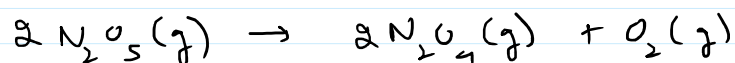


## Question

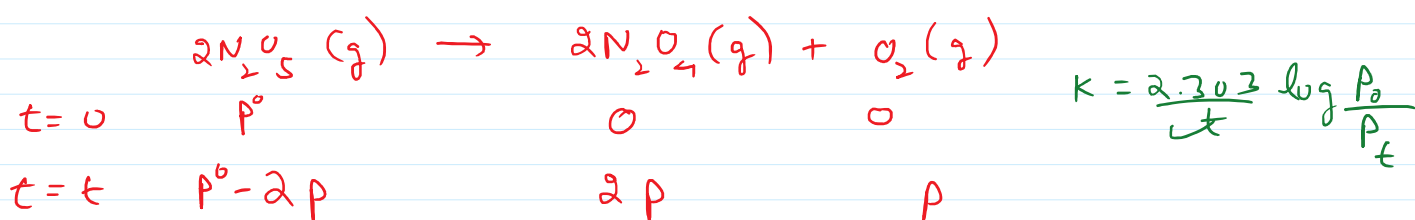
The following data were obtained during the first order thermal decomposition of  $N_2O_5(g)$  at constant volume



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

Calculate rate constant of reaction.

## Answer



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

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

$$p^0 + p = 0.512$$

From above two equations  $p = 0.012 \text{ atm}$

For first order reaction rate constant is given as:

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

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

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

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

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

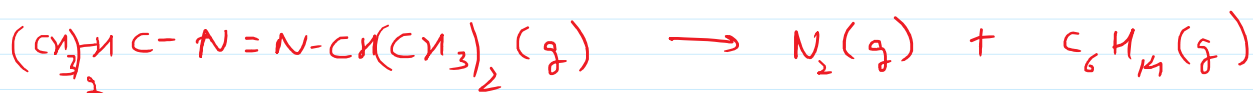
Question

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

Calculate the rate constant.

Answer:



t=0	P <sup>0</sup>	0	0
t=t	P <sup>0</sup> - P	P	P

At time t total pressure (P<sub>T</sub>) is:

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

$$P_T = P^0 + P$$

$$P = P_T - P^0$$

After time t pressure of azoisopropane (P<sub>t</sub>) is:

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

For first order reaction

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

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

$$= \frac{2.303}{t} \log \frac{35}{35 - P_T}$$

$$\text{At } t = 360 \text{ s, } P_T = 54$$

$$k = \frac{2.303}{360} \log \frac{35}{35 \times 2 - 54} = 2.175 \times 10^{-3} \text{ s}^{-1}$$

$$\text{At } t = 720 \text{ s, } P_T = 63$$

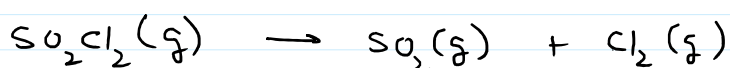
$$k = \frac{2.303}{720} \log \frac{35}{35 \times 2 - 63} = 2.235 \times 10^{-3} \text{ s}^{-1}$$

Taking average of above two

$$k = \frac{2.175 \times 10^{-3} + 2.235 \times 10^{-3}}{2} = 2.21 \times 10^{-3} \text{ s}^{-1}$$

Question

The following data were obtained during the first order thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume.

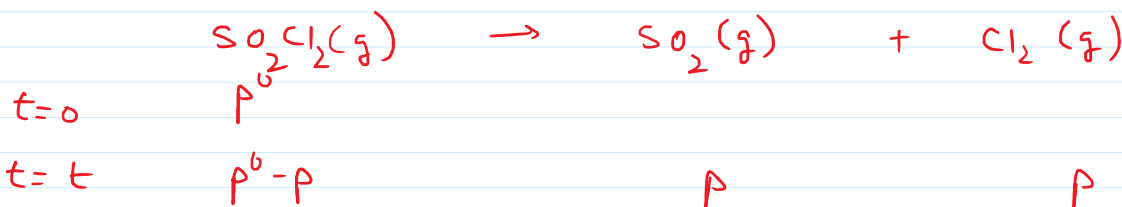


Experiment	Time (s)	Total pressure (atm)
1	0	0.5
2	100	0.6

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

Answer:

$$r = k P_{\text{SO}_2\text{Cl}_2}^1$$



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  $\text{SO}_2\text{Cl}_2$  ( $P_t$ ) is :

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

For first order reaction

$$\begin{aligned}k &= \frac{2.303}{t} \log \frac{P^0}{P_t} \\&= \frac{2.303}{t} \log \frac{P^0}{2P^0 - P_t} \\&= \frac{2.303}{100} \log \frac{0.5}{2 \times 0.5 - 0.6} \\&= \frac{2.303}{100} \left( \log \frac{5}{4} \right) \\&= \frac{2.303}{100} (\log 5 - \log 4) \\&= \frac{2.303}{100} (0.7 - 0.6) \\&= 2.303 \times 10^{-3} \text{ s}^{-1}\end{aligned}$$

For first order reaction rate of reaction

$$r = kP_t = k(2P^0 - P_t)$$

when  $P_t = 0.65 \text{ atm}$

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