Chemical Kinetics

The goal of kinetics is to establish a quantitative relationship between the **concentrations of reactants and/or products** and the **rate of the reaction**.

$$A + B \longrightarrow P$$

$$\text{rate} = k[A]^m[B]^n$$

Kinetics experiments are often useful when chemists seek to determine a reaction mechanism. However, kinetics only serve to support or refute a reaction mechanism; they can **never prove** a mechanism.

For relevant reading, see OGC, Chapter 18

Chemical Kinetics: Rate Laws

A **rate law** is an equation expressing the rate of a reaction in terms of the molar concentrations of the species involved in the reaction. The rate law is independent of the stoichiometry.

$$A + B \longrightarrow P$$

$$rate = k[A]^m[B]^n = d[P]/dt$$

In this rate law, **m** and **n** are **orders** of the reaction components

k is the **rate constant**

The **overall reaction rate** has an order that is **m** + **n**

Chemical Kinetics: Rate Laws

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$$A + B \longrightarrow P$$

$$\text{rate} = k[A]^m[B]^n = d[P]/dt$$

0th **order:** reaction rate is independent of a given reagent
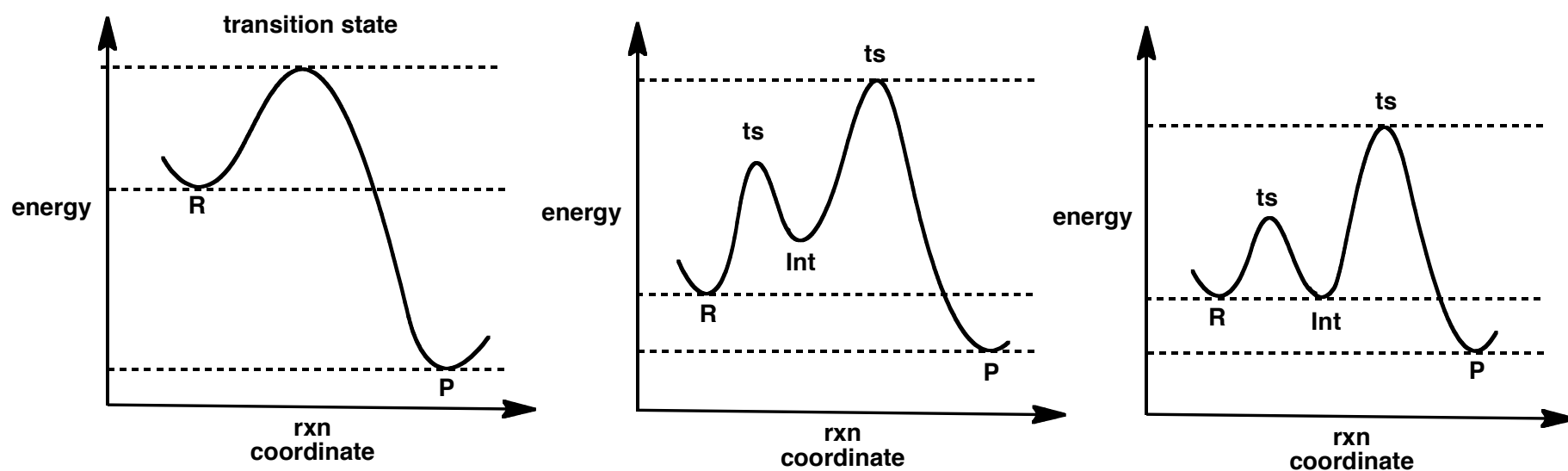1st **order**: reaction rate doubles as [reagent] doubles
2nd **order**: reaction rate quadruples as [reagent] doubles

The **overall reaction rate** has an order that is $m + n$

Chemical Kinetics

Consider a chemical reaction that converts **reactants (R)** to **products (P)**.

Transition state: a stationary point with one, and only one, negative eigenvalue. A transition state is a maximum on the reaction coordinate. The lifetime of the transition state is no longer than a vibration.

