reaction rate at a particular time, *i.e.*, $\Delta T \rightarrow 0$. It may be defined as the rate of change of concentration per unit time. It is determined by taking slope of a tangent at a point of the curve to the graph of concentration $[A]$ versus time t , corresponding to the specified time.

20. From Expt. 1 and 2

$$(i) \text{ Rate} \propto [\text{Cr}(\text{H}_2\text{O})_6]^{3+a} [\text{SCN}^-]^b$$

$$\frac{2.0 \times 10^{-11}}{2.0 \times 10^{-10}} \propto \frac{(1.0 \times 10^{-4})^a (0.10)^b}{(1.0 \times 10^{-3})^a (0.10)^b}$$

$$0.1 \propto (0.1)^a \Rightarrow a = 1$$

The order of the reactant $[\text{Cr}(\text{H}_2\text{O})_6]^{3+a}$ is 1.

From Expt. 3 and 4,

$$\frac{6.0 \times 10^{-10}}{1.5 \times 10^{-9}} \propto \frac{(1.5 \times 10^{-3})^a (0.20)^b}{(1.5 \times 10^{-3})^a (0.50)^b}$$

$$0.4 \propto (0.4)^b \Rightarrow b = 1$$

The order of the reactant $[\text{SCN}^-]$ is 1.

(ii) Rate law

$$\text{Rate} = k[\text{Cr}(\text{H}_2\text{O})_6]^{3+a} [\text{SCN}^-]^1$$

$$\text{Rate} = k[\text{Cr}(\text{H}_2\text{O})_6]^{3+a} [\text{SCN}^-]$$

$$\begin{aligned} (iii) \text{ Rate constant, } k &= \frac{\text{Rate}}{[\text{Cr}(\text{H}_2\text{O})_6]^{3+a} [\text{SCN}^-]} \\ &= \frac{2.0 \times 10^{-11} \text{ Ms}^{-1}}{(1.0 \times 10^{-4} \text{ M})(0.10 \text{ M})} = 2.0 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

21. For a first order reaction, $k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$

For the first case : $t = 72 \text{ min}$; $x = 75\%$ $a = 0.75a$

$$k = \frac{2.303}{72} \log \frac{a}{a-0.75a} = \frac{2.303}{72} \log 4 = 0.01925 \text{ min}^{-1}$$

For the second case, $t_{50\%} = ?$, $x = a/2$

$$k = \frac{2.303}{t_{50\%}} \log \frac{a}{a-(a/2)} = \frac{2.303}{t_{50\%}} \log 2$$

$$t_{50\%} = \frac{2.303}{0.01925} \log 2 = 36 \text{ minutes}$$

\therefore The reaction was half completed in 36 minutes.

OR

For a first order reaction in X , $k = \frac{2.303}{t} \log \left(\frac{a}{a-x} \right)$
 $t = 1 \text{ hour}$, $x = a/2$

$$k = \frac{2.303}{1} \log \frac{a}{a-a/2} = 2.303 \log 2$$

$$= 2.303 \times 0.3010 = 0.6932 \text{ hr}^{-1}$$

For a second case, $t = 2 \text{ hours}$, $a - x = ?$

$$k = \frac{2.303}{2} \log \left(\frac{a}{a-x} \right)$$

$$\log \left(\frac{a}{a-x} \right) = \frac{0.6932 \times 2}{2.303} = 0.602$$

$$\frac{a}{a-x} = \text{antilog}(0.602) = 3.999$$

$$a = 3.999(a-x)$$

$$(a-x) = \frac{a}{3.999} = \frac{1000}{3999} a = 0.25006a$$

\therefore The amount of the reactant left at the end of 2 hours = 0.25006 of the original material.

$$0.25006 \times 100\% = 25.006\%$$

22. (a) For a first order reaction

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.2 \times 10^{-5} \text{ sec}^{-1}} = 31500 \text{ sec}$$

$$(b) k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

$$2.2 \times 10^{-5} = \frac{2.303}{7200} \log \frac{10}{[A]_t} \Rightarrow \log \frac{10}{[A]_t} = 0.06877$$

$$\frac{10}{[A]_t} = \text{antilog}(0.06877) = 1.1715$$

$$\frac{10}{1.1715} = [A]_t \Rightarrow [A]_t = 8.53 \text{ g}$$

\therefore 85.3% is unreacted

23. (i) The order of reaction is defined as the sum of the exponents to which the concentration terms are raised in the rate law equation.

