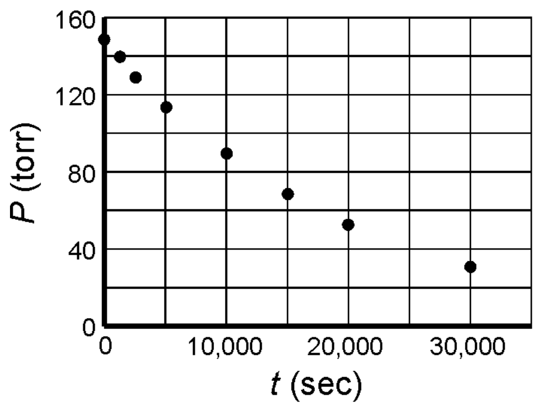
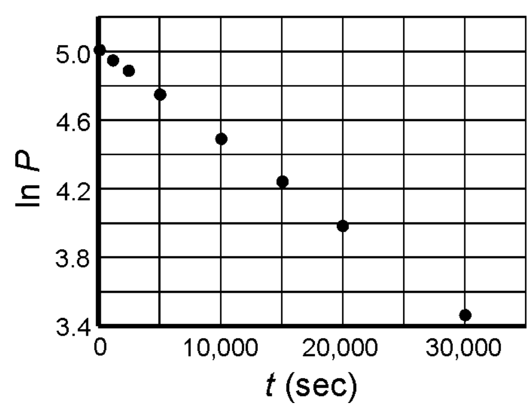
Chemistry 4011/8011 Wednesday, September 27

Discussion Question

1. Although gaseous methyl isocyanide (CH_3NC) can be stably isolated and bottled at low temperature, at 273 K it isomerizes over the course of hours to acetonitrile (CH_3CN), which condenses from the gas as a liquid. The graphs below show how the measured pressure in a sealed container of CH_3NC drops with time as the gas is converted to CH_3CN liquid.

$$H_3C{-}N{=}C\!: \longrightarrow H_3C{-}C{\equiv}N$$





a) Are these graphs consistent with first-order kinetics (in CH_3NC)? Can you estimate a rate constant *k* from these graphs?

b) From the integrated rate law for this process and your rate constant *k*, estimate the half-life $t_{½}$ for this reaction (where $[CH_3NC]_t /[CH_3NC]_0 = 0.5$). Does this calculated $t_{½}$ match the data on the graph?

