

## Speed Test-46

$$1. (d) k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{24} \log \frac{1}{\frac{1}{8}} = \frac{2.303}{24} \log 8$$

2. (b) Since doubling the concentration of B does not change half life, the reaction is of 1st order w.r.t. B.  
Order of reaction with respect to A = 1 because rate of reaction doubles when concentration of A is doubled keeping concentration of B constant.

∴ Order of reaction = 1 + 1 = 2 and units of second order reaction are  $\text{L mol}^{-1} \text{sec}^{-1}$ .

3. (d) The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction. Thus the reaction involving two different reactant can never be unimolecular.

4. (a) Let the rate law be  $r = k[A]^x[B]^y$

$$\text{Divide (3) by (1)} \quad \frac{0.10}{0.10} = \frac{[0.024]^x [0.035]^y}{[0.012]^x [0.035]^y}$$

$$\therefore 1 = [2]^x, x = 0$$

$$\text{Divide (2) by (3)} \quad \frac{0.80}{0.10} = \frac{[0.024]^x [0.070]^y}{[0.024]^x [0.035]^y}$$

$$\therefore 8 = (2)^y, y = 3$$

$$\text{Hence rate equation, } R = k[A]^0[B]^3 = k[B]^3$$

5. (a) If we write rate of reaction in terms of concentration of  $\text{NH}_3$  and  $\text{H}_2$ , then

$$\text{Rate of reaction} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\text{So, } \frac{d[\text{NH}_3]}{dt} = -\frac{2}{3} \frac{d[\text{H}_2]}{dt}$$

6. (a) As doubling the initial conc. doubles the rate of reaction, order = 1

7. (b) Rate law has to be determined experimentally as  $\text{Cl}_2$  is raised to power  $\frac{1}{2}$  in rate law whereas its stoichiometric coefficient in balanced chemical equation is 1.

8. (a)

$$9. (c) \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}; \quad \frac{120}{240} = \left(\frac{4 \times 10^{-2}}{8 \times 10^{-2}}\right)^{n-1}; n = 2$$

10. (b)

12. (c) Activation energy is lowered in presence of +ve catalyst.

13. (d) Overall order = sum of orders w.r.t. each reactant.  
Let the order be x and y for G and H respectively

Exp.No.	[G]mole litre <sup>-1</sup>	[H]mole litre <sup>-1</sup>	rate(mole litre <sup>-1</sup> time <sup>-1</sup> )
1	a	b	r
2	2a	2b	8r
3	2a	b	2r

∴ For (1) and (3), the rate is doubled when conc. of G is doubled keeping that of H constant i.e.,

$$\text{rate} \propto [\text{G}] \therefore x = 1$$

From (2) and (3),  $y = 2$

∴ Overall order is 3.

14. (b) For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{0.1}{0.025}$$

$$= \frac{2.303}{40} \log 4 = \frac{2.303 \times 0.6020}{40}$$

$$= 3.47 \times 10^{-2} \text{ min}^{-1}$$

$$\text{Rate} = k[A] = 3.47 \times 10^{-2} \times 0.01$$

$$= 3.47 \times 10^{-4} \text{ M/min}$$

15. (c) Third order

16. (c) For a first order reaction

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$\text{when } t = t_{1/2}$$

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{a-a/2}$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log_{10} 2 = \frac{\ln 2}{k}$$

17. (d) The integrated rate equations are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

18. (b)  $T_2 = T$  (say),  $T_1 = 25^\circ\text{C} = 298\text{K}$ ,  
 $E_a = 104.4 \text{ kJ mol}^{-1} = 104.4 \times 10^3 \text{ J mol}^{-1}$   
 $k_1 = 3 \times 10^{-4}$ ,  $k_2 = ?$ ,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J mol}^{-1}}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \left[ \frac{1}{298} - \frac{1}{T} \right]$$

$$\text{As } T \rightarrow \infty, \frac{1}{T} \rightarrow 0$$

$$\therefore \log \frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log \frac{k_2}{3 \times 10^{-4}} = 18.297, \quad \frac{k_2}{3 \times 10^{-4}} = 1.98 \times 10^{18}$$

$$k_2 = (1.98 \times 10^{18}) \times (3 \times 10^{-4}) = 6 \times 10^{14} \text{ s}^{-1}$$

19. (c) Adsorption lowers the activation energy.

