16.(67%)

$$\ln\left\{\frac{k(40°C)}{k(25°C)}\right\} = \frac{E_a}{R}\left(\frac{15}{298\times 313}\right) = \frac{70\times 10000}{8.314}\times\frac{15}{298\times 313} = 1.35$$

$$\Rightarrow \quad \frac{k(40°C)}{k(25°C)} = 3.87$$

$$\text{Also } k(25°C) = \frac{1}{20}\ln\frac{100}{75} = \frac{1}{20}\ln\frac{4}{3}$$

$$\Rightarrow \quad k(40°C) = 3.87\times k(25°C) = 3.87\times\frac{1}{20}\ln\frac{4}{3} = 55.66\times 10^{-3}\,\text{min}^{-1}$$

$$\text{Now} \quad k(40°C)\times 20 = \ln\frac{100}{100-x}$$

$$\Rightarrow \quad 55.66\times 10^{-3}\times 20 = \ln\frac{100}{100-x} \qquad \Rightarrow \quad x = 67\%$$

17.(0.75 atm)

$$CH_3 - O - CH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

At 12 min : $0.40 - p$ $\quad p \quad p \quad p$

Total pressure = $0.4 + 2P$

$$\text{Also } k\times 12 = \ln\frac{0.40}{0.40-p} = \frac{\ln 2}{14.5}\times 12 = 1.77 \qquad \Rightarrow \qquad p = 0.175$$

$\Rightarrow$ Total pressure = $0.4 + 2p = 0.4 + 2\times 0.175 = 0.75$ atm

18. **(i)** 2 **(ii)** 1.2 **(iii)** 0.1 mole^{-1} hr^{-1}

(i) According to the figure, in the given time of 4 hours (1 to 5) concentration of A falls from 0.5 to 0.3 M, while in the same time concentration of B increases from 0.2 M to 0.6 M.

Decrease in concentration of A in 4 hours

$= 0.5 - 0.3 = 0.2\,M$

Increase in concentration of B in 4 hours

$= 0.6 - 0.2 = 0.4\,M$

Thus increase in concentration of B in a given time is twice then the decrease in concentration of A. Thus $n = 2$.

(ii) $K = \dfrac{[B^2]_{eq}}{[A]_{eq}} = \dfrac{(0.6)^2}{0.3} = 1.2\,M$

(iii) Initial rate of conversion of A

= Change in conc. of A during 1 h

$= \dfrac{0.6-0.5}{1} = 0.1$ mole^{-1} hr^{-1}

19. 1.76×10^{-4}

20. **(i)** A = 2, B = 1 **(ii)** $K = 2.66\times^{8} s^{-1}L^2mol^{-2}$ **(iii)** $A = 1.2\times 10^{18}$

Comparing the data of experiment number 2 and 3 :

$$\frac{R_3}{R_2} = \frac{1.6\times 10^{-2}}{4\times 10^{-3}} = \left(\frac{1.0\times 10^{-3}}{5\times 10^{-4}}\right)^m \qquad \Rightarrow \qquad m = 2, \text{ order w.r.t. } A$$

Now comparing the data of experiment number 1 and 2 :

$$\frac{R_2}{R_1} = \frac{4\times 10^{-3}}{5\times 10^{-4}} = \left(\frac{5\times 10^{-4}}{2.5\times 10^{-4}}\right)^2\left(\frac{6.0\times 10^{-5}}{3.0\times 10^{-5}}\right)^n$$

$\Rightarrow$ $8 = (2)^2(2)^n \Rightarrow$ n = 1, order w.r.t B.

(i) Order with respect to A = 2, order with respect to B = 1.

(ii) At 300 K, $R = k[A]^2[B]$

$$\Rightarrow \quad k = \frac{R}{[A]^2[B]} = \frac{5.0\times10^{-4}}{(2.5\times10^{-4})^2(3.0\times10^{-5})} = 2.66\times10^{8}\,s^{-1}L^2mol^{-2}$$

(iii) From first experiment :

Rate (320 K) = k(320 K) $(2.5 \times 10^{-4})2\ (3.0 \times 10^{-5})$

$$\Rightarrow \quad k(320K) = \frac{2\times10^{-3}}{(2.5\times10^{-4})^2(3.0\times10^{-5})} = 1.066\times10^{9}\,s^{-1}L^2mol^2\,.$$

$$\Rightarrow \quad \ln\left\{\frac{k(320K)}{k(300K)}\right\} = \frac{E_a}{R}\left(\frac{T_2-T_1}{T_1T_2}\right) \quad \Rightarrow \quad \ln\left(\frac{1.066\times10^9}{2.66\times10^8}\right) = \frac{E_a}{8.314}\left(\frac{20}{300\times320}\right)$$

$$\Rightarrow \quad E_a = 55.42\,kJ\ mol^{-1}$$

Now $\ln k = \ln A - \frac{E_a}{RT}$

At 300 K : $\ln(2.66\times10^8) = \ln A - \frac{55.42\times10^3}{8.314\times300}$

Solving : ln A = 41.62 $\Rightarrow$ $A = 1.2\times10^{18}$

21.(20.74 min)

