31. $1.005 \times 10^{-4}\ \text{min}^{-1}$

Let the number of moles of A left after $100\,\text{min} = x$

Total number of moles after $100\,\text{m} = x + 12 + 0.525$

$$P_{\text{mix}} = P_A + P_B = \left(\frac{x}{12+x} \times 300\right) + \left(\frac{12}{12+x} \times 500\right) = \frac{6000 + 300x}{12+x}$$

According to Raoult's law

$$\frac{\left(\dfrac{6000+300x}{12+x}\right) - 400}{\dfrac{6000+300x}{12+x}} = \frac{0.525}{x + 12 + 0.525}$$

On solving, we get $x = 9.9$

Now according to first-order kinetics, $k = \dfrac{2.303}{100} \log \dfrac{10}{9.9} = 1.005 \times 10^{-4}\,\text{min}^{-1}$

32. 24.14 min $r_2 = k_1 c_1$ and $r_2 = k_2 c_2$

Since rate of first-order reaction is directly proportional to the concentration of its reactant,

$$\therefore \qquad \frac{r_1}{r_2} = \frac{c_1}{c_2} = \frac{0.04}{0.03}$$

According to first-order reaction $k = \dfrac{2.303}{t_{20} - t_{10}} \log \dfrac{c_1}{c_2}$

On substituting the various values $k = 0.0287\,\text{min}^{-1}$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287} = 24.14\,\text{min}$$

33. **(a)** Rate = k[A] **(b)** $0.5\,\text{sec}^{-1}$

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{0.05}{0.10} = \frac{1}{2} = \left(\frac{1}{2}\right)^a \Rightarrow a = 1 \text{ ; order w.r.t A}$$

Order w.r.t B = 0

(a) Rate = k[A] **(b)** $k = \dfrac{\text{Rate}}{[A]} = \dfrac{0.05}{0.10} = 0.5\ s^{-1}$

34. **(i) 1** **(ii)** $6.93 \times 10^{-3}\,\text{min}^{-1}$ **(iii) 200 min** **(iv) 950 mm Hg**

(a) Partial pressure becomes half of initial in every 100 min, therefore, order = 1.

(b) $k \times 100 = \ln \dfrac{800}{400} = \ln 2 \Rightarrow k = 6.93 \times 10^{-3}\,\text{min}^{-1}$

(c) For 75% reaction; time required = $2 \times \text{half} - \text{life} = 200\,\text{min}$

(d)

$$\begin{array}{ccc} 2X(g) & \longrightarrow 3Y(g) & + \ 2Z(g) \\ 800 - x & \dfrac{3}{2}x & x \end{array}$$

Total pressure $= 800 + \dfrac{3}{2}x$

Also $800 - x = 700 \Rightarrow \quad x = 100$

$\Rightarrow$ **Total pressure** $= 800 + \dfrac{3}{2} \times 100 = 950$ **mm Hg**

35.(B) The required reaction is $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; K = ?

From the given equations, we have

$$k_1 = \frac{[Ag(NH_3)]^+}{[Ag^+][NH_3]} \; ; \; k_2 = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+\,[NH_3]}$$

If equations are added, their rate constants are multiplied.

$\therefore$ The value of K is given by

$$K = k_1 \times k_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 1.08 \times 10^{-5}$$

36.(D) Order w.r.t. G is 2.
Order w.r.t. H is 1.
Overall order = 2 + 1 = 3

37.(A) $k_1 = \frac{0.693}{40} \quad r_0 = \frac{1.386}{2 \times 20} \quad \frac{k_1}{r_0} = 0.5\,\text{mol}^{-1}\text{dm}^3$

38.(D) $k = AC^{-Ea/RT}$

$$\Rightarrow \quad \log_{10} K = \log_{10} A = \frac{Ea}{2.303RT} \quad \Rightarrow \quad \log A = 6 \Rightarrow A = 10^6 s^{-1} \Rightarrow \frac{Ea}{2.303R} = 200 \Rightarrow Ea = 2000 \times 2.303$$

$$\Rightarrow \quad Ea = 38.3\,\text{kJ / mol}$$

39.(0) The ratio of reaction do not depend upon initial concentration.

40.(ABD) In first order reaction the half life do not depend upon initial concentration of the reactant.

41.(9) $$\frac{\log\left(\frac{A_0}{1/8A_0}\right)}{\log\left(\frac{A_0}{1/10A_0}\right)} \times 10 = 9$$

42.(D) Since time taken for 75% reaction of P is twice the time taken for 50% reaction of P. Hence reaction is first order w.r.t. P.
Analysis of graph of Q w.r.t. time shows, reaction of Q is of zero order.
Hence overall order of the reaction is one.

43.(B) $r = k[M]^a$

$$\frac{r'}{r} = \frac{(2M)^a}{(M)^a} = 8 \qquad \Rightarrow \quad a = 3$$

44.(9) $${}^{238}_{92}U \longrightarrow {}^{206}_{82}Pb + 8\alpha + 6\beta$$

α on getting neutralized forms He gas.

So 1 mole ${}^{238}_{92}U$ produces 8 moles He

Initial number of mole of gases = 1 mole
Final number of mole of gases = 1 + 8 = 9 moles

Ratio of final pressure to initial $= \frac{9}{1} = 9 \;\; (P \propto n)$

45.(BCD) $k = Ae^{-\frac{Ea}{RT}}$

High activation energy means lower value of k and slow reaction.
On increasing temperature energy of particles increases hence greater number of collisions occur whose energy exceeds the activation energy.
Rate of increase of k with temperature is higher when Ea has a large value
Pre-exponential factor is a measure of frequency of collisions.

