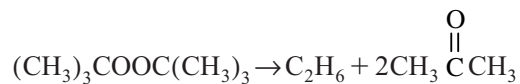***PRS Solved Problem Example 5–1   Differential Method of Analysis of Pressure–Time Data***

Determine the reaction order for the gas-phase decomposition of di-*tert*-butyl peroxide,

$$(CH_3)_3COOC(CH_3)_3 \rightarrow C_2H_6 + 2CH_3 \overset{\overset{\displaystyle O}{\|}}{C} CH_3$$

This reaction was carried out in the laboratory in an isothermal batch system in which the total pressure was recorded at various times during the reaction.[1] The data given in Table E5-1.1 apply to this reaction. Only pure di-*tert*-butyl peroxide was initially present in the reaction vessel.

TABLE E5-1.1   PRESSURE–TIME DATA

Time (min)	Total Pressure (mmHg)
0.0	7.5
2.5	10.5
5.0	12.5
10.0	15.8
15.0	17.9
20.0	19.4

While the proper SI units of pressure are pascal (Pa) or kilopascal (kPa), a significant amount of kinetic data in past literature are reported in units of mmHg (torr), atmospheres, or psi. Consequently, we must be able to analyze pressure–time rate data in any one of these units.

$$1 \text{ atm} \equiv 14.7 \text{ psi} \equiv 1.103 \text{ bar} \equiv 101.3 \text{ kPa} \equiv 760 \text{ mmHg}$$

Solution

Let A represent di-*tert*-butyl peroxide.

1. Postulate a rate law.

$$-r_A = kC_A^\alpha$$

A combination of the *mole balance* on a constant-volume batch reactor and the *rate law* gives

$$\frac{-dC_A}{dt} = -r_A = kC_A^\alpha \tag{E5-1.1}$$

Need
$C_A = f(P)$

where α and k are to be determined from the data listed in Table E5-1.1.

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[1] A. F. Trotman-Dickenson, *J. Chem. Educ., 46*, 396 (1969).

2. Rewrite the design equation in terms of the measured variable. When there is a net increase or decrease in the total number of moles in a gas-phase reaction, the reaction order may be determined from experiments performed with a constant-volume batch reactor by monitoring the total pressure as a function of time. The total pressure data **should not be converted** to conversion and then analyzed as conversion-time data just because the design equations are written in terms of the variable conversions. Rather, **transform the design equation to the measured variable**, which in this case is pressure. Consequently, we need to *express the concentration in terms of total pressure* and then substitute for the concentration of A in Equation (E5-1.1).

Processing data in terms of the measured variable, P

For the case of a constant-volume batch reactor, we recall Equations (3-26) and (3-38):

$$C_A = C_{A0}(1 - X) \tag{3-26}$$

$$V = V_0 \frac{P_0}{P} (1 + \varepsilon X) \frac{T}{T_0} \tag{3-38}$$

For isothermal operation and constant volume, Equation (3-38) solves to

$$X = \frac{1}{\varepsilon P_0} (P - P_0) = \frac{1}{y_{A0} \delta P_0} (P - P_0)$$

$$X = \frac{1}{\delta P_{A0}} (P - P_0) \tag{E5-1.2}$$

where

$$P_{A0} = y_{A0} P_0$$

Combining Equations (3-26) and (E5-1.2) gives

$$C_A = \frac{P_{A0} - [(P - P_0)/\delta]}{RT} \tag{E5-1.3}$$

For pure di-*tert*-butyl peroxide, initially $y_{A0} = 1.0$ and therefore $P_{A0} = P_0$. Stoichiometry gives $\delta = 1 + 2 - 1 = 2$.

$$C_A = \frac{P_0 - [(P - P_0)/2]}{RT} = \frac{3P_0 - P}{2RT} \tag{E5-1.4}$$

Substitute Equation (E5-1.4) into (E5-1.1) to get

$$\frac{1}{2RT} \frac{dP}{dt} = k\left(\frac{3P_0 - P}{2RT}\right)^\alpha$$

Let $k' = k(2RT)^{1-\alpha}$; then

$$\boxed{\frac{dP}{dt} = k'(3P_0 - P)^\alpha} \tag{E5-1.5}$$

Taking the natural logarithm of both sides gives us

$$\ln\frac{dP}{dt} = \alpha \, \ln\,(3P_0 - P) + \ln k' \qquad \text{(E5-1.6)}$$

Observe that the reaction order, α, can be determined from the slope of a plot of $\ln(dP/dt)$ versus $\ln\,(3P_0 - P)$. Once α is known, the constant k' may be calculated from the ratio

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

at any point.

3. Look for simplifications. We have assumed the reaction is irreversible. Check to see if any terms in the equation can be neglected [e.g., the term εX in $(1 + \varepsilon X)$ when $(\varepsilon X \ll 1)$].