Chemical Kinetics

The **molecularity** of a chemical reaction is the number of molecules involved in the transition state of a reaction. The term can only be applied to single step reactions, or the elementary steps for a multi-step reaction

**unimolecular**: a single molecule in the transition state
bimolecular: two molecules in the transition state
termolecular: three molecules in the transition state (these are rare

Chemical Kinetics

The **molecularity** of a chemical reaction is the number of molecules involved in the transition state of a reaction. The term can only be applied to single step reactions, or the elementary steps for a multi-step reaction.

the **rate** of the reaction is determined by the energy of the **highest transition state** along the reaction coordinate ($\Delta G^{\ddagger)}$
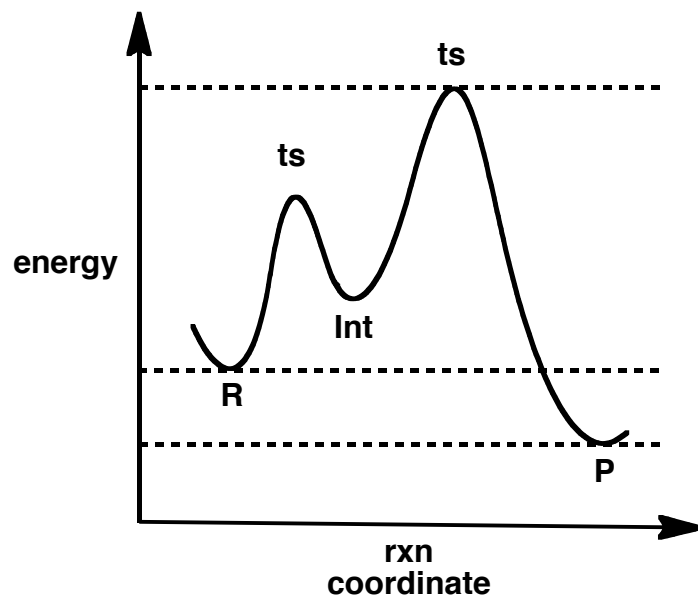
Transition State Theory

Transition state theory (TST) assumes the reactants and activated complex are in pre-equilibrium.

• TST allows us to use statistical mechanics to calculate the concentration of the transition state and to determine the activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for a reaction.

consider:

$$A + B \longrightarrow P$$

$$dP/dt = k[A][B]$$
$$dP/dt = k^{\ddagger}[AB^{\ddagger}]$$

$$k = k^{\ddagger}K^{\ddagger}$$

$$[AB^{\ddagger}] = K^{\ddagger}[A][B]$$

Transition State Theory

Transition state theory (TST) assumes the reactants and activated complex are in pre-equilibrium.

$$A + B \longrightarrow P \qquad k = k^{\ddagger}K^{\ddagger}$$
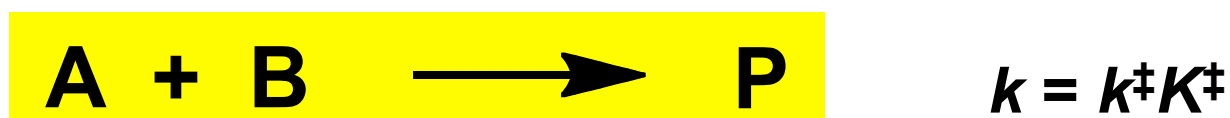
Need to solve for $K^{\ddagger}$. Passage over the transition state is correlated to a vibrational mode that tips it along the reaction coordinate toward the products

$$k^{\ddagger} = \kappa\nu$$

$$K^{\ddagger} = \left(\frac{k_BT}{h\nu}\right)K^{\ddagger\prime} \qquad\qquad k = \kappa\left(\frac{k_BT}{h}\right)K^{\ddagger\prime}$$

$$K^{\ddagger\prime} = \left(\frac{-\Delta G}{RT}\right) \qquad\qquad \textbf{Eyring equation}$$

The Eyring Equation

The **Eyring equation** can be used to determine activation parameters

$$k = \kappa \left(\frac{k_B T}{h} \right) K^{\ddagger\prime}$$

Eyring equation

$$k = \kappa \left(\frac{k_B T}{h} \right) e^{(-\Delta G^\ddagger/RT)} = 2.083 \times 10^{10}\, T\, e^{(-\Delta G^\ddagger/RT)}$$

$$k = \kappa \left(\frac{k_B T}{h} \right) e^{(-\Delta H^\ddagger/RT)}\, e^{(\Delta S^\ddagger/R)}$$