(ii) The first order rate equation is given by

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} \Rightarrow t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t}$$

When $t = t_{1/2}$; $[A]_t = [A]_0/2$

On substituting the values, we get

$$\begin{aligned} t_{1/2} &= \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/2} = \frac{2.303}{k} \log 2 \\ &= \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k} \end{aligned}$$

Hence, the half-life of a first order reaction is independent of the concentration of the reactant.

OR

(i) (a) For a zero order reaction, Rate = $k[A]^0 = k$

So, the unit of k is same as that of rate *i.e.*, $\text{mol L}^{-1}\text{s}^{-1}$ for a zero order reaction.

(b) For a first order reaction, Rate = $k[A]$

$$k = \frac{\text{Rate}}{[A]} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{\text{mol L}^{-1}} = \text{s}^{-1}$$

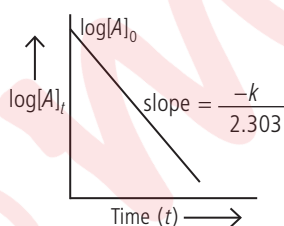
So, the unit of k is s^{-1} for a first order reaction.

(ii) For a first order reaction ;

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{t} [\log [A]_0 - \log [A]_t]$$

$$\text{or } \log [A]_t = \frac{-kt}{2.303} + \log [A]_0$$

When we plot a graph between logarithm of a reactant concentration and time, we will get a straight-line graph. It is a linear graph. This proves that the reaction is of first order reaction.



24. (i) The minimum amount of extra energy required by reactant molecules to participate in a chemical reaction is called activation energy. The rate of a reaction increases with increase in temperature. The Arrhenius equation; $k = Ae^{-E_a/RT}$ relates to the activation energy, temperature and the rate constant. The equation shows that, for a given value of activation energy, as the temperature increases the value of the rate constant increases. The increase of temperature increases the fraction of molecules that have energies in excess of the activation energy.

$$(ii) \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\begin{aligned} E_a &= \frac{2.303R \times T_1 \times T_2}{(T_2 - T_1)} \log \frac{k_2}{k_1} \\ &= \frac{2.303 \times 8.314 \times 298 \times 308}{10} \log \left(\frac{13.50 \times 10^{-5}}{3.46 \times 10^{-5}} \right) \end{aligned}$$

$$= 103907.6 \text{ J mol}^{-1} = 103.907 \text{ kJ mol}^{-1}$$

25. (i) If f is the fraction that has reacted, then $(1 - f)$ is the fraction that remains after $t = 1$ hour = 3600 seconds.

$$t = \frac{2.303}{k} \log \left(\frac{1}{1-f} \right)$$

$$\log \left(\frac{1}{1-f} \right) = \frac{kt}{2.303} = \frac{1.5 \times 10^{-4} \text{ s}^{-1} \times 3600 \text{ s}}{2.303} = 0.234476$$

$$\frac{1}{1-f} = \text{antilog}(0.234476) = 1.7158$$

$$1-f = \frac{1}{1.7158} = 0.5828$$

(ii) For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{6 \text{ min}^{-1}} \log \frac{0.8}{0.08} = 0.38 \text{ min}$$

26. (i) For a first order reaction, the rate of reaction is directly proportional to the concentration of the reactant.

$$\text{Rate} = \frac{-d[A]}{dt} = k[A] \Rightarrow \frac{-d[A]}{[A]} = kdt$$

On integrating this above equation, we get

$$-\ln[A] = kt + I \quad [\because \text{At } t = 0; [A] = [A]_0]$$

$$-\ln[A]_0 = I$$

Substituting the value of I in above equation

$$-\ln[A] = kt - \ln[A]_0$$

$$kt = \ln[A]_0 - \ln[A] = \ln \frac{[A]_0}{[A]}$$

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

This is the integrated rate expression for the first order reaction.