1. a) $P \propto [CH_3NC]$, so

$$\frac{P_t}{P_0} = \frac{[CH_3NC]_t}{[CH_3NC]_0} .$$

If the reaction displayed first-order kinetics, the graph could be fit to

$$\frac{P_t}{P_0} = e^{-kt} ,$$

or to

$$\ln P_t = \ln P_0 - kt .$$

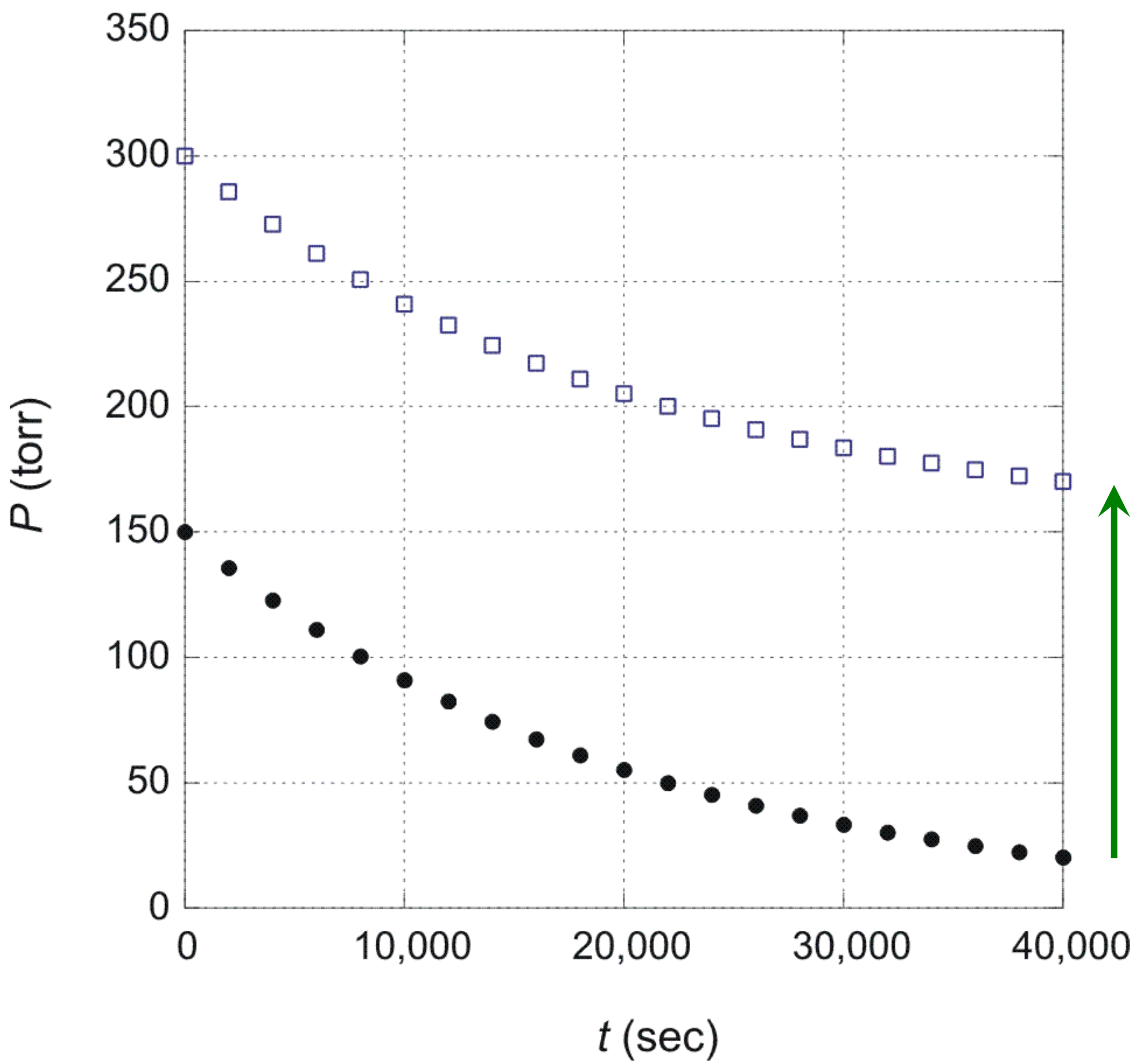
If you use this second equation, the slope of the graph is equal to k. Here, $k \sim 5 \times 10^{-5}$ /sec.

