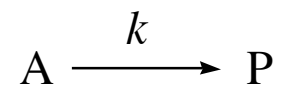




II. Irreversible 1st-Order Reaction

A. Given:



We will routinely let...

A and B = starting materials

C and D = intermediates

P = product



II. Irreversible 1st-Order Reaction

B. Rate Equation:

$$-d[A]/dt = d[P]/dt = k[A]$$

- “Differential form” of the rate equation.
- It is not necessary to know mathematics, only mathematicians.
- References to integral numbers in the *CRC Handbook of Chemistry and Physics* (CRC) will serve as a reminder that all the requisite math has been done previously. Therefore...



II. Irreversible 1st-Order Reaction

rearrange and integrate... (CRC #1,9)

$$\ln\{[A]/[A_0]\} = -kt \quad (1)$$

Taking the inverse natural log...

$$[A] = [A_0]e^{-kt} \quad (2)$$

or...

$$[A]/[A_0] = e^{-kt} \quad (3)$$

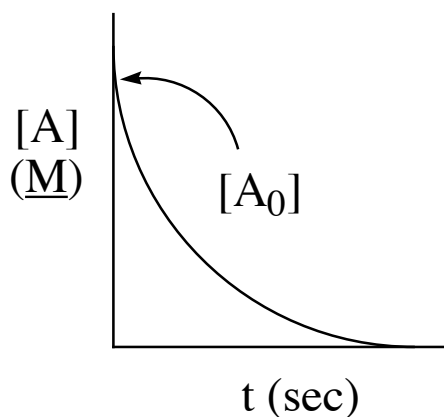
“Integral forms” of the rate equation.

II. Irreversible 1st-Order Reaction

C. Graphics:

1. Zeroth-Order Plot:

- Derives the name from the fact that a zeroth-order dependence on $[A]$ affords linearity (*vide infra*).



The fitting function is written as...

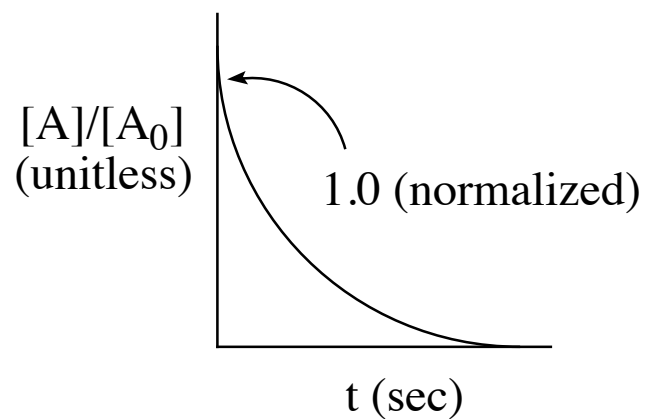
$$f(x) = ae^{bx}$$

such that...

$$f(x) = [A] \quad x = t \quad a = [A_0] \quad b = -k$$

II. Irreversible 1st-Order Reaction

Alternatively...



The fitting function is written as...

$$f(x) = e^{bx}$$

such that...

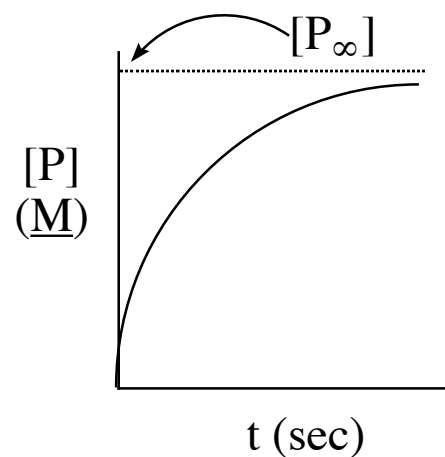
$$f(x) = [A]/[A_0] \quad x = t \quad b = -k$$

II. Irreversible 1st-Order Reaction

We can also follow formation of product. Thus,...