Chemical Kinetics: Determining the Orders of a Chemical Reaction

There are two common experimental methods that help us determine the orders of a reaction:

• the method of **isolation** puts all but one reactant in such a large excess that their concentration change over the course of the reaction is essentially zero
    ✓ the order determined for the remaining reactant is a **pseudo-order** for the reaction
    ✓ the pseudo-orders can be determined for each reactant, and can be used to give the overall order

• the method of **initial rates** measures the rate at the beginning of the reaction (<10% conversion) for several initial concentrations of the reactant

Using the Initial Rates Method

Example: the initial rate of a reaction depended on the concentration of a substance **A** as follows:

$[A]_0$ (10^{-3} M)	5.0	8.2	17	30
$rate_0$ (10^{-7} M s^{-1})	3.6	9.6	41	130

Initial Rates Method assumes that **$[A]_0$** isn't changing during course of measurements

*The concentration of reactant **A** can be determined by spectroscopic methods (^{1}H NMR, UV, IR, etc)*

*The initial rate was determined for each of four reactions with different initial concentrations of **A***

Using the Initial Rates Method

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$[A]_0$ (10^{-3} M)	5.0	8.2	17	30
rate$_0$ (10^{-7} M s^{-1})	3.6	9.6	41	130

*When we start with more **A**, the initial rate is faster. The rate is clearly dependent on the **[A]**.*
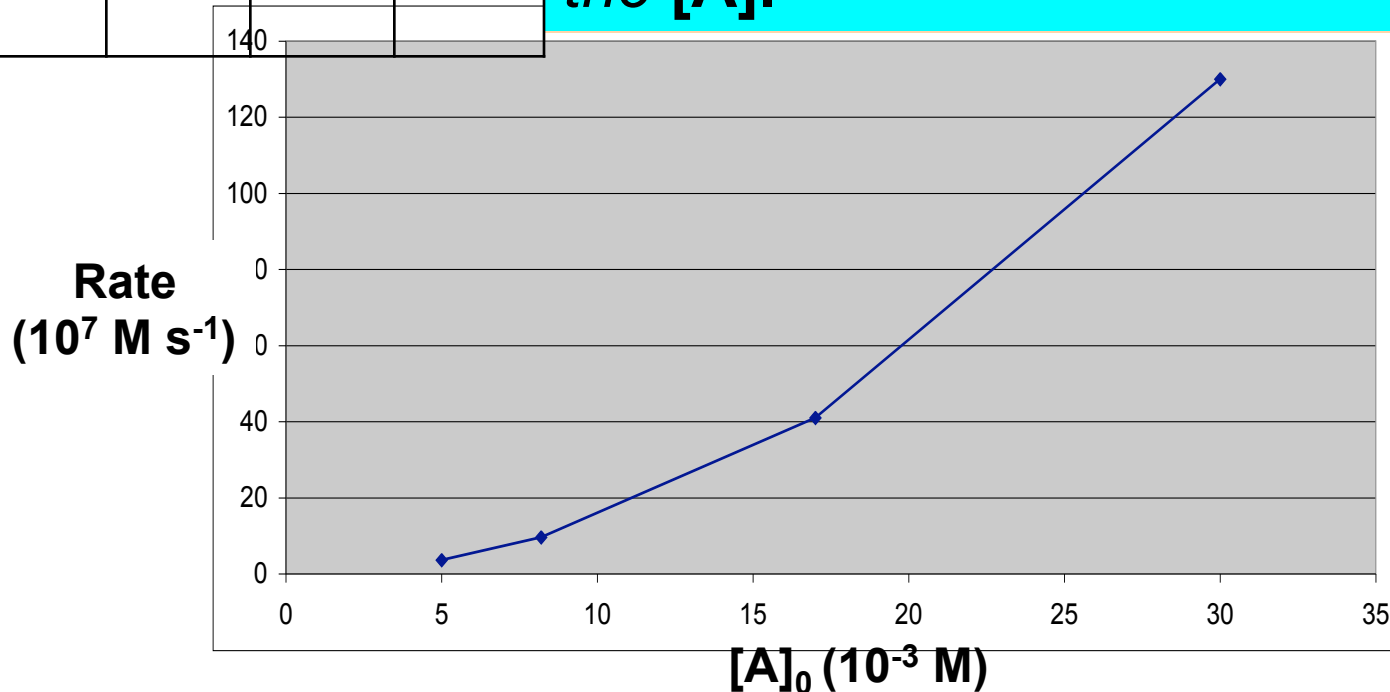
Rate (10^7 M s^{-1})