b) $$\frac{P_t}{P_0} = \frac{[CH_3NC]_t}{[CH_3NC]_0} = 0.5 = e^{-kt}.$$

$$t_{1/2} = \frac{\ln(0.5)}{k}$$

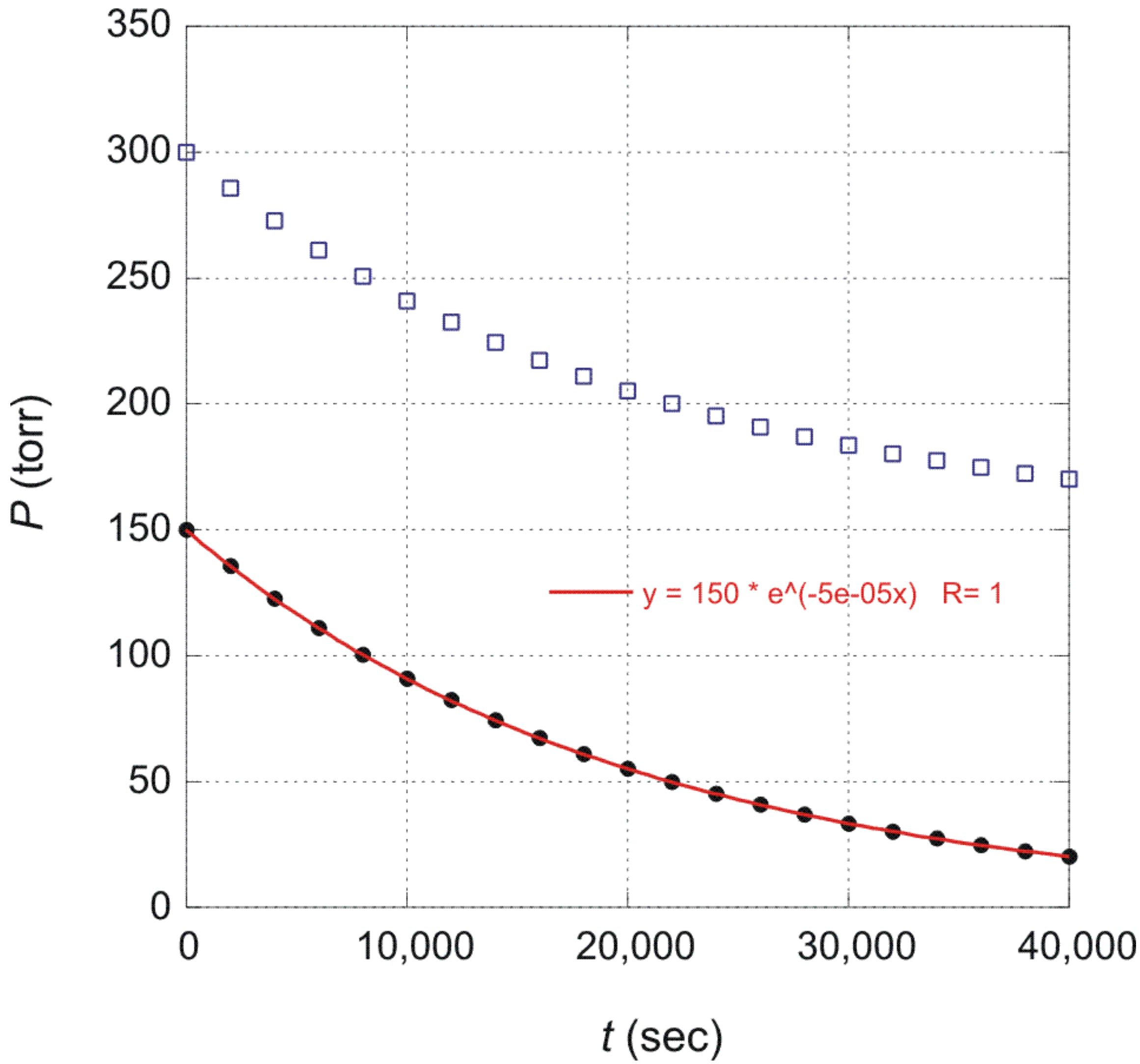
$$= 14{,}000 \text{ sec.}$$

Background Signal in Kinetic Data



What if the CH_3NC was contaminated with 150 torr of air?