$$[P] = [A_0] - [A] = [A_0] - [A_0]e^{-kt}$$

$$[P] = [P_\infty](1 - e^{-kt}) \text{ (such that } [P_\infty] = [A_0])$$



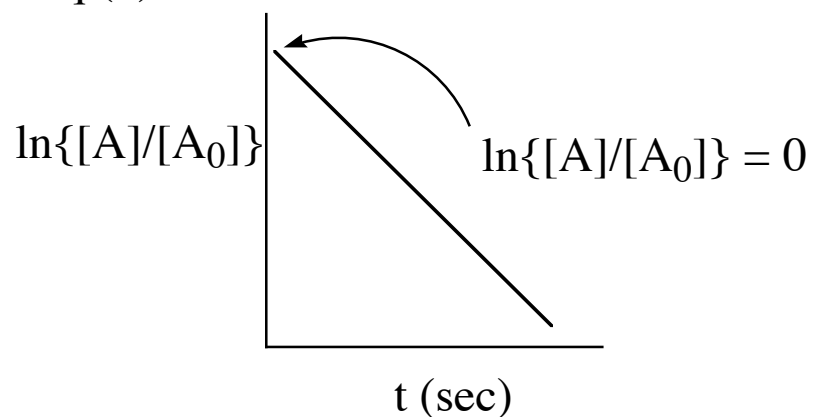
The fitting function is written as...

$$f(x) = a(1 - e^{bx})$$

II. Irreversible 1st-Order Reaction

2. First-Order Plot:

From eq (1)...



The fitting function is written as...

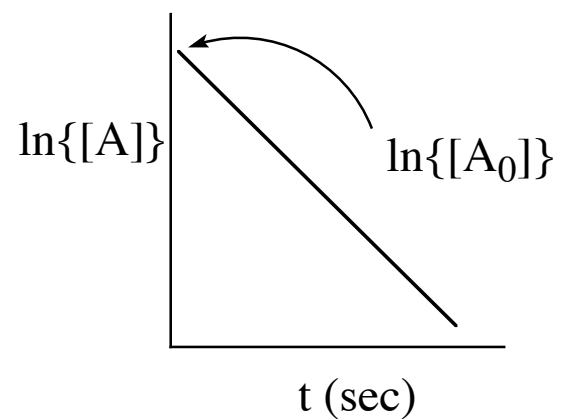
$$f(x) = ax$$

such that...

$$f(x) = \ln\{[A]/[A_0]\} \quad x = \text{time} \quad a = -k$$

II. Irreversible 1st-Order Reaction

Alternatively...



The fitting function is written as...

$$f(x) = ax + b$$

such that...

$$f(x) = \ln[A] \quad x = t \quad a = -k \quad b = \ln\{[A_0]\}$$



II. Irreversible 1st-Order Reaction

3. Summary

a. First-Order Plot:

- i. Visually retrievable order (i.e., linearity indicates first order)
- ii. Easily plotted and visualized
- iii. Inadvertent non-linear weighting due to the natural log

b. Zeroth-Order Plot:

- i. All orders (except zeroth) show curvature
- ii. Easy to plot with computers
- iii. No inadvertent weighting

c. Compromise:

- i. Present the linear 1st-order plot
- ii. Determine the rate constant via the non-linear, zeroth-order fit.



II. Irreversible 1st-Order Reaction

4. Concentrations vs. Physical Properties:

- The treatments employing a normalized dependent variable ($[A]/[A_0]$) appear to be advantageous. However this is not necessarily so.
- While we typically describe rate behaviors in terms of concentrations, you never actually measure a concentration, but rather a property related to concentration. This might be a GC peak intensity or an IR absorbance intensity that (hopefully) correlates with concentration. This poses technical problems that, while relatively minor in most cases, require further consideration.



II. Irreversible 1st-Order Reaction

a. Gas Chromatography:

i. Monitoring the Disappearance of Starting Material:

- At $t = 0$, the absorbance (abs_0) provides a direct measure of the absorbance at a known molarity.
- However, as the absorbance (abs) decreases as a function of time, it must be monitored relative to the absorbance of an internal GC standard (abs_{st}) that remains constant throughout the course of the reaction.