$[A]_0$ (10^{-3} M)

Using the Initial Rates Method

Example: the initial rate of a reaction depended on the concentration of a substance **A** as follows:

$[A]_0$ $(10^{-3}\ M)$	5.0	8.2	17	30
$rate_0$ $(10^{-7}\ M\ s^{-1})$	3.6	9.6	41	130

note that as $[A]_0$ goes up by 2, the $rate_0$ goes up by 2^2

*Find the **order** of the reaction with respect to **A** and the rate constant (**k**).*

what do we know?
$$rate_0 = k[A]_0^n$$

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*Find the **order** of the reaction with respect to **A** and the rate constant.*

what do we know?

rate$_0$ = $k[A]_0^n$

log rate$_0$ = log k + nlog $[A]_0$

plot this function

Using the Initial Rates Method

$$\log \text{rate}_0 = \log k + n\log[A]_0$$

	Coefficients
Intercept **(log k)**	-0.84439
slope **(n)**	**2.000498**

Slope = 2.0 = order

Log k = -0.84; k=0.14 M^{-1} s^{-1}

Regression Statistics	
R-squared	0.999973

a word of caution: log-log plots tend to be linear, no matter what!
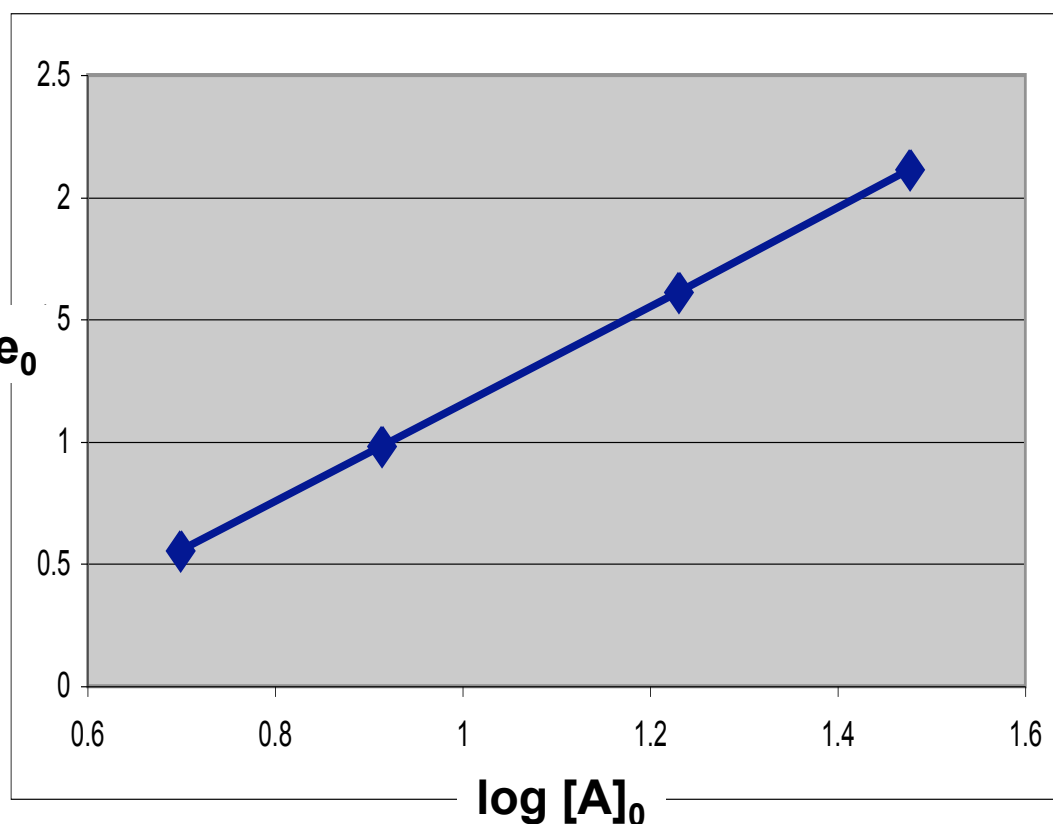
from a few experiments, we get a lot of useful information

A Systematic Look at Rate Laws

- **discussion of commonly observed rate laws**
- **determining rate laws**
    - *monitor the disappearance of a reactant or the appearance of a product*
    - *use graphical methods to distinguish between different reaction type*

Zero Order Rates

What if the plot looked like this instead?