Background Signal in Kinetic Data



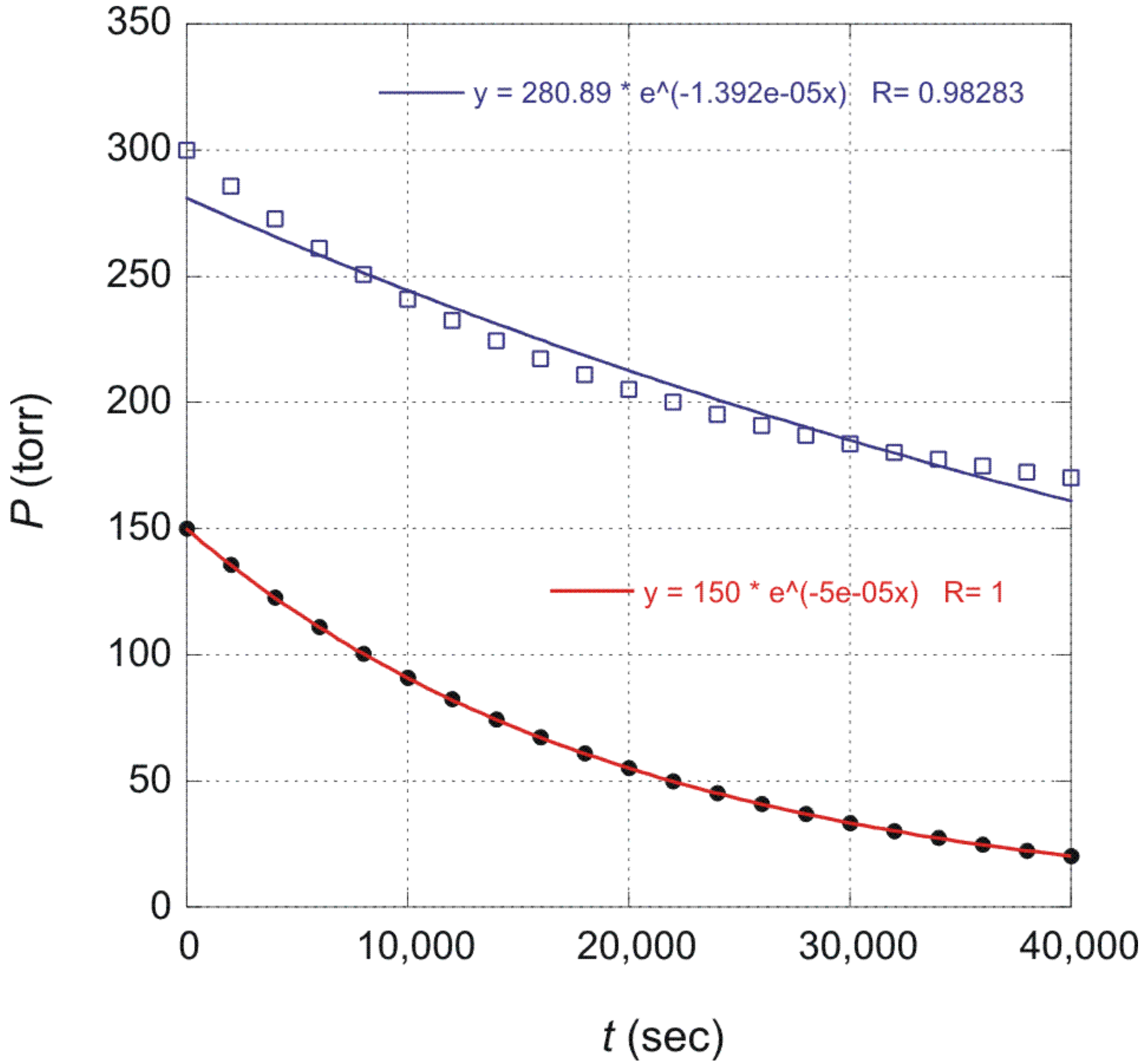
Fit to

$$Y_t = Y_0 e^{-kt}$$

$[A]_0$ = 150 torr

$k = 5 \times 10^{-5}$ /sec

Background Signal in Kinetic Data



Fit to

$$Y_t = Y_0 e^{-kt}$$

Y_0 = 281 torr

$k = 1.4 \times 10^{-5}$ /sec

wrong!

