Using this probability and the energy dependence of Z_{AB} derived from the Boltzmann distribution, the reaction rate can be obtained. The result is:

Where $Z_{AB} = \pi(\sigma_{AB})^2 \langle u_{rel} \rangle (N_A/V)(N_B/V)$

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

Often k_R is written $k_R = A\, e^{-E_A/RT}$

Since $<u_{rel}> = (8kT/\pi\mu)^{1/2}$, A increases linearly with
 square root of T.

Temperature Dependence of k_R

There are two places where T comes into the expression for k_R

Orientation Effects: The Steric Factor

We have left out one consideration in our model for R, the reaction rate.

For example, in the reaction of $NO+O_2$ to form NO_2, the one O from O_2 must attach to the N in NO, not the O in NO!

Might expect collisions between NO and O_2 that occur at the nitrogen end of NO will be more effective in producing NO_2 than collisions at the O end of NO!
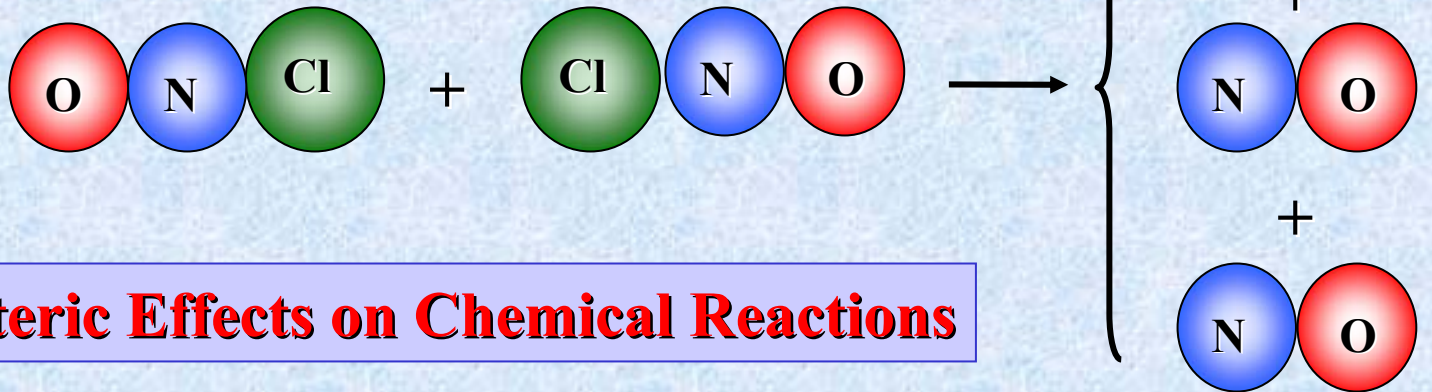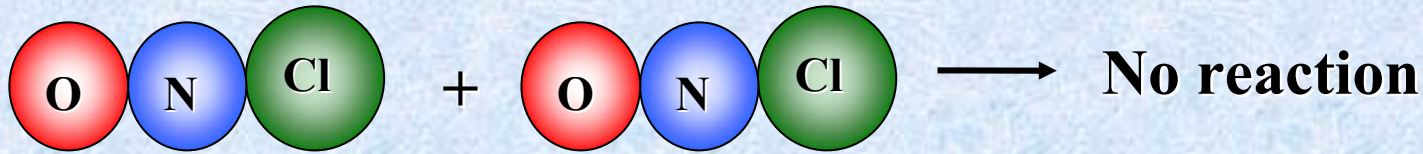
Steric Effects on Chemical Reactions

Units (cgs) and typical numbers:

Chemical Kinetics: Laboratory Measurements

We now have a model for chemical reactions (Binary Collision Model) and need to deal with practical issue of how to make observations in the laboratory.

This will involve both analyzing chemical reaction data from laboratory measurements and extending our models.

A) Consider the reaction
2A → B + C

**Rate ≡ time rate of change of concentration of any of the
substances involved - reactants or products.**

Usual convention: $R = -\dfrac{1}{2}\dfrac{dC_A}{dt} = \dfrac{dC_B}{dt} = \dfrac{dC_C}{dt}$

