**In the Binary Collision Model we made a good case for the rate expression:**

$$R=\{\pi(\sigma_{AB})^2 \langle u_{rel} \rangle e^{-E_A/RT}\} (N_A/V)(N_B/V)$$

**Often, $N_A/V$ and $N_B/V$ are concentrations in units of molecules per ml. To get these in moles per liter, just multiply by $1000/N_0$!**

**So the Binary Collision Model predicts $R=k_R C_A C_B$**

**Basically, the Binary Collision Model predicts a reaction rate that is first order in A, first order in B and second order overall.**

**B) First Order Reactions [will need a model later!]**

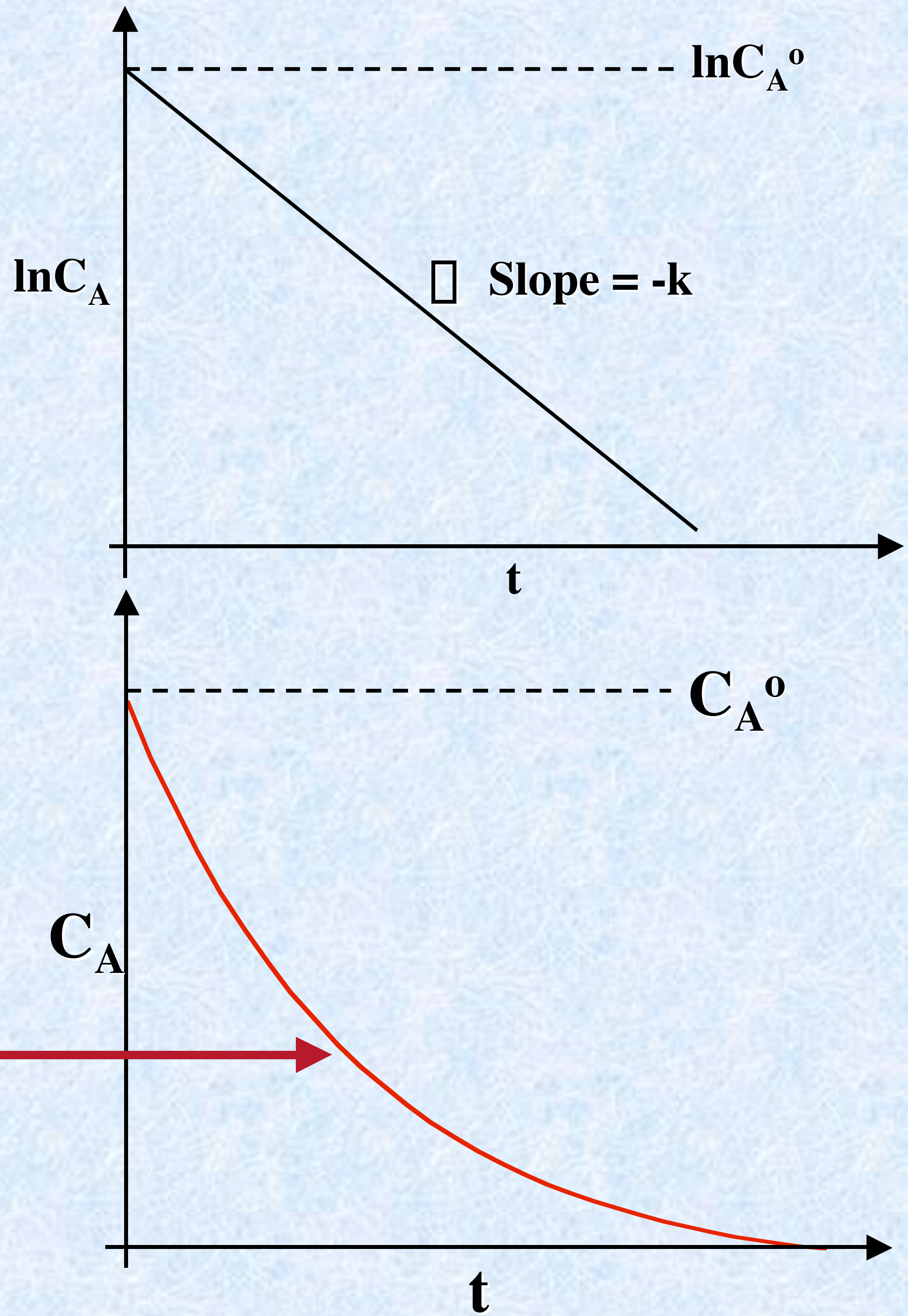