Fit to

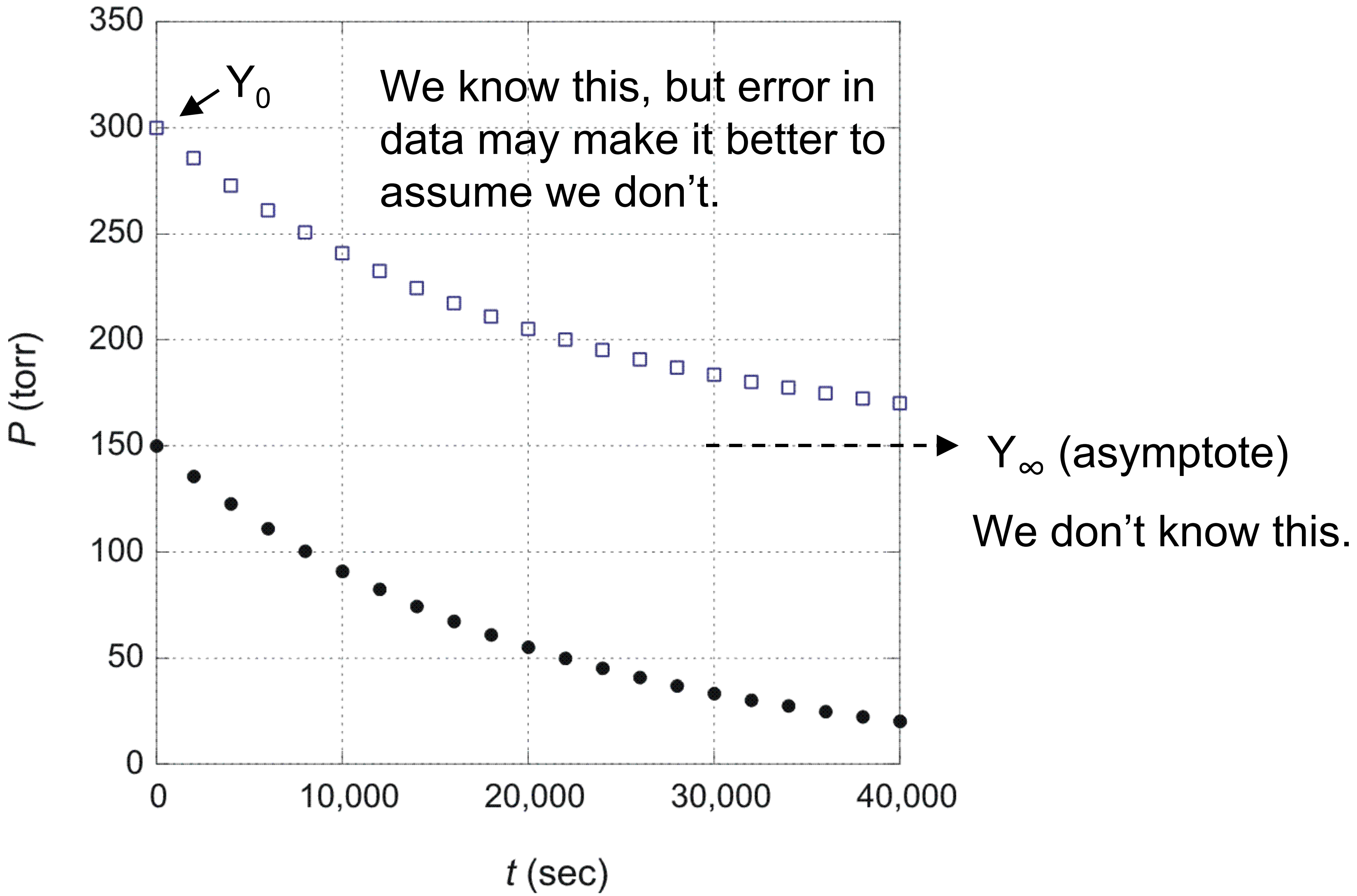
$$Y_t = Y_0 e^{-kt}$$

Y_0 = 150 torr