20. (a) For the change  $2A + 3B \rightarrow \text{products}$

$$-\frac{1}{2} \frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt}, \quad \frac{1}{2} t_1 = \frac{1}{3} t_2, \quad 3t_1 = 2t_2$$

21. (c) The  $t_{1/2}$  is 15 minutes. To fall the concentration from 0.1 to 0.025 we need two half-lives i.e., 30 minutes.

22. (b) According to Arrhenius equation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$= -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

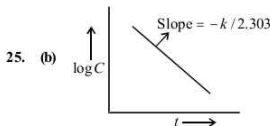
$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

23. (c)  $t_{1/4} = \frac{2.303}{k} \log \frac{1}{3/4} = \frac{2.303}{k} \log \frac{4}{3}$
- $$= \frac{2.303}{k} (\log 4 - \log 3) = \frac{2.303}{k} (2 \log 2 - \log 3)$$
- $$= \frac{2.303}{k} (2 \times 0.301 - 0.4771) = \frac{0.29}{k}$$

24. (d) For a zero order reaction,  
 $t_{1/2} \propto a_0$  (initial concentration or initial pressure)  
 $(t_{1/2})_1 \propto P_1$   
 $(t_{1/2})_2 \propto P_2$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{P_2}{P_1}, \quad \frac{(t_{1/2})_2}{45} = \frac{16}{4}$$

$$(t_{1/2})_2 = \frac{16}{4} \times 45 = 180 \text{ min}$$



26. (b) Plot given is for zero order reaction.

27. (c) Since for every  $10^\circ\text{C}$  rise in temperature rate doubles for  $50^\circ\text{C}$  rise in temperature increase in reaction rate  $= 2^5 = 32$  times

28. (a)  $k = \frac{2.303}{1386} \log \frac{100}{100 - 75}$  On solving we get  $k = 10^{-3}$

29. (a)

30. (a) Presence of catalyst does not affect enthalpy change of reaction  $\Delta H_R = E_f - E_b = 180 - 200 = -20 \text{ kJ/mol}$

31. (c) Given  $t_{1/2} = 15$  minutes

$$\text{Total time } (T) = 1 \text{ hr} = 60 \text{ min}$$

$$\text{From } T = n \times t_{1/2}$$

$$n = \frac{60}{15} = 4$$

$$\text{Now from the formula } \frac{N}{N_0} = \left( \frac{1}{2} \right)^n$$

$$= \left( \frac{1}{2} \right)^4 = \frac{1}{16}$$

Where  $N_0$  = initial amount

$N$  = amount left after time  $t$

hence the amount of substance left after 1 hour will

$$\text{be } \frac{1}{16}$$

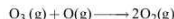
32. (d)  $\text{Rate}_1 = k[A]^n [B]^m$

$$\text{Rate}_2 = k[2A]^n \left[ \frac{1}{2} B \right]^m$$

$$\therefore \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[2A]^n \left[ \frac{1}{2} B \right]^m}{k[A]^n [B]^m} = (2)^n \left( \frac{1}{2} \right)^m$$

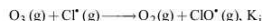
$$= 2^n \cdot (2)^{-m} = 2^{n-m}$$

33. (a) On adding eq. (i) and eq. (ii) we get



$$\text{Hence overall rate constant} = K_1 \times K_{ij}$$

$$= 5.2 \times 10^9 \times 2.6 \times 10^{10} \approx 1.4 \times 10^{20} \text{ mol}^{-1} \text{ L s}^{-1}$$



34. (b)  $k = A e^{-E_a/RT}$   $\log k = \log A - \frac{E_a}{2.303R} \cdot \frac{1}{T}$

$$\text{Plot of } \log k \text{ Vs. } \frac{1}{T}$$

$$\text{Straight line Slope} = \frac{-E_a}{2.303R}$$

35. (b)  $r = k[\text{O}_2][\text{NO}]^2$ . When the volume is reduced to  $1/2$ , the conc. will double

$$\therefore \text{New rate} = k[2\text{O}_2][2\text{NO}]^2 = 8k[\text{O}_2][\text{NO}]^2$$

The new rate increases to eight times of its initial.