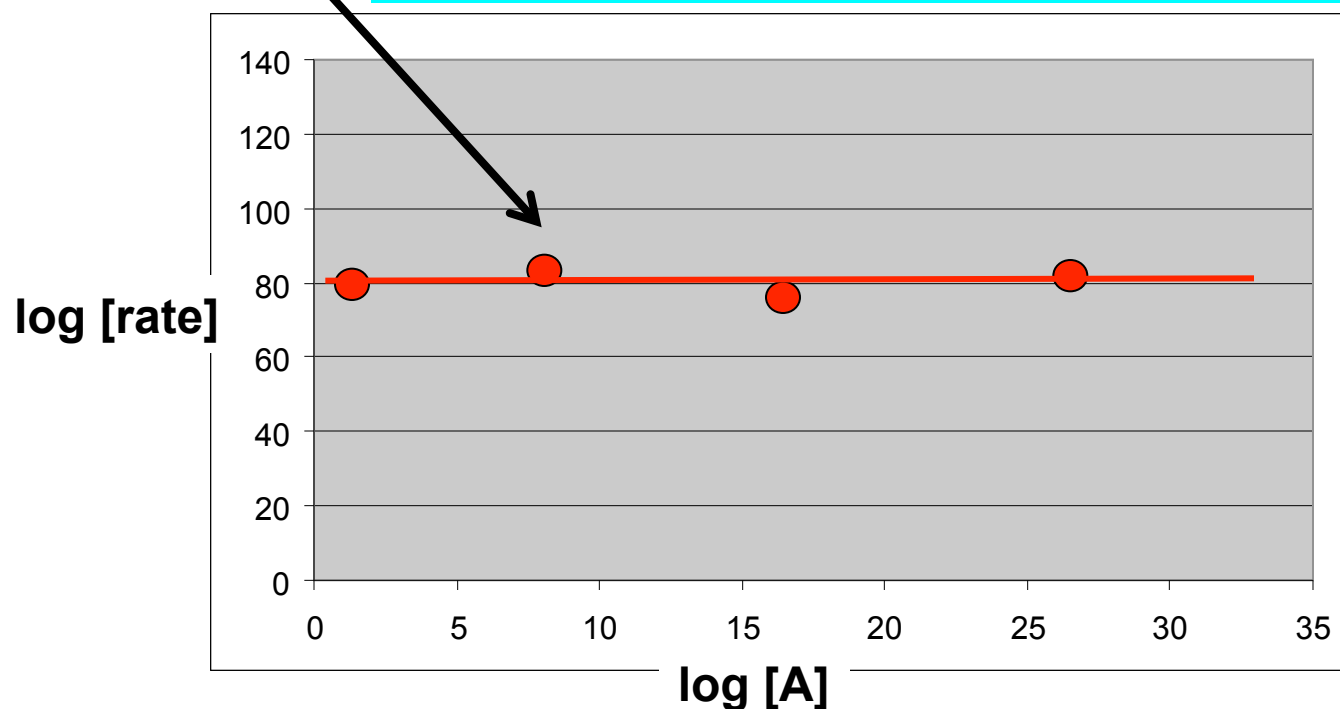*the rate is **independent** of the concentration of **A***
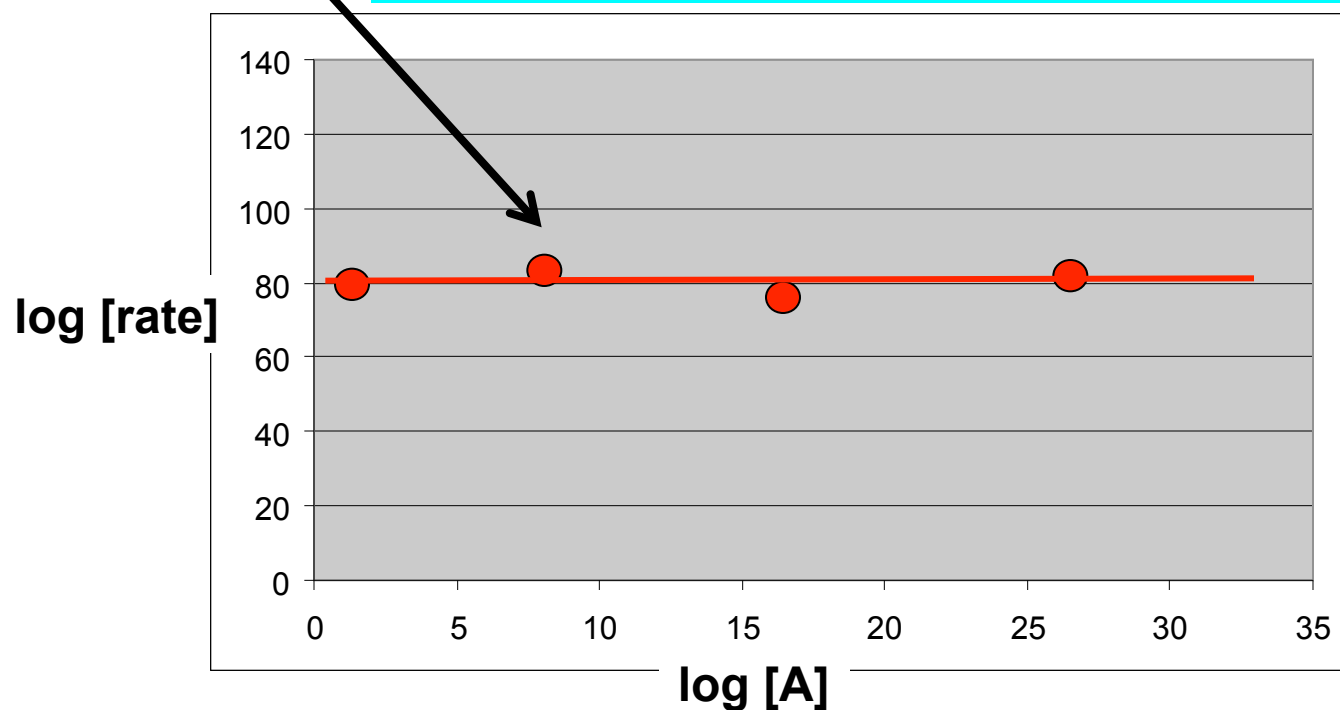
How can we get the rate constant?