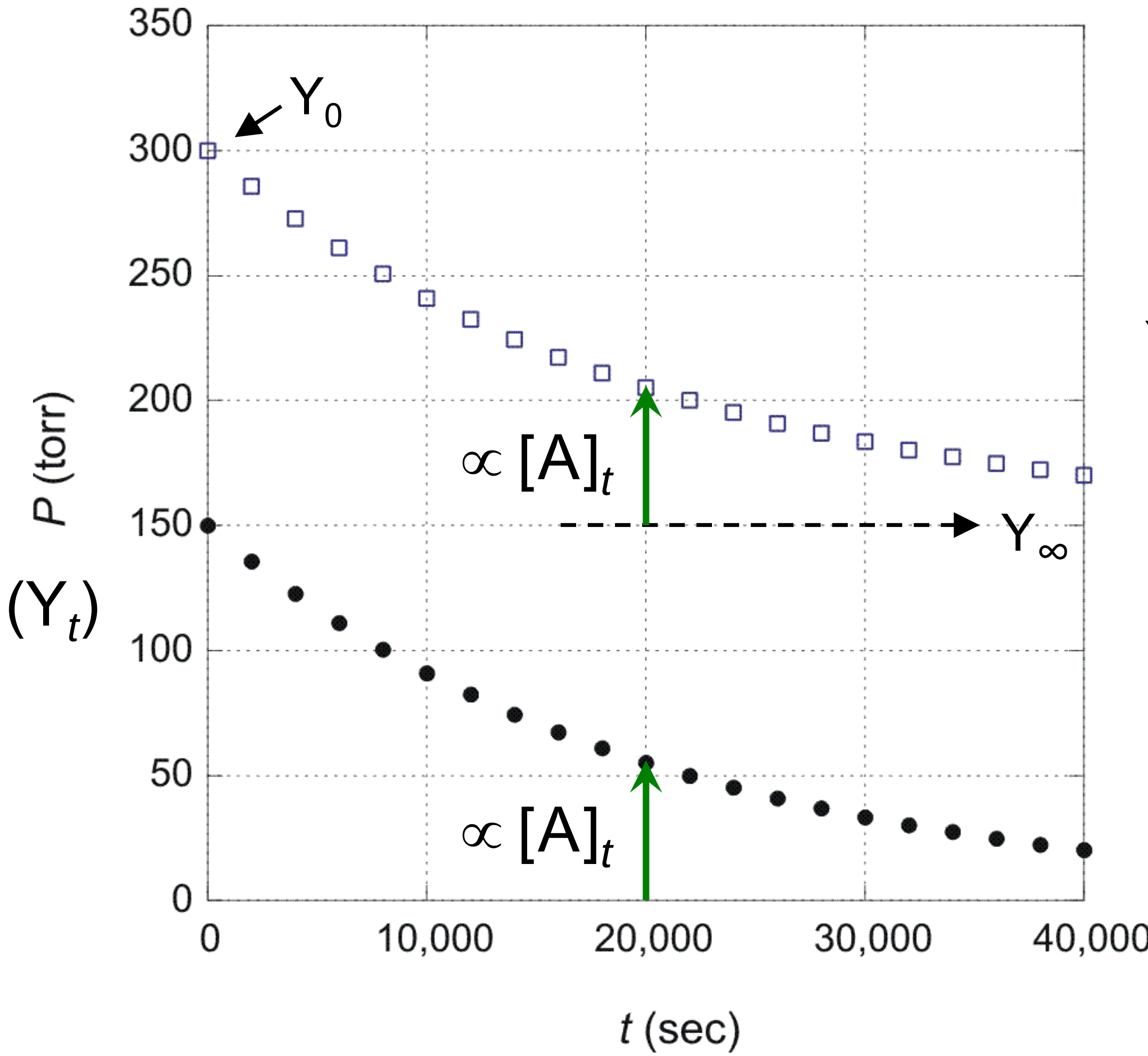
$k = 5 \times 10^{-5}$ /sec

Fits search for only 2 variables (Y_0 and *k*).