36. (d) From rate law

$$-\frac{1}{2} \frac{d\text{SO}_2}{dt} = -\frac{d\text{O}_2}{dt} = \frac{1}{2} \frac{d\text{SO}_3}{dt}$$

$$\begin{aligned}\therefore -\frac{d\text{SO}_2}{dt} &= -2 \times \frac{d\text{O}_2}{dt} \\ &= -2 \times 2.5 \times 10^{-4} \\ &= -5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

37. (c)
- $k_1 = A_1 e^{-E_{a1}/RT}$
- .....(i)

$$k_2 = A_2 e^{-E_{a2}/RT}$$
 .....(ii)

On dividing eqn (i) from eqn. (ii)

$$\frac{k_1}{k_2} = \frac{A_1}{A_2} (E_{a2} - E_{a1}) / RT$$
 .....(iii)

$$\text{Given } E_{a2} = 2E_{a1}$$

On substituting this value in eqn. (iii)

$$k_1 = k_2 A \times e^{E_{a1}/RT}$$

38. (d) Enthalpy of reaction (
- $\Delta H$
- ) =
- $E_{a(f)} - E_{a(b)}$
- 
- to be positive
- 
- $E_{a(b)} < E_{a(f)}$

39. (d)

$$40. (a) \ln \frac{K_1}{K_2} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln 4 = \frac{E_a}{8.314} \left( \frac{310-300}{310 \times 300} \right)$$

$$2 \ln 2 = \frac{E_a}{8.314} \left( \frac{310-300}{310 \times 300} \right)$$

$$E_a = \frac{0.693 \times 2 \times 8.314 \times 300 \times 310}{10} = 107.2 \text{ kJ/mol}$$

41. (d) Since the slow step is the rate determining step hence if we consider option (A) we find

$$\text{Rate} = k [\text{Cl}_2] [\text{H}_2\text{S}]$$

Now if we consider option (B) we find

$$\text{Rate} = k [\text{Cl}_2] [\text{HS}^-] \quad \dots(i)$$

For equation,



$$K = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$\text{or } [\text{HS}^-] = \frac{K [\text{H}_2\text{S}]}{[\text{H}^+]}$$

Substituting this value in equation (i) we find

$$\text{Rate} = k [\text{Cl}_2] K \frac{[\text{H}_2\text{S}]}{[\text{H}^+]} = k' \frac{[\text{Cl}_2] [\text{H}_2\text{S}]}{[\text{H}^+]}$$

Thus slow step should involve 1 molecule of  $\text{Cl}_2$  and 1 molecule of  $\text{H}_2\text{S}$ .

hence only, mechanism (A) is consistent with the given rate equation.

42. (a) Arrhenius equation is given by

$$k = A e^{-E_a/(2.303RT)}$$

Taking log on both sides, we get

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

Arrhenius plot a graph between  $\log k$  and  $\frac{1}{T}$  whose

$$\text{slope is } \frac{-E_a}{2.303R}$$

43. (d) The graph show that reaction is exothermic.

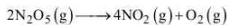
$$\log k = \frac{-\Delta H}{RT} + 1$$

For exothermic reaction  $\Delta H < 0$ 

$\therefore \log k$  Vs  $\frac{1}{T}$  would be negative straight line with positive slope.

44. (a) As per Arrhenius equation (
- $k = A e^{-E_a/RT}$
- ), the rate constant increases exponentially with temperature.

45. (a) Rate law for first order reaction =
- $k[\text{N}_2\text{O}_5]$



$$t = 0 \text{ min} \quad 50 \quad 0 \quad 0$$

(Pressure in mm Hg)

$$t = 30 \text{ min} \quad 50 - 2p \quad 4p \quad p$$

(Pressure in mm Hg)

$$\text{Total pressure } 50 - 2p + 4p + p = 50 + 3p$$

$$= 87.5 \text{ mm Hg}$$

$$\therefore P = 12.5 \text{ mm Hg}$$

$$\therefore P_0 = 50 \text{ \& } P(t = 30 \text{ min})$$

$$= 25 \text{ for } \text{N}_2\text{O}_5 \text{ reactant}$$

$$\therefore k = \frac{2.303}{30 \text{ min}} \times \log \left( \frac{50}{25} \right) = \frac{2.303}{60 \text{ min}} \times \log \left( \frac{50}{x} \right)$$

On solving  $x = 12.5 \text{ mm Hg} = 50 - 2p$ 

$$\therefore P = 18.75 \text{ mm Hg}$$

$$\therefore \text{Total pressure} = 50 + 3P = 106.25 \text{ mm Hg}$$