4. Determine dP/dt **from the pressure–time data and then the reaction order** α. The data are reported in terms of total pressure as a function of time; *consequently*, we must differentiate the data either numerically or graphically before we can use Equations (E5-1.6) and (E5-1.7) to evaluate the reaction order and specific reaction rate. First we shall evaluate dP/dt by graphical differentiation. Many prefer the graphical analysis because they use it to visualize the discrepancies in their data.

Graphical Method. The derivative dP/dt is determined by calculating and plotting $\Delta P / \Delta t$ as a function of time, t, and then using the equal-area differentiation technique (Appendix A.2) to determine (dP/dt) as a function of P and t. First we calculate the ratio $\Delta P / \Delta t$ from the first two columns of Table E5-1.2; the result is written in the third column. Next we use Table E5-1.2 to plot the third column as a function of the first column in Figure E5-1.1. Using equal-area differentiation, the value of dP/dt is read off the figure (represented by the arrows) and then it is used to complete the fourth column of Table E5-1.2.

TABLE E5-1.2.   PROCESSED DATA

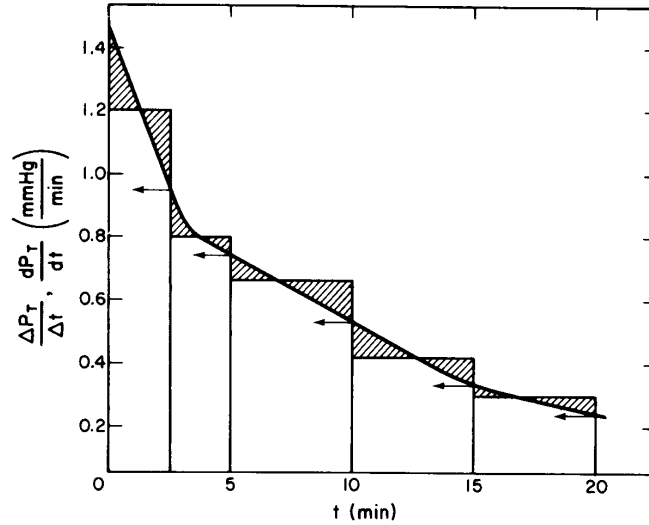| t (min)	P (mmHg)	$\dfrac{\Delta P}{\Delta t}$ (mmHg/min)	$\dfrac{dP}{dt}$ (mmHg/min)
0.0	7.5		1.44
		1.20	
2.5	10.5		0.95
		0.80	
5.0	12.5		0.74
		0.66	
10.0	15.8		0.53
		0.42	
15.0	17.9		0.34
		0.30	
20.0	19.4		0.25
Temperature $= 170°C$			

Figure E5-1.1   Graphical differentiation.

Finite Difference. Next we calculate *dP/dt* from finite difference formulas (5-8) through (5-10):

$$t = 0: \quad \left(\frac{dP}{dt}\right)_0 = \frac{-3P_0 + 4P_1 - P_2}{2\Delta t} = \frac{-3(7.5) + 4(10.5) - 12.5}{2(2.5)} = 1.40$$

Calculating

$$t = 2.5: \quad \left(\frac{dP}{dt}\right)_1 = \frac{P_2 - P_0}{2\Delta t} = \frac{12.5 - 7.5}{2(2.5)} = 1.0$$

$t = 5$: Here we have a change in time increments Δt, between
P_1 and P_2 and between P_2 and P_3. Consequently, we
have two choices for evaluating $(dP/dt)_2$:

(a) $$\left(\frac{dP}{dt}\right)_2 = \frac{P_3 - P_0}{2(\Delta t)} = \frac{15.8 - 7.5}{2(5)} = 0.83$$

(b) $$\left(\frac{dP}{dt}\right)_2 = \frac{-3P_2 + 4P_3 - P_4}{2(\Delta t)} = \frac{-3(12.5) + 4(15.8) - 17.9}{2(5)} = 0.78$$

$$t = 10: \quad \left(\frac{dP}{dt}\right)_3 = \frac{17.9 - 12.5}{2(5)} = 0.54$$

$$t = 15: \quad \left(\frac{dP}{dt}\right)_4 = \frac{19.4 - 15.8}{2(5)} = 0.36$$

$$t = 20: \quad \left(\frac{dP}{dt}\right)_5 = \frac{P_3 - 4P_4 + 3P_5}{2\Delta t} = \frac{15.8 - 4(17.9) + 3(19.4)}{2(5)} = 0.24$$

Polynomial (Polymath). Another method to determine dP/dt is to fit the total pressure to a polynomial in time and then to differentiate the resulting polynomial. Choosing a fourth-order polynomial

$$P = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 \tag{E5-1.8}$$

we use the Polymath software package to express pressure as a function of time. Here we first choose the polynomial order (in this case fourth order) and then type in the values of P at various times t to obtain

$$P(t) = 7.53 + 1.31t - 0.0718t^2 + 0.00276t^3 - 4.83 \times 10^{-5}t^4 \tag{E5-1.9}$$