Could measure the rate by measuring the composition of the reaction vessel as a function of time. Example:

t = 0 N_A^o = moles A $N_B^o = N_C^o = 0$

t = t_1 N_A' = moles A $N_B' = N_C'$ = moles B, C

Consider the reaction
2A → B + C

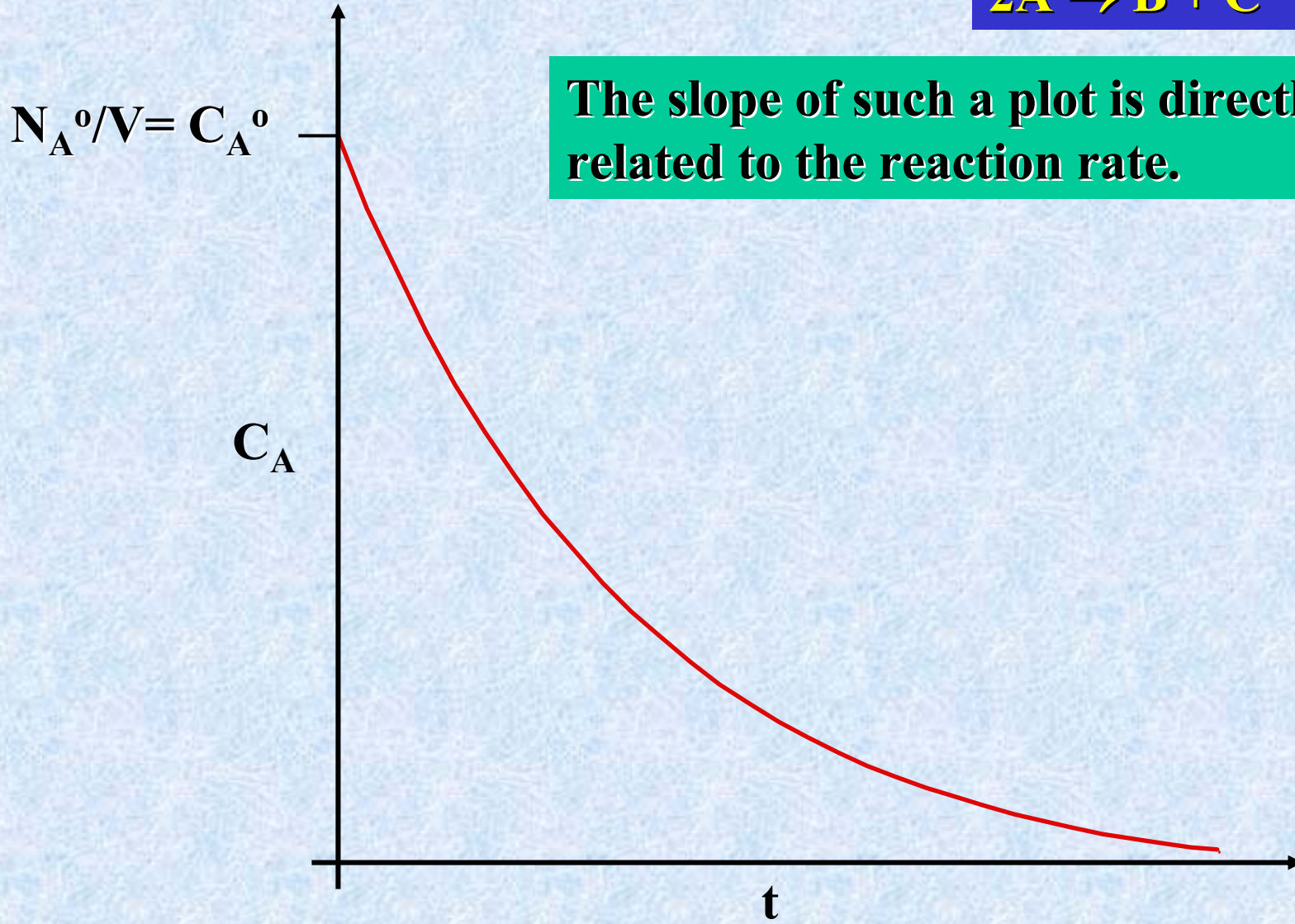**Two moles of A gives one mole of B. Or moles of B formed must equal half the number of moles of A reacted.**

t = 0 N_A^o = **moles A** $N_B^o = N_C^o = 0$

t = t$_1$ N_A' = **moles A** $N_B' = N_C'$ = **moles B, C**

Take deerivative of both sides with respect to t $\rightarrow$

Consider the reaction
$2A \rightarrow B + C$

The slope of such a plot is directly related to the reaction rate.

$N_A^o/V = C_A^o$

C_A

t

In general the rate for such a reaction turns out to be a function of the concentrations of all of the substances involved

f could have any form. In many cases f has the form

k is a constant called the **rate constant**. α is the **order** of the reaction for the component A

$\alpha = 1 \equiv 1^{st}$ order in A

$\alpha = 3 \equiv 3^{rd}$ order in A

<u>Overall order of a reaction</u> =
$\alpha + \beta + \gamma$. <u>The order has absolutely nothing to do with the</u>
<u>stoichiometry of the reaction,</u>

The point is that one knows nothing about α, β, γ from
looking at the chemical equation for the reaction.