**Assume this is first order to get □**

$$-\frac{dC_A}{dt} = kC_A \text{ if reaction is 1}^{st}\text{ order}$$

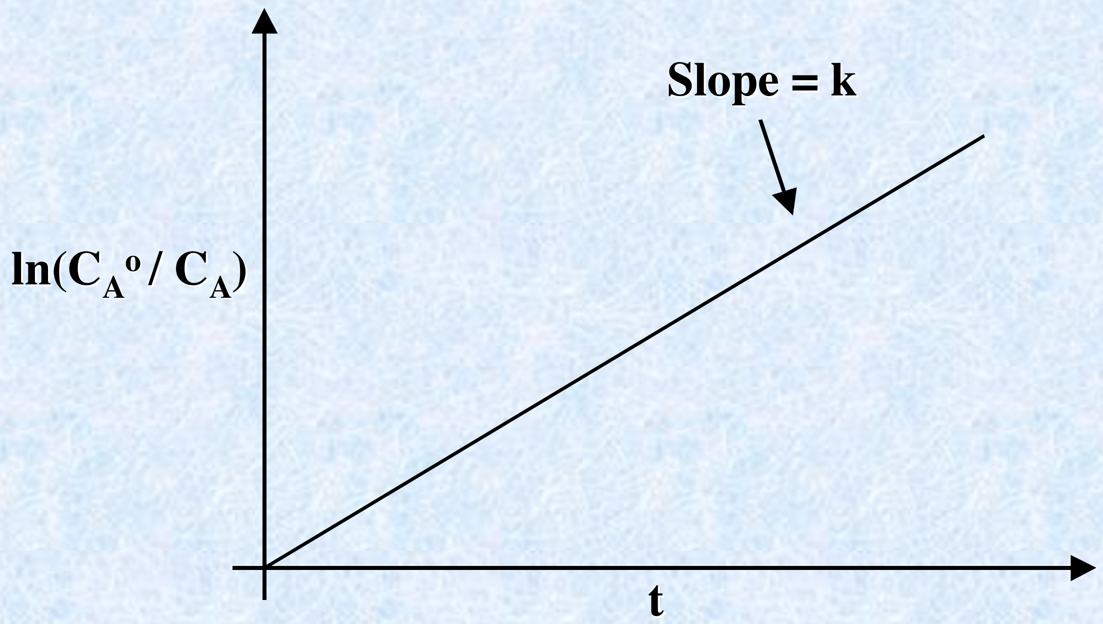
Integrate both sides: $+\int[dC_A/C_A] = -\int kdt$

Need to find g from initial conditions.

$\ln C_A^{o} = -k\,(0) + g$




$$C_A = C_A^0 e^{-kt}$$




**Equations for first order reactions are very important. In the laboratory almost ALL reactions can be made to APPEAR First Order.**