46.(BD) N/P can be increased by β^+ decay and K electron capture. In both processes number of protons decreases and number of protons increases.

47.(AC) $K = P \cdot Z\, e^{-Ea/RT}$ (According to Arrhenius equation)

$K = A\,e^{-Ea/RT}$

$$P = \frac{A}{Z}$$

According to collision theory, P value is generally less than unity but for some reactions P is greater than one and for such reactions, observed rate is greater than rate predicted from Arrhenius equation. For a reaction with P value greater than 1, implies that the experimentally determined value of frequency factor (A) is higher than that predicted by Arrhenius equations and such reactions proceeds rapidly without the use of a catalyst.

48.(AD)

49.(AD) $A(g) \rightarrow 2B(g) + C(g)$

First order reaction

$$\begin{array}{llll} & A(g) & \rightarrow\ 2B(g) & +\ C(g) \\ t = 0 & [A]_0 & - & - \\ t = t & [A]_0 - x & 2x & x \end{array}$$

$$\begin{array}{lll} [A_0] + 2x & \alpha & P_t \\ 2x & \alpha & (P_t - P_0) \\ x & \alpha & \frac{(P_t - P_0)}{2} \end{array}$$

$$\ln\frac{A_0}{A_t} = kt \Rightarrow \ln\frac{A_0}{A_0 - x} = kt$$

$$\Rightarrow \quad \ln\frac{P_0}{P_0 - \left[\frac{P_t - P_0}{2}\right]} = kt \quad \Rightarrow \quad \ln\frac{2P_0}{3P_0 - P_t} = kt \quad \Rightarrow \quad \ln 2P_0 - \ln(3P_0 - P_t) = kt$$

$$\Rightarrow \quad \underset{\underset{y}{\downarrow}}{\ln(3P_o - P_t)} = \underset{\underset{C}{\downarrow}}{\ln 2P_o} - \underset{\underset{mx}{\downarrow}}{kt} \qquad \text{(so slope} = -k \text{ (-ve))}$$

$$\Rightarrow \quad t_{1/3} = \frac{1}{K}\ell n3\,; \quad t_{1/3} \text{ is independent of } [A]_0\,; \text{ k is constant.}$$

50.(ABD) ${}^{238}_{92}U \xrightarrow{-X_1} {}^{234}_{90}Th \xrightarrow{-X_2} {}^{234}_{91}Pa \xrightarrow{-X_3} {}^{234}Z \xrightarrow{-X_4} {}^{230}_{90}Th$

X_1	:	α particle	X_2	:	β^- particle
X_3	:	β^- particle	X_4	:	α particle

Z : ${}^{234}_{92}Z$ (isotope of uranium)

51.(6.75) $r = k[A]^x[B]^y[C]^z$

$6 \times 10^{-5} = k(0.2)^x(0.1)^y(0.1)^z$ .... **(i)**

$6 \times 10^{-5} = k(0.2)^x(0.2)^y(0.1)^z$ .... **(ii)**

$1.2 \times 10^{-4} = k(0.2)^x(0.1)^y(0.2)^z$ .... **(iii)**

$9 \times 10^{-5} = k(0.3)^x(0.1)^y(0.1)^z$ .... **(iv)**

From (i) & (ii) $\Rightarrow$ $y = 0$

From (i) & (iii) $\Rightarrow$ $z = 1$

From (i) & (iv) $\Rightarrow$ $x = 1$

$\therefore$ $r = k[A][C]$

From equation (i)

$6 \times 10^{-5} = k(0.2)(0.1)$

$k = \frac{6 \times 10^{-5}}{2 \times 10^{-2}} = 3 \times 10^{-3}$ $\therefore$ $r = 3 \times 10^{-3}[A][C]$

For $[A] = 0.15\,\text{mol dm}^{-3}$, $[B] = 0.25\,\text{mol dm}^{-3}$ & $[C] = 0.15\,\text{mol dm}^{-3}$

$r = 3 \times 10^{-3} \times 0.15 \times 0.15$

$r = 6.75 \times 10^{-5}$ $\therefore$ $y = 6.75$

52.(4.6) $2N_2O_5(g) \longrightarrow 2N_2O(g) + O_2(g)$

	$2N_2O_5(g)$	$2N_2O(g)$	$O_2(g)$
$t = 0$	1 atm		
$t = 4 \times 10^{-3} s^{-1}$	$1-2p$	$2p$	p

Total pressure $= 1 + p = 1.45$

$p = 0.45$

At $t = y \times 10^3$, pressure of $N_2O_5 = 1 - (2 \times 0.45) = 0.1\,\text{atm}$

$\Rightarrow$ unit of rate constant, shows first order reaction

$\Rightarrow$ $kt = \ell n \frac{p_o}{p_t}$

$\Rightarrow$ $t = \frac{1}{k} \ell n \frac{p_o}{p_t}$ $\Rightarrow$ $y \times 10^3 = \frac{1}{5 \times 10^{-4}} \ell n \frac{1}{0.1}$

$y = \frac{1}{5 \times 10^{-4} \times 10^3} \ell n 10$

$= 4.6$