Zero Order Rates

What if the plot looked like this instead?

*the rate is **independent** of the concentration of **A***

How can we get the rate constant?

*Consider monitoring the disappearance of **A** with time.*

Zero Order Rates

In the previous example,
log rate$_0$ = 2 log[A]$_0$ + log k   this reaction was 2nd order in **A**

Often, **n = 0**. *The reaction is 0-order in* **A***; the rate is independent of* **[A]**.

log rate$_0$ = 0 log[A]$_0$ + log k

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instead, let's think about it like this:

$$-\frac{d[A]}{dt} = k[A]^0 = k$$ this is the rate law, sometimes it's referred to as the differential rate law.

$$-\ d[A]\ = k \cdot dt$$

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$$-\,[A] = kt$$ this is the integrated rate law   units for k = concentration time^{-1}

Zero Order Rates

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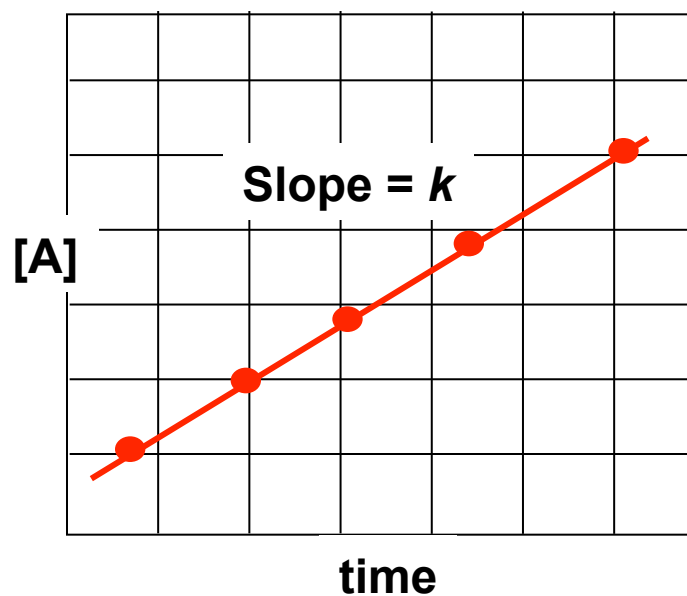
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$$-\,[A] = kt$$