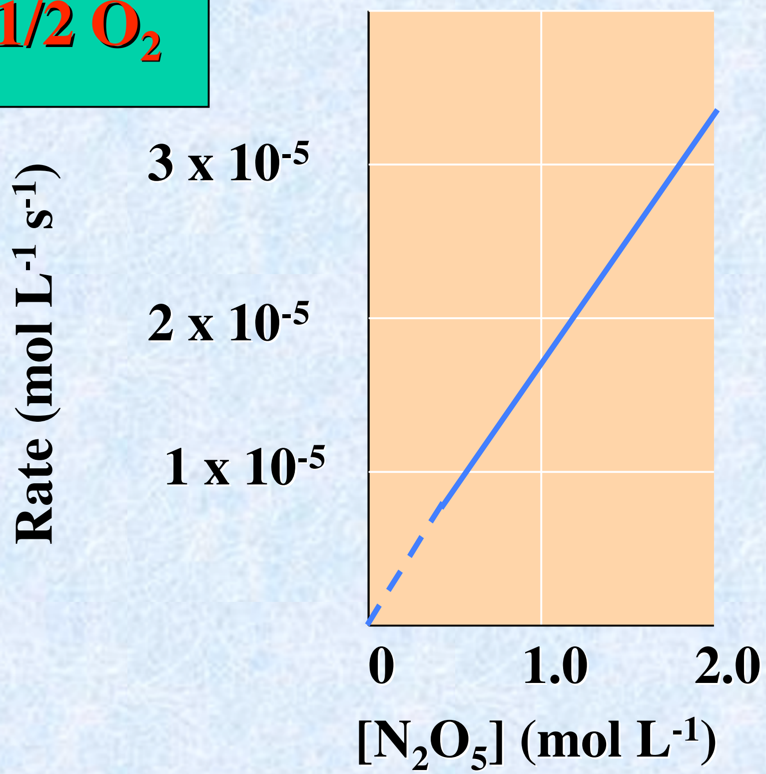
**Bonus * Bonus * Bonus * Bonus * Bonus * Bonus**

## Half Life or Half Time

$$\ln\left(\frac{C_A}{C_A^\circ}\right) = -kt$$

$N_2O_5$  $2NO_2 + 1/2\ O_2$

**Rate =**
**$-d[N_2O_5]/dt = k[N_2O_5]$**




**Example of a first order reaction.**

## C) 2nd Order Kinetics: $A \rightarrow$ Products

$$-\int dC_A/[C_A]^2 = k\int dt \quad \Longrightarrow \quad \boxed{1/[C_A] = kt + g}$$

$t = t_0$, $C_A = C_A^0$ — Initial conditions

$$\frac{1}{C_A} = \frac{1}{C_A^{\;0}} + k(t - t_0), \quad \text{Take } t_0 = 0 \Rightarrow$$

