Determining the Rate Law from Pressure Data

Problem 14-80

The decomposition of ethylene oxide at 690 K is monitored by measuring the *total* gas pressure as a function of time. The data obtained are t =10 min, P_{tot} = 139.14 mmHg; 20 min, 151.67 mmHg; 40 min, 172.65 mmHg; 60 min, 189.15 mmHg; 100 min, 212.34 mmHg; 200 min, 238.66 mmHg; ∞, 249.88 mmHg. What is the order of the reaction

$$(CH_3)_2O(g) \rightarrow CH_4(g) + CO(g)$$

Solution:

This is a challenging problem because of the total pressure component. Nevertheless, it is quite straightforward if Dalton's law of partial pressures is understood and remembering the stoichiometry of gases.

First things first… the initial pressure must be determined. Our handle on the initial pressure is the final pressure of 249.88 mmHg which is a combination of the partial pressures of CH_4 and CO.

$$P^{\text{initial}}_{(CH_3)_2O} = \frac{1 \text{ mol } (CH_3)_2O}{2 \text{ mol products}} \times 249.88 \text{ mmHg} = 124.94 \text{ mmHg}$$

Now, calculate the current partial pressure of $(CH_3)_2O$ at each time, t:

t = 10 min

$$P_{\text{total}} = P_{(CH_3)_2O} + P_{CH_4} + P_{CO} \quad \text{and} \quad P_{CH_4} = P_{CO} \quad \text{so}$$

$$P_{\text{total}} = P_{(CH_3)_2O} + 2P_{CH_4}$$

Keeping in mind the stoichiometry

$P_{(CH_3)_2O} + P_{CH_4} = 124.94$ mmHg at every t, so...

$$P_{\text{total}} = P_{(CH_3)_2O} + 2\left(124.94 \text{ mmHg} - P_{(CH_3)_2O}\right) = P_{(CH_3)_2O} + 249.88 \text{ mmHg} - 2P_{(CH_3)_2O}$$

$$P_{(CH_3)_2O} = 249.88 \text{ mmHg} - P_{\text{total}}$$

$$P_{(CH_3)_2O} = 249.88 \text{ mmHg} - 139.14 \text{ mmHg} = 110.74 \text{ mmHg}$$

$t = 20$ min

$$P_{(CH_3)_2O} = 249.88 \text{ mmHg} - 151.67 \text{ mmHg} = 98.21 \text{ mmHg}$$

$t = 40$ min

$$P_{(CH_3)_2O} = 249.88 \text{ mmHg} - 172.65 \text{ mmHg} = 77.23 \text{ mmHg}$$

$t = 60$ min

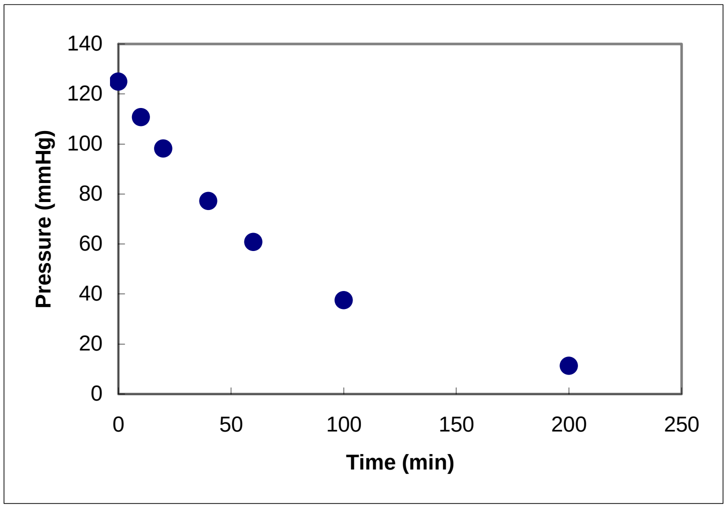
$$P_{(CH_3)_2O} = 249.88 \text{ mmHg} - 189.15 \text{ mmHg} = 60.73 \text{ mmHg}$$

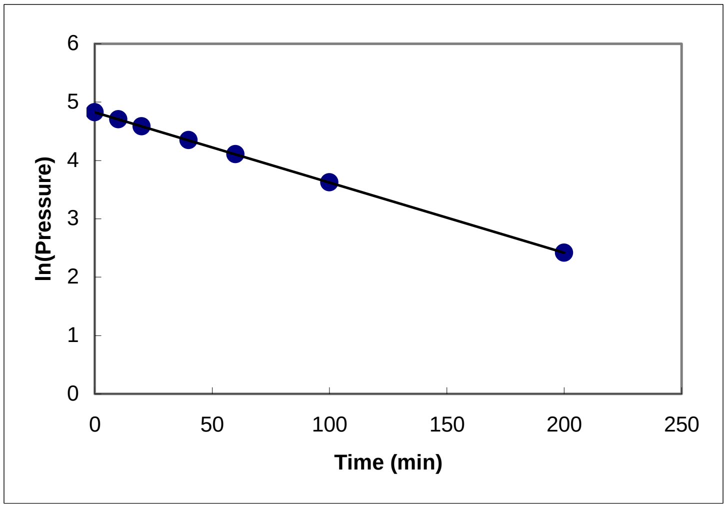
$t = 100$ min

$P_{(CH_3)_2O} = 249.88 \text{ mmHg} - 212.34 \text{ mmHg} = 37.54 \text{ mmHg}$

$t = 200$ min

$P_{(CH_3)_2O} = 249.88 \text{ mmHg} - 238.66 \text{ mmHg} = 11.22 \text{ mmHg}$





Since the data are linear when plotted as the natural logarithm, the order of the reaction is 1.