(ii) Let the initial concentration of the reaction, $A = 100\%$

$$t_{20\%} = \frac{2.303}{k} \log \frac{100}{100-20} \Rightarrow 20 \text{ min} = \frac{2.303}{k} \log 1.25$$

$$t_{80\%} = \frac{2.303}{k} \log \left(\frac{100}{100-80} \right) = \frac{2.303}{k} \log 5$$

$$\frac{t_{80\%}}{t_{20\%}} = \frac{2.303}{k} \log 5 \times \frac{k}{2.303} \times \frac{1}{\log 1.25}$$

$$\frac{t_{80\%}}{20} = \frac{\log 5}{\log 1.25} = \frac{0.6989}{0.0969} = 7.213$$

$$\therefore t_{80\%} = 7.213 \times 20 = 144.3 \text{ min}$$

$$\begin{aligned} \text{27. (i) Rate} &= -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{2} \times 1 \times 10^{-2} \\ &= 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

$$(ii) \text{Rate} = \frac{-d[A]}{dt} = \frac{-1}{2} \frac{d[B]}{dt} = +\frac{1}{3} \frac{d[C]}{dt}$$

Rate of change in concentration of A,

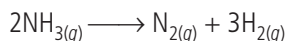
$$= -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = 0.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

Rate of change in concentration of C,

$$= +\frac{d[C]}{dt} = -\frac{3}{2} \frac{d[B]}{dt} = \frac{3}{2} \times 10^{-2} = 1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

OR

The reaction is



Here : $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

The order of reaction is 0 i.e.,

Rate = k [Reactant]⁰

Rate = $2.5 \times 10^{-4} \times 1 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\text{Rate of reaction} = \frac{+d[\text{N}_2]}{dt} = \frac{+1}{3} \frac{d[\text{H}_2]}{dt}$$

The rate of formation of $\text{N}_2 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$$\text{Again, } 2.5 \times 10^{-4} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\therefore \frac{d[\text{H}_2]}{dt} = 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Therefore, rate of formation of $\text{H}_2 = 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

28. (i) Let rate law for the disappearance of N_2O_5 is

Rate = $k[\text{N}_2\text{O}_5]^a$

$$\text{Then } \frac{r_1}{r_2} = \frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{k(1.13 \times 10^{-2})^a}{k(0.84 \times 10^{-2})^a}$$

$$\text{or, } \frac{34}{25} = \left(\frac{113}{84}\right)^a \text{ or } a = 1$$

Thus, order of reaction = 1

(ii) $r = k[\text{N}_2\text{O}_5]$ or, $34 \times 10^{-5} = k \times 1.13 \times 10^{-2}$

$$\text{or, } k = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}} = 3.0 \times 10^{-2} \text{ min}^{-1}$$

(iii) Rate law = $k[\text{N}_2\text{O}_5]$

29. (i) $k_1 = 6.0 \times 10^{-4} \text{ s}^{-1}$, $T_1 = 300 \text{ K}$,
 $E_a = 3.05 \times 10^5 \text{ J mol}^{-1}$, $k_2 = ?$, $T_2 = 310 \text{ K}$

Using Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{k_2}{k_1} = \frac{3.05 \times 10^5 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left[\frac{310 \text{ K} - 300 \text{ K}}{300 \text{ K} \times 310 \text{ K}} \right]$$

$$\log \frac{k_2}{k_1} = \frac{3.05 \times 10^5 \text{ J mol}^{-1} \times 10}{1780684.2 \text{ J mol}^{-1}}$$

$$\log \frac{k_2}{k_1} = 1.71 \Rightarrow \frac{k_2}{k_1} = \text{antilog}(1.71)$$

$$\frac{k_2}{6 \times 10^{-4}} = 51.28 \text{ or } k_2 = 3.07 \times 10^{-2} \text{ s}^{-1}$$