Background Signal in Kinetic Data



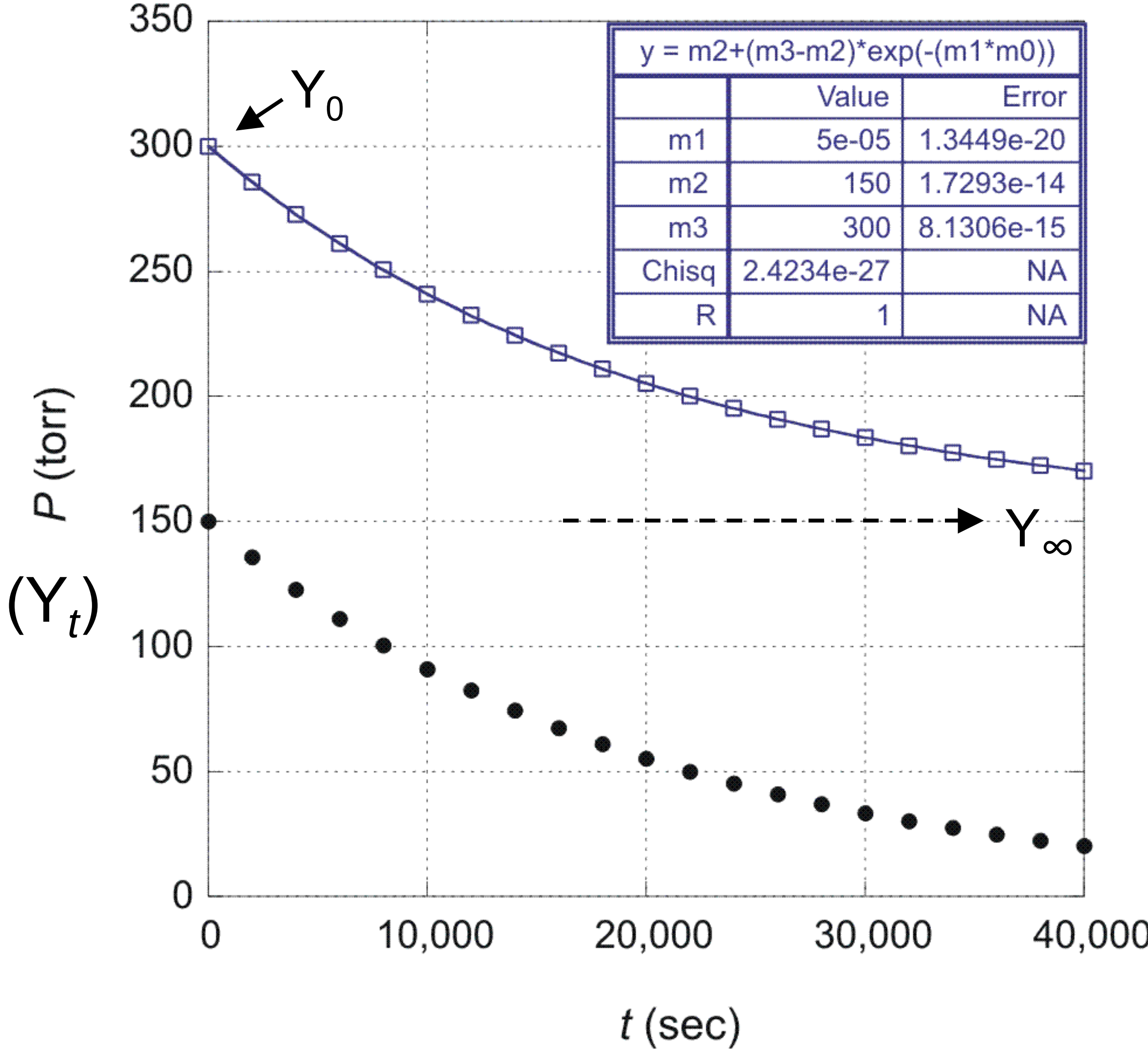
Background Signal in Kinetic Data



$$\frac{[A]_t}{[A]_0} = \frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = e^{-kt}$$

$$Y_t = Y_\infty + (Y_0 - Y_\infty)e^{-kt}$$

Background Signal in Kinetic Data



$$\frac{[A]_t}{[A]_0} = \frac{Y_t - Y_\infty}{Y_0 - Y_\infty} = e^{-kt}$$

$$Y_t = Y_\infty + \left(Y_0 - Y_\infty\right)e^{-kt}$$

Optimize for Y_0, Y_∞, k simultaneously.

Because function cannot be expressed in terms of $y = mx + b$, is fit by non-linear least-squares.