For 1st order reaction :

$$k \propto \frac{1}{t_{1/2}}$$

$$\Rightarrow \quad \ln\left\{\frac{k\,(450°C)}{k(380°C)}\right\} = \ln\left\{\frac{t_{1/2}(380°C)}{t_{1/2}(450°C)}\right\} = \frac{E_a}{R}\left(\frac{450-380}{723\times653}\right)$$

$$\Rightarrow \quad \ln\left\{\frac{360}{t_{1/2}(450°C)}\right\} = \frac{200\times10^3}{8.314}\times\frac{70}{723\times653} = 3.54$$

$\Rightarrow$ $t_{1/2}(450°) = 10.37\,min$ $\Rightarrow$ Time for 75% reaction at 450°C

$= 2\times t_{1/2} = 2\times10.37 = 20.74$ min

22. $T = \infty$

23. **(i)** $E_a = 239.33$ kJ / mol **(ii)** 669 K

(i) The Arrhenius equation is $\log k = \log A - \frac{E_a}{2.303\,RT}$

Comparing with the given equation :

$$1.25\times10^4 = \frac{E_a}{2.303\,R} \quad \Rightarrow \quad E_a = 239.33\ kJ\ mol^{-1}$$

(ii) When half-life = 256 min, $k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{256\times60}s^{-1} = 4.5\times10^{-5}s^{-1}$

$$\Rightarrow \quad \frac{1.25\times10^4}{T} = 14.34 - \log 4.5\times10^{-5} = 16.68 \Rightarrow \quad T = \frac{1.25\times10^4}{16.68} = 669\ K$$

24. **(i)** E_a = 22kJ $A = 5.42\times10^{10}s^{-1}$ **(ii)** X = 0.375

(i) $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

$$\Rightarrow \quad \ln\left(\frac{4.5\times10^{7}}{1.5\times10^{7}}\right)=\frac{E_a}{8.314}\left(\frac{50}{323\times373}\right) \quad \Rightarrow \quad E_a = 22\text{kJ}$$

Also $\ln k = \ln A - \dfrac{E_a}{RT}$

At 50° C : $\ln A = \ln (1.5 \times 10^7) - \dfrac{22\times1000}{8.314\times323} = 8.33 \quad \Rightarrow \quad A = 4.15\times10^{3}\text{s}^{-1}$

(ii) $N_2O_5(g) \longrightarrow 2NO_2(g) + \dfrac{1}{2}O_2(g)$

$600 - p \qquad 2p \qquad \dfrac{p}{2}$

Total pressure $960 = 600 + \dfrac{3}{2}p \Rightarrow p = 240\text{mm}$

$\Rightarrow$ Partial pressure of $N_2O_5(g)$ remaining = 600 – 240 = 360 mm

Mole fraction = $\dfrac{360}{960} = 0.375$

25.(AD) $k = \dfrac{[A]_0 - [A]_t}{[A]_0} = 1 - e^{-kt}$; Units of A = units of R

26.(ABD) The relevant expressions are as follows.

(A) $k_p = A e^{-\Delta H/RT}$

$\ln k_p = \ln A \dfrac{-\Delta H}{RT}$

$\log k_p = \log A - \dfrac{\Delta H}{2.030R}\times\dfrac{1}{T}$

$\log k_p = \dfrac{-\Delta H}{2.303R}\dfrac{1}{T} + \log A \quad \Rightarrow y = mx + c$

(B) $k = \dfrac{2.303}{t}\log\dfrac{[x_0]}{[x]} \quad \Rightarrow \log\dfrac{[x_0]}{[x]} = \dfrac{kt}{2.303} \quad \Rightarrow \log\dfrac{[x]}{[x_0]} = \dfrac{-kt}{2.303}$

(D) $p \propto \dfrac{1}{v} \Rightarrow p = k\times\dfrac{1}{v} \Rightarrow y = mx$

27. 3.42×10^{-3} mol/min

$kt = \ln\dfrac{[A]_0}{[A]}$

$\Rightarrow \quad 4.5\times10^{-3}\times60 = \ln\dfrac{1}{[A]} \quad \Rightarrow \quad [A] = 0.76\text{M}$

$\Rightarrow$ Rate $= k[A] = 4.5\times10^{-3}\times0.76 = 3.42\times10^{-3}\text{molL}^{-1}\text{min}^{-1}$

28. **100 kJ/mol**

$k_{500} = Ae^{-E_1/RT_1}$

$k_{400} = Ae^{-E_2/RT_2}$

$\because \quad k_{500} = k_{400} \quad \Rightarrow \quad \dfrac{E_1}{RT_1} = \dfrac{E_2}{RT_2} \quad \Rightarrow \quad \dfrac{E_2}{E_1} = \dfrac{T_2}{T_1} = \dfrac{400}{500} = \dfrac{4}{5}$

Also $E_1 = E_2 + 20000\,\text{J} \quad \Rightarrow \quad \dfrac{E_1 - 20{,}000}{E_1} = \dfrac{4}{5} \quad \Rightarrow \quad E_1 = 100{,}000\text{ J} = 100\text{kJ mol}^{-1}$

29.(D) As per units of rate constant, it follows first order kinetics w.r.t. N_2O_5

$$[N_2O_5] = \frac{\text{rate}}{k} = \frac{3.90 \times 10^{-5}}{1.3 \times 10^{-5}} = 3M$$

30.(B) The rate of photochemical process varies with the intensity of absorption.
Since greater is the intensity of absorbed light more photons will fall at a point, and further each photon causes one molecular to undergo reaction.