At $t_{1/2}$, $C_A = (C_A^0 / 2)$ and $1/[C_A] = 1/[C_A^0] + kt$

$$t_{1/2} = 1 / kC_A^0$$

## 2) Initial Rates Method

### 1st order reaction

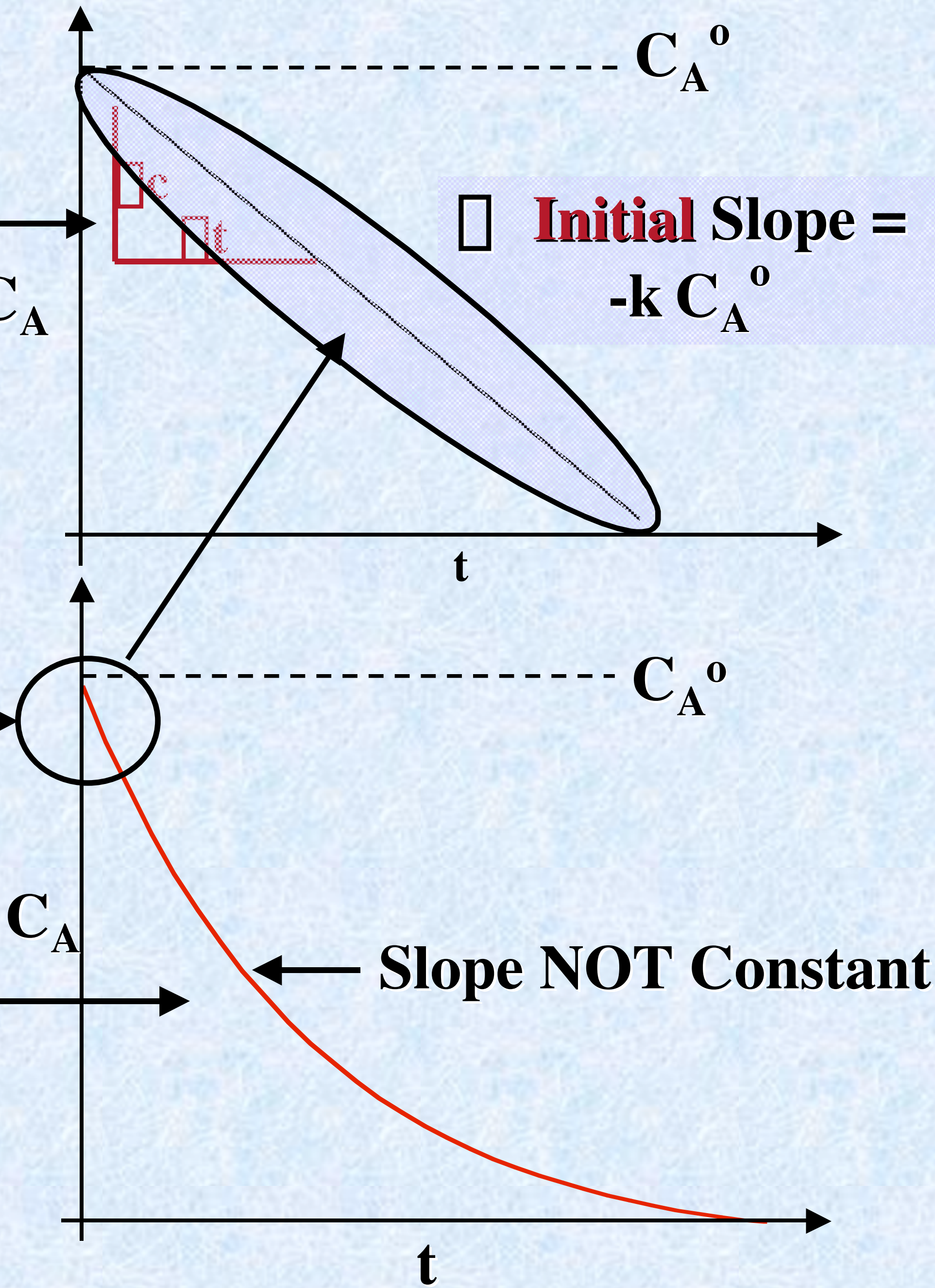
**$c = c_0 - x$**
**Where $c_0$ is the initial concentration and $x$ is a function of time, $x = x(t)$. $x$ is simply the amount reacted.**

**If $x \ll c_0$ □ $dx/dt = \text{const} = kc_0$ (sure to be true if $t$ is small enough!)**

**Initial part of curve will look like a straight line if t is small!**

$\Delta c / \Delta t = -k\, C_A^{o}$

∴ **Initial** Slope = $-k\, C_A^{o}$




Blow up first one percent of $C_A$ vs t curve

$dC_A/dt = -kC_A$

**Measure $\Delta c$ vs. $\Delta t$ for first 1% of reaction. Here, $c_0 >> x$,**

**$\Delta c \approx dx$ and $\Delta t \approx dt$ $\Rightarrow$**

**Know $c_0$ , measure $\Delta c$ and $\Delta t$, $\Rightarrow$ obtain k**

## $n^{th}$ Order Reactions

**$A + B + C \rightarrow$ products**

**a= initial conc of A**
**b= initial conc of B**
**c= initial conc of C**

**Bonus * Bonus * Bonus * Bonus * Bonus * Bonus**

$$\left(\frac{dx}{dt}\right)_2 = ka_2^{\,n_1} b_1^{\,n_2} c_1^{\,n_3}$$ **(Note, have kept b, c constant!)**

**$(dx/dt)_1$ and $(dx/dt)_2$ are measured in the laboratory, while $a_1$ and $a_2$ are known quantities.**

**Can do a similar trick for $n_2$ , $n_3$**

# Mechanism Concept

1) Exponents in rate law do not depend on stoichiometric coefficients in chemical reactions.

2)What is the detailed way in which the reactants are converted into products? This is not described by the chemical equation, which just accounts for mass balance.

3) Rate at which reaction proceeds and equilibrium is achieved, depends on the **Mechanism** by which reactants form products.

**Elementary Reactions:** these are hypothetical constructs, or our guess about how reactants are converted to products.

The **Mechanism** is a **set** of **Elementary Reactions**!