PRS Sovled Problems Example 5–2 Integral Method of Analysis of Pressure–Time Data

Use the integral method to confirm that the reaction order for the di-*tert*-butyl peroxide decomposition described in Example 5-1 is first order.

Solution

Recalling Example 5-1, the combined mole balance and rate law for a constant-volume batch reactor can be expressed in the form

$$\frac{dP}{dt} = k'(3P_0 - P)^{\alpha} \quad \text{(E5-1.7)}$$

For $\alpha = 1$,

$$\frac{dP}{dt} = k'(3P_0 - P) \quad \text{(E5-2.1)}$$

Integrating with limits $P = P_0$ when $t = 0$ yields

Assuming a first-order reaction

$$\ln \frac{2P_0}{3P_0 - P} = k't \quad \text{(E5-2.2)}$$

If the reaction is first order, a plot of $\ln[2P_0/(3P_0 - P)]$ versus t should be linear.

TABLE E5-2.1. PROCESSED DATA

t (min)	P (mmHg)	$2P_0/(3P_0 - P)$ (−)
0.0	7.5	1.00
2.5	10.5	1.25
5.0	12.5	1.50
10.0	15.8	2.24
15.0	17.9	3.26
20.0	19.4	4.84

After completing Table E5-2.1, using the raw data, a plot of $2P_0/(3P_0 - P)$ as a function of time was made using semilog paper as shown in Figure E5-2.1.

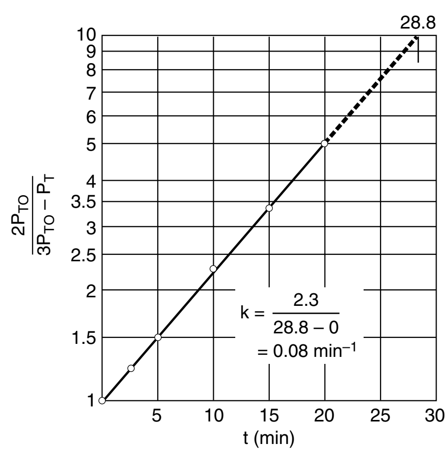

Figure E5-2.1 Plot of processed data.

From the plot we see that $\ln[2P_0/(3P_0 - P)]$ is indeed linear with time, and we therefore conclude that the decomposition of di-*tert*-butyl peroxide follows first-order kinetics. From the slope of the plot in Figure E5-2.1, we can determine the specific reaction rate, $k = 0.08\ \text{min}^{-1}$. [Recall $k' = k$ because $\alpha = 1$ (E5-1.5)]

We found the plot of $\ln[2P_{t0}/(3P_{t0} - P_t)]$ versus t was linear, indicating that the reaction is first order (i.e., $\alpha = 1$). If we try zero, first, or second order as shown on the CD-ROM, and they do not seem to describe the reaction rate equation, it is usually best to try some other method of determining the reaction order, such as the differential method.