A plot of P versus t and the corresponding fourth-order polynomial fit is shown in Figure E5-1.2. Differentiating Equation (E5-1.9) yields

$$\frac{dP}{dt} = 1.31 - 0.144t + 0.00828t^2 - 0.000193t^3 \tag{E5-1.10}$$
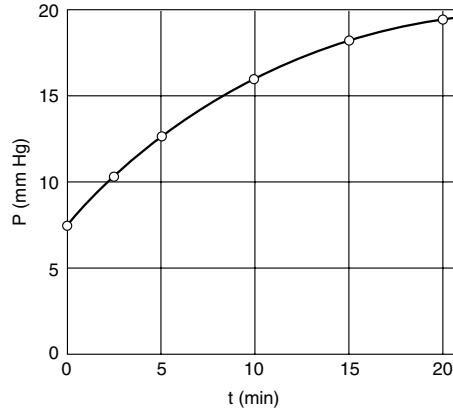

Figure E5-1.2   Polynomial fit.

To find the derivative at various times we substitute the appropriate time into Equation (E5-1.10) to arrive at the fourth column in Table E5-1.3. We can see that there is quite a close agreement between the graphical technique, finite difference, and Polymath polynomial analysis. The second, third, fourth, and fifth columns of the processed data in Table E5-1.3 are plotted in Figure E5-1.3 to determine the reaction order and specific reaction rate.

Next, plot $\dfrac{dP}{dt}$ versus the appropriate function of total pressure

We shall determine the reaction order, α, from the slope of a log-log plot of dP/dt as a function of the appropriate function of pressure $f(P)$, which for the initial conditions and stoichiometry of this reaction turns out to be $(3P_0 - P)$ (see Table E5-1.3).[2] Recall that

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[2] If you are unfamiliar with any method of obtaining slopes from plots on log-log or semilog graphs, read Appendix D before proceeding.
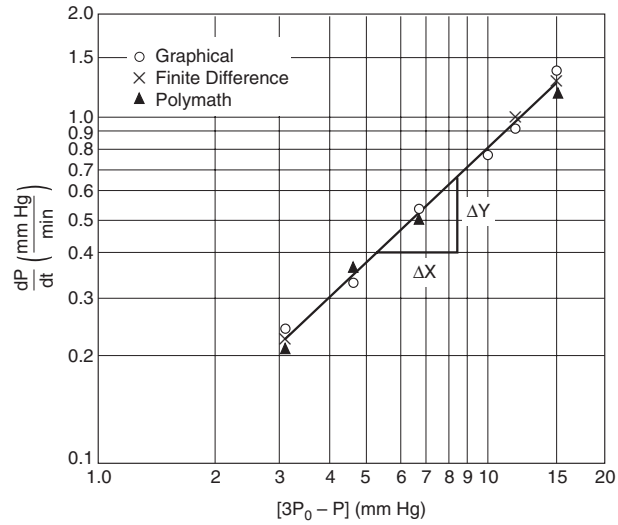
Figure E5-1.3. Plot to determine k and α.

TABLE E5-1.3.   SUMMARY OF PROCESSED DATA

t (min)	dP/dt (mmHg/min) Graphical	dP/dt (mmHg/min) Finite Difference	dP/dt (mmHg/min) Polymath	$3P_0 - P$ (mmHg)
0.0	1.44	1.40	1.31	15.0
2.5	0.95	1.00	1.0	12.0
5.0	0.74	0.78	0.78	10.0
10.0	0.53	0.54	0.51	6.7
15.0	0.34	0.36	0.37	4.6
20.0	0.25	0.24	0.21	3.1

$$\ln\frac{dP}{dt} = \alpha \ln(3P_0 - P) + \ln k' \qquad \text{(E5-1.6)}$$

Using the line through the data points in Figure E5-1.3 yields

$$\alpha = \text{slope} = \frac{\Delta y}{\Delta x} = \frac{1.2 \text{ cm}}{1.2 \text{ cm}} = 1.0$$

The reaction order is

$$\alpha = 1.0$$

$$k' = k(2RT)^{1-\alpha} = k \qquad \text{(E5-1.11)}$$

$$-r_A = kC_A \qquad \text{(E5-1.12)}$$

5. Determine the specific reaction rate. The specific reaction rate can be determined using Equation (E5-1.7) with $\alpha = 1$ and then evaluating the numerator and denominator at any point, p.

$$k' = k = \frac{(dP/dt)_p}{(3P_0 - P)_p}$$

At $(3P_0 - P) = 5.0$ mmHg,

$$\frac{dP}{dt} = 0.4 \text{ mmHg/min}$$

From Equation (E5-1.5),

$$k = \left. \frac{\left(\dfrac{dP}{dt}\right)_p}{(3P_0 - P)_p} \right| = \frac{0.4 \text{ mmHg/min}}{5.0 \text{ mmHg}} = 0.08 \text{ min}^{-1}$$

The rate law is

$$\boxed{-r_A = \frac{0.08}{\text{min}} C_A} \qquad \text{(E5-1.13)}$$