Since...

$$[A] \propto \text{abs}/\text{abs}_{\text{st}}$$

then...

$$[A]/[A_0] = (\text{abs}/\text{abs}_{\text{st}})/(\text{abs}_0/\text{abs}_{\text{st}})$$



II. Irreversible 1st-Order Reaction

Substituting into eq (3)...

$$(\text{abs}/\text{abs}_{\text{st}})/(\text{abs}_0/\text{abs}_{\text{st}}) = e^{-kt}$$

and rearranging gives...

$$(\text{abs}/\text{abs}_{\text{st}}) = (\text{abs}_0/\text{abs}_{\text{st}})e^{-kt}$$

A plot of $\text{abs}/\text{abs}_{\text{st}}$ vs. time will afford the first-order rate constant from the function...

$$f(x) = ae^{bx}$$

such that...

$$f(x) = \text{abs}/\text{abs}_{\text{st}} \quad x = \text{time (sec)} \quad a = \text{abs}_0/\text{abs}_{\text{st}} \quad b = -k$$

This particular mathematical form has notable latent features. The value of $\text{abs}_0/\text{abs}_{\text{st}}$ frequently is not known since the time required for mixing and thermal equilibration distorts the data at early reaction times. By this method, $\text{abs}_0/\text{abs}_{\text{st}}$ is an *extrapolation* to $t = 0$, calculated as an adjustable parameter.



II. Irreversible 1st-Order Reaction

- To exclude autocatalysis, autoinhibition, non-first-order behavior, and reactions that afford balanced equilibria, fit the data to...

$$f(x) = ae^{bx} + c$$

- Clean first-order kinetics will afford a value for c (corresponding to unaccounted for absorbance of starting material at $t = \infty$) that is very small relative to a .



II. Irreversible 1st-Order Reaction

ii. Monitoring Appearance of Product:

- This is a more challenging problem, placing a greater reliance on adjustable parameters. We previously showed that...

$$[P] = [P_{\infty}](1 - e^{-kt}) \quad (4)$$

such that...

$$[P_{\infty}] = [P] \text{ at } t = \infty$$

and...

$$[A_0] = [P_{\infty}]$$



II. Irreversible 1st-Order Reaction

- We probably can assume and, if necessary, experimentally confirm that the peak area of \underline{P} is proportional to $[P]$. That is...

$$[P]/[P_{\infty}] = \text{abs}/\text{abs}_{\infty}$$

or more practically written as...

$$[P]/[P_{\infty}] = (\text{abs}/\text{abs}_{\text{st}})/(\text{abs}_{\infty}/\text{abs}_{\text{st}})$$

such that...

abs_{∞} = the absorbance of \underline{P} at $t = \infty$

abs_{st} = the absorbance of the GC standard.

Dividing through eq (4) by $[P_{\infty}]$ and substituting gives...

$$(\text{abs}/\text{abs}_{\text{st}})/(\text{abs}_{\infty}/\text{abs}_{\text{st}}) = 1 - e^{-kt}$$

or...

$$\text{abs}/\text{abs}_{\text{st}} = \text{abs}_{\infty}/\text{abs}_{\text{st}}(1 - e^{-kt})$$



II. Irreversible 1st-Order Reaction

- We may not be able to estimate abs_∞ accurately. Once again, substantial advantage of the latter mathematical form allows $\text{abs}_\infty / \text{abs}_{\text{st}}$ to be determined in each kinetic run as an adjustable parameter. Thus...

$$f(x) = a(1 - e^{-bx})$$

such that...

$$f(x) = \text{abs} / \text{abs}_{\text{st}}$$

$$x = t \quad a = \text{abs}_\infty / \text{abs}_{\text{st}} \quad b = k$$



II. Irreversible 1st-Order Reaction

b. IR Spectroscopy:

- The problems associated with using an IR absorbance as a measure of concentration are similar to the corresponding problems associated with the GC analysis.

- From Beer's Law...

$$[A]/[A_0] = (\text{abs} - \text{abs}_\infty)/(\text{abs}_0 - \text{abs}_\infty)$$

While deviations from Beer's law are a concern, it is easy to show an adherence to it.

- The problem is simplified by the absolute absorbance scale, eliminating the need for an internal standard.
- The problem is complicated when abs_∞ is not readily measured, placing a greater demand on adjustable parameters rather than standardized absorbance measurements.