Question

The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at constant volume

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

S.no.	Time (s)	Total pressure (atm)
1.	0	0.5
2.	100	0.512

Calculate rate constant of reaction.

Answer

	$2N_2O_5(g)$	$\rightarrow$ $2N_2O_4(g)$	$+ O_2(g)$
$t=0$	p^0	0	0
$t=t$	p^0-2p	$2p$	p

$$K = \frac{2.303}{t}\log\frac{P_0}{P_t}$$

Total pressure at $t=0$ is $p^0+0+0 = p^0 = 0.5$

Total pressure at $t=100$ s is $(p^0-2p)+2p+p = 0.512$

$p^0+p = 0.512$

From above two equations $p = 0.012$ atm

For first order reaction rate constant is given as:

$$K = \frac{2.303}{t}\log\frac{P_{N_2O_5}(t=0)}{P_{N_2O_5}(t=t)}$$

$$= \frac{2.303}{100}\log\frac{p^0}{p^0-2p}$$

$$= \frac{2.303}{100}\log\left(\frac{0.5}{0.5-2\times 0.012}\right)$$

$$= \frac{2.303}{100} \log \frac{0.5}{0.476}$$

$$= 4.98 \times 10^{-4} s^{-1}$$

Question

For the decomposition of azoisopropane to hexane and nitrogen at 543K, the following data are obtained

t (sec)	P (mm of Hg)
0	35.0
360	54.0
720	63.0

Calulate the rate constant.

Answer:

$$(CH_3)_2HC-N=N-CH(CH_3)_2(g) \longrightarrow N_2(g) + C_6H_{14}(g)$$

t=0	p^0	0	0
t=t	p^0-p	p	p

At time t total pressure (P_T) is:

$$P_T = (p^0 - p) + p + p$$

$$P_T = p^0 + p$$

$$p = P_T - p^0$$

After time t pressure of azoisupropane (P_t) is:

$$P_t = p^0 - p = p^0 - (P_T - p^0) = 2p^0 - P_T$$

For first order reaction

$$k = \frac{2.303}{t} \log \frac{p^0}{P_t}$$

$$= \frac{2.303}{t} \log \frac{p^0}{2p^0 - P_T}$$

$$= \frac{2.303}{t} \log \frac{35}{\ldots}$$

$35\times2 - P_T$

At $t = 360\,s$, $P_T = 54$

$$k = \frac{2.303}{360}\log\frac{35}{35\times2-54} = 2.175\times10^{-3}\,s^{-1}$$

At $t = 720\,s$, $P_T = 63$

$$k = \frac{2.303}{720}\log\frac{35}{35\times2-63} = 2.235\times10^{-3}\,s^{-1}$$

Taking average of above two

$$k = \frac{2.175\times10^{-3} + 2.235\times10^{-3}}{2} = 2.21\times10^{-3}\,s^{-1}$$

Question

The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time (s)	Total pressure (atm)
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Answer:

$r = k\,P^1_{SO_2Cl_2}$

	$SO_2Cl_2(g)$	$\longrightarrow$	$SO_2(g)$	+	$Cl_2(g)$
$t=0$	P^0				
$t=t$	$P^0 - P$		P		P

After time t total pressure (P_T) is:

$P_T = (P^0 - P) + P + P = P^0 + P$

$P = P_T - P^0$

After time t pressure of SO_2Cl_2 (P_t) is :

$$P_t = p^0 - p = p^0 - (p_T - p^0) = 2p^0 - P_T$$

For first order reaction

$$K = \frac{2.303}{t} \log \frac{p^0}{P_t}$$

$$= \frac{2.303}{t} \log \frac{p^0}{2p^0 - P_T}$$

$$= \frac{2.303}{100} \log \frac{0.5}{2 \times 0.5 - 0.6}$$

$$= \frac{2.303}{100} \left(\log \frac{5}{4} \right)$$

$$= \frac{2.303}{100} (\log 5 - \log 4)$$

$$= \frac{2.303}{100} (0.7 - 0.6)$$

$$= 2.303 \times 10^{-3} \ s^{-1}$$

For first order reaction rate of reaction

$$r = kP_t = k (2p^0 - P_T)$$

when $P_T = 0.65$ atm

$$r = 2.303 \times 10^{-3} (2 \times 0.5 - 0.65) = 8 \times 10^{-4} \text{ atm } s^{-1}$$