Slope = k

[A]

time

plot looks like this

First Order Rates

Often, **n = 1**. *The reaction is 1st order in* **A***; the rate is dependent on* **[A]**.

log rate$_0$ = 1 log[A]$_0$ + log *k*

First Order Rates

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log rate$_0$ = 1 log[A]$_0$ + log k

$$-\frac{d[A]}{dt} = k[A]^1 = k[A] \quad \boxed{\text{differential rate law}}$$

$$\frac{d[A]}{[A]} = -k \cdot dt \quad \boxed{\textit{how do we determine the rate constant?}}$$

*again, monitor the disappearance of **A***

First Order Rates

Often, **n = 1**. *The reaction is 1st order in* **A**; *the rate is dependent on* **[A]**.

log rate$_0$ = 1 log[A]$_0$ + log k

$$-\frac{d[A]}{dt} = k[A]^1 = k[A]$$

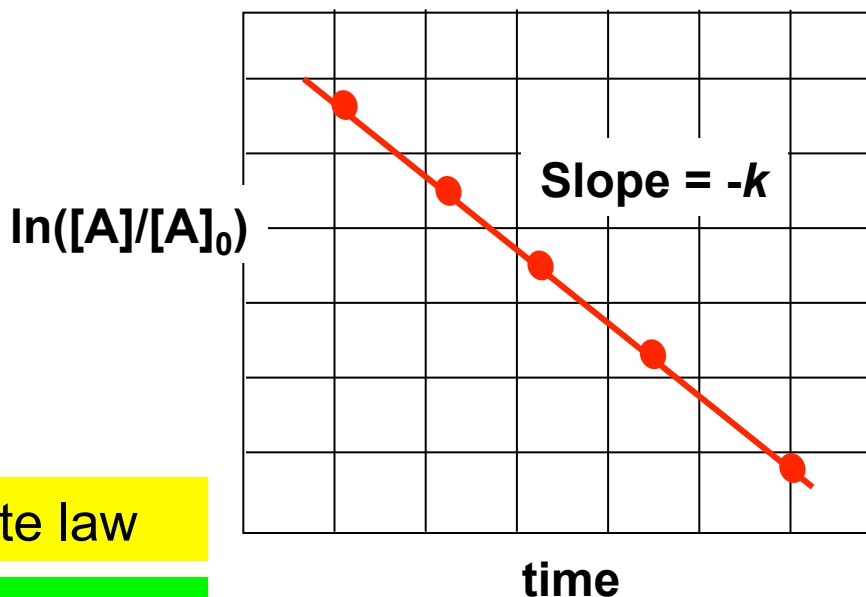$$\frac{d[A]}{[A]} = -k \cdot dt$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k \cdot t$$

integrated rate law

units for k = time^{-1}

This plot is a litmus test for 1st order reactions!

Plot looks like this

ln([A]/[A]$_0$)