(ii) Here $k_2 = 2k_1$, $T_1 = 298 \text{ K}$, $T_2 = 308 \text{ K}$
 $E_a = ?$

$$\therefore \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{2k_1}{k_1} = \frac{E_a}{2.303R} \left[\frac{308 - 298}{308 \times 298} \right]$$

$$\log 2 = \frac{E_a}{2.303R} \left[\frac{10}{91784} \right]$$

$$0.3010 = \frac{1.089 \times 10^{-4} E_a}{2.303 \times 8.314}$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314}{1.089 \times 10^{-4}} = 52922.77 \text{ J mol}^{-1}$$

OR

20% decomposition means that $x = 20\%$ of $a = 0.20 a$

For first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a-x}$

$$= \frac{2.303}{15} \log \frac{a}{a-0.20a} = \frac{2.303}{15} \log \frac{a}{0.80a} = \frac{2.303}{15} \log 1.25$$

$$= \frac{2.303}{15} \times 0.0969 = 0.0148 \text{ min}^{-1}$$

(ii) It is due to improper orientation. Energy more than threshold energy and proper orientation are the two main factors which are responsible for a reaction to occur.

30. (i) Order of a reaction : It is defined as "the sum of the powers or exponents to which the concentration terms are raised in the rate law expression."

If rate = $k[A]^m [B]^n$, then order = $m + n$.

(a) $\text{L}^{-1} \text{ mol s}^{-1}$ – Zero order reaction

(b) $\text{L mol}^{-1} \text{ s}^{-1}$ – Second order reaction

Rate expression is a way of expressing rate of reaction in terms of concentration of reactants, e.g., for a general reaction,
 $aA + bB \longrightarrow cC + dD$

Rate = $k[A]^x [B]^y$

Rate constant (k) is equal to the rate of reaction when molar concentration of reactant is unity. Its units depends upon the order of reaction.

(ii) Given reaction is



Initially : 0.80 0.20 0

At equil. : 0.80 - x 0.20 - x 2x

According to law of mass action, $K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$

$$\text{or } 1.0 \times 10^{-5} = \frac{(2x)^2}{(0.80 - x)(0.20 - x)}$$

x is very small hence can be neglected in the denominator. Thus,

$$1.0 \times 10^{-5} = \frac{4x^2}{0.8 \times 0.2} \text{ or } 1.0 \times 10^{-5} = \frac{4x^2}{0.16}$$

$$\text{or, } 4x^2 = 1.0 \times 10^{-5} \times 0.16 \text{ or } 4x^2 = 16 \times 10^{-7}$$

$$\text{or, } x^2 = 4 \times 10^{-7} \text{ or } x = 6.32 \times 10^{-4}$$

$$\therefore [\text{N}_2] = 0.80 - 0.000632 = 0.7994 \text{ mol L}^{-1}$$

$$[\text{O}_2] = 0.20 - 0.000632 = 0.199 \text{ mol L}^{-1}$$

$$[\text{NO}] = 2x = 2 \times 0.000632 = 0.001264 \text{ mol L}^{-1}$$

OR

(i) Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate

of a chemical reaction for which the concentration of each of the reacting species is unity.

Unit for k : $(\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$

(a) For a zero order reaction : $\text{mol L}^{-1} \text{ s}^{-1}$

(b) For a first order reaction : s^{-1} .

$$\text{(ii) (a) } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \text{ min}} = 0.0693 \text{ min}^{-1}$$

$$\text{(b) } N = N_0 \left(\frac{1}{2}\right)^n, \text{ where, } n = \frac{\text{Total time}}{t_{1/2}} = \frac{60}{10} = 6$$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^6 = \frac{1}{64} \quad \dots(1)$$

[where N_0 = initial amount of reactant and N = amount of reactant left after time, t].

