## VII. Reversible 1st-Order Reaction:

A. Given:

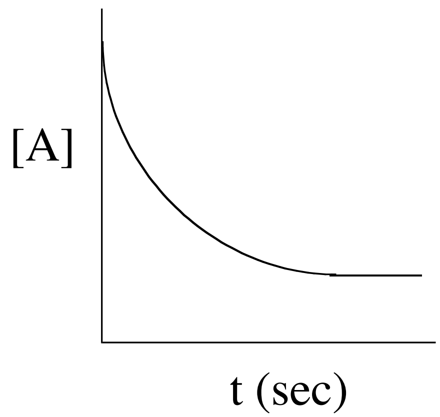
$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} P$$

- If $k_f >> k_r$, then the scheme reduces to an irreversible 1st-order reaction. However, if $k_f < 10k_r$, then A and P are both observable at equilibrium and the scheme is treated differently.

## VII. Reversible 1st-Order Reaction:

B. Graphics:

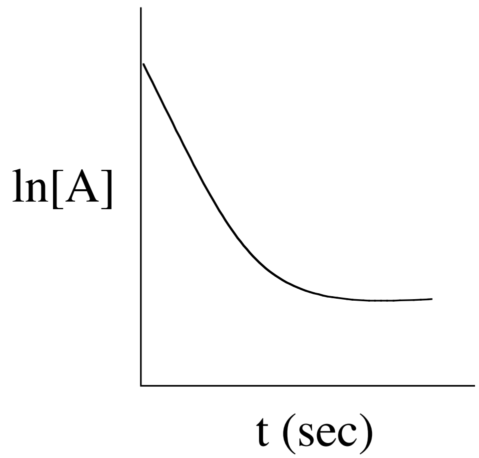
1. Zeroth-Order Plot:




• The failure to approach full conversion in the limit is easily missed by inspection, yet easily detected by floating an additional constant corresponding to $[A_\infty]/[A_0]$ (described in Section II.C.4.a.i).

## VII. Reversible 1st-Order Reaction:

2. <u>First-Order Plot</u>:




• This is easily confused with a 2nd-order dependence at high conversion or with a simple 1st-order dependence if the reaction is not followed to nearly full conversion.

## VII. Reversible 1st-Order Reaction:

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

$$-d[A]/dt = k_f[A] - k_r[P] \quad (1)$$

Since at t = 0...

$$[A_0] = [A] \text{ and } [P] = 0.$$

Then...

$$[A_0] = [A] + [P]$$

Substituting for [P] into eq (1)...

$$-d[A]/dt = k_f[A] - k_r([A_0] - [A])$$

## VII. Reversible 1st-Order Reaction:

Integrate... (CRC #27)

$$\underbrace{\ln\left\{\frac{k_f[A_o]}{(k_f + k_r)[A] - k_r[A_o]}\right\}}_{\text{adjustable parameters embedded in f(x)}} = (k_f + k_r)t \qquad (2)$$

Cross-check: as $k_f >> k_r$, the expression reduces to 1st order.

We need another (simultaneous) equation to solve for $k_f$ and $k_r$. Thus,...

$$k_f/k_r = [P_{eq}]/[A_{eq}]$$

or...

$$k_f[A_{eq}] = k_r[P_{eq}]$$

## VII. Reversible 1st-Order Reaction:

Substituting for $[P_{eq}]$...

$$k_f[A_{eq}] = k_r([A_0] - [A_{eq}]) \qquad (3)$$

$$[A_{eq}] = \frac{k_r}{k_f + k_r}[A_o] \qquad (4)$$

Going back to eq (2), substituting in $[A_{eq}]$ from eq (4) with rearrangement gives...

$$\ln\left\{\frac{(k_f/k_r)[A_{eq}]}{[A]-[A_{eq}]}\right\} = (k_f + k_r)t$$

Substituting in from eq (3) and rearranging...

$$\ln\left\{\frac{[A]-[A_{eq}]}{[A_o]-[A_{eq}]}\right\} = -(k_f + k_r)t$$

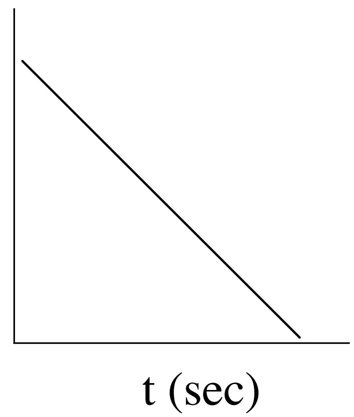
- Crosscheck: if $[A] >> [A_{eq}]$ (i.e., $k_f >> k_r$), the expression reduces to 1st order.

## VII. Reversible 1st-Order Reaction:

C. <u>Graphics</u>:

1. <u>Linear Fit</u>:

$$\ln\left\{\frac{[A]-[A_{eq}]}{[A_o]-[A_{eq}]}\right\}$$




Let...

$$f(x) = ax$$

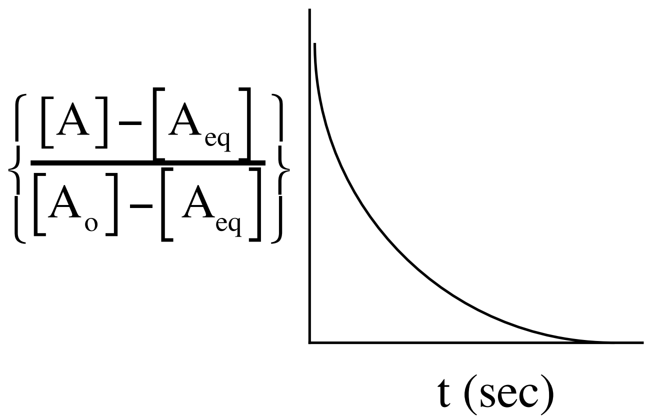
such that...

$$f(x) = \ln\left\{\frac{[A]-[A_{eq}]}{[A_o]-[A_{eq}]}\right\} \qquad x = t \qquad a = -(k_f + k_r)$$

(measured displacements from equilibrium)

## VII. Reversible 1st-Order Reaction:

2. Non-Linear Fit:




Let...

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

such that...

$$f(x) = \left\{\frac{[A]-[A_{eq}]}{[A_o]-[A_{eq}]}\right\} \qquad x = t \qquad a = -(k_f + k_r)$$

Parameter $\underline{a}$ provides $k_f + k_r$. We obtain $k_r$ and, in turn, $k_f$ from eq (4).