III. Irreversible 2nd-Order Reaction

A. <u>Given</u>:

$$\mathrm{A} + \mathrm{A} \xrightarrow{k} \mathrm{P}$$

B. <u>Rate Equation</u>:

$$-d[\mathrm{A}]/d\mathrm{t} = 2d[\mathrm{P}]/d\mathrm{t} = k[\mathrm{A}]^2$$

Integrate... (CRC #7)

$$1/[\mathrm{A}] = 1/[\mathrm{A}_0] + k\mathrm{t} \qquad (1)$$

• Some treatments that include stoichiometric coefficients will show the rate constant as "2*k*t" rather than "*k*t".

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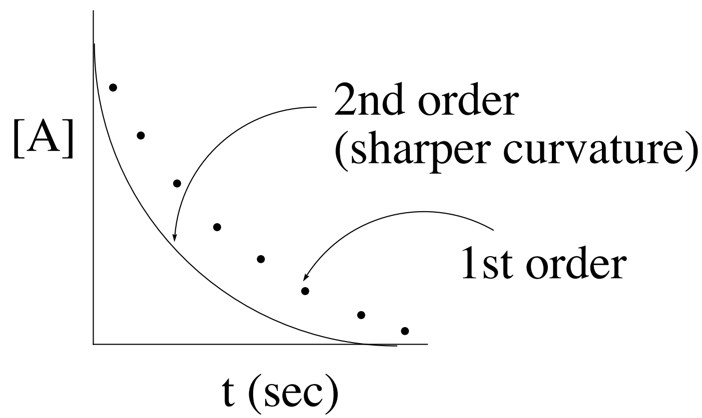
C. Graphics:

1. Zeroth-Order Plot:



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For a 2nd-order reaction, rearranging eq (1) provides...

$$[A] = [A_0]/(1+[A_0]kt)$$

with the fitting function written as...

$$f(x) = a/(1+bx)$$

such that...

$$a = [A_0] \qquad b = [A_0]k$$

• The sharper curvature of a second-order reaction compared to a 1st-order reaction is <u>not</u> readily detected by the naked eye.

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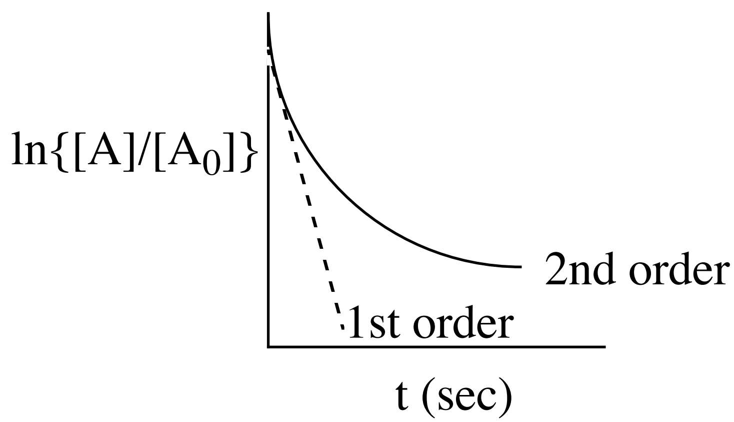
2. <u>1st-Order Plot</u>:



• Upward curvature (i.e., anomalous slowing) relative to lst order.

• Curvature will not be obvious in 1st half-life.

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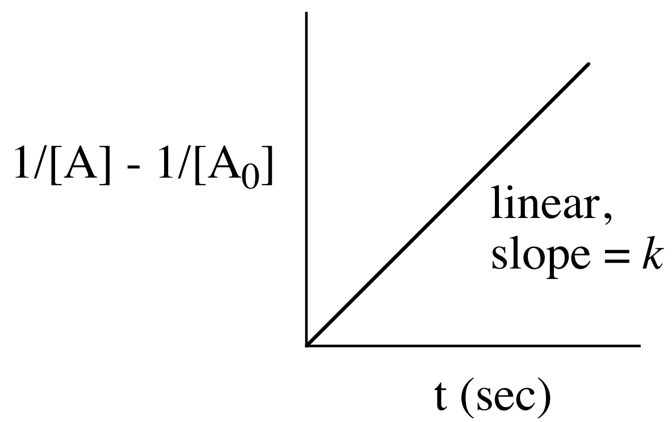
3. <u>2nd-Order Plot</u>:

Since

$$1/[A] - 1/[A_0] = kt$$



Let...

$$f(x) = ax$$

such that...

$f(x) = 1/[A] - 1/[A_0]$ $\qquad a = k\ (M^{-1}sec^{-1})$

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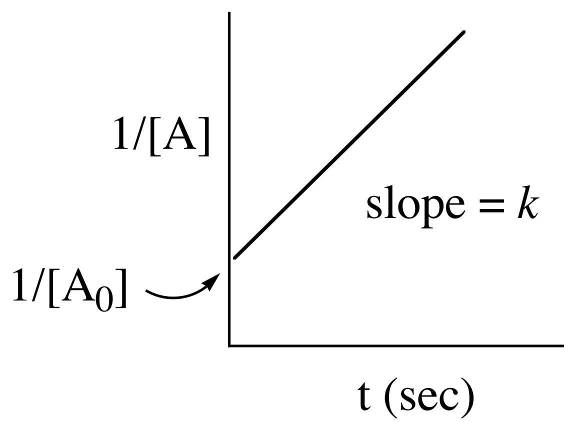
Alternatively…



Let…

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

such that…

$$f(x) = 1/[A] \qquad a = k\ (M^{-1}sec^{-1}) \qquad b = 1/[A_0]$$

The latter treatment is important if $[A_0]$ (i.e., the monitored property of <u>A</u> at t = 0) is not known.