Slope = -k
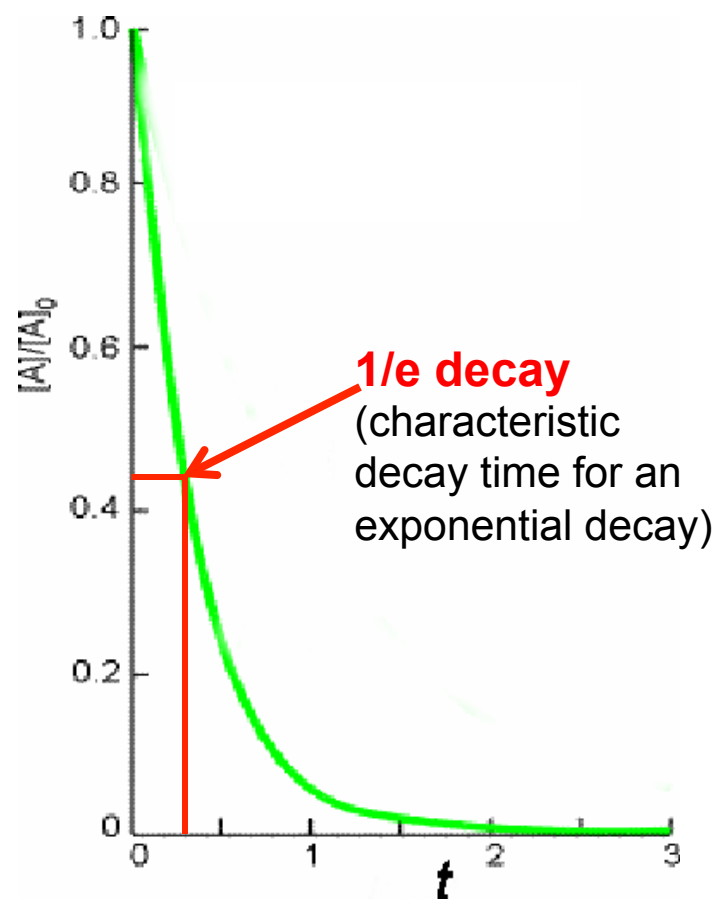
time

First Order Rates

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$$\ln\left(\frac{[A]}{[A]_0}\right) = -\,k{\cdot}t$$

can also use this form:

$$[A] = [A]_0 \exp(-k{\cdot}t)$$

and plot $[A]/[A]_0$ *versus t*

1/e decay
(characteristic decay time for an exponential decay)

First Order Rates

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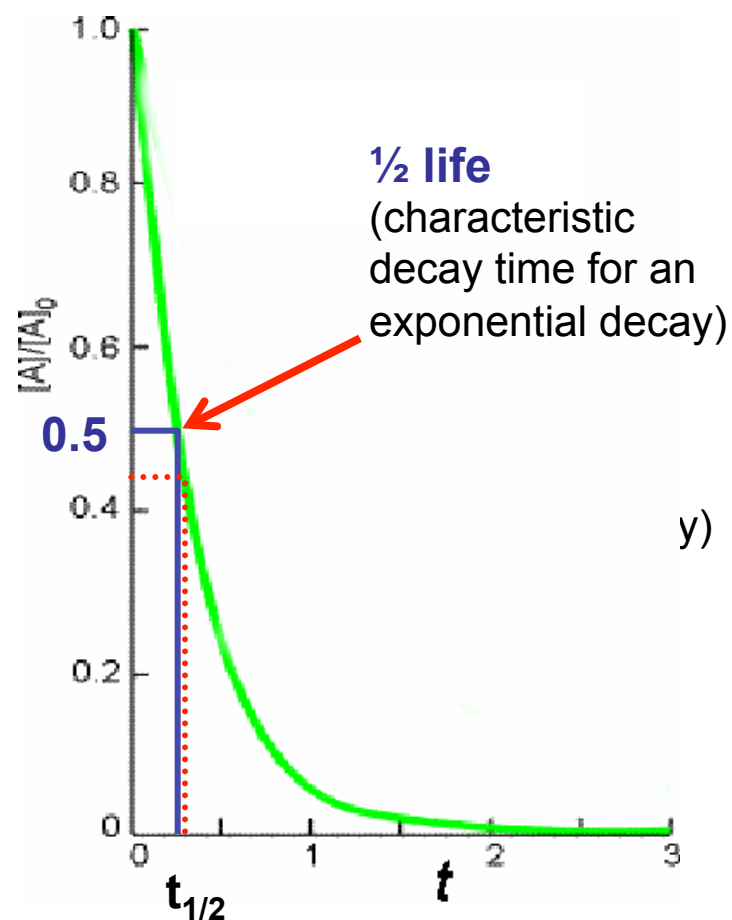
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can also use this form:

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and plot $[A]/[A]_0$ *versus t*

half-life can be calculated:
$t_{1/2} = \ln(2)/k = 0.693/k$

½ **life**
(characteristic decay time for an exponential decay)

y)

An Example

The concentration of N_2O_5 in liquid bromine was recorded over time:

t (s)	0	200	400	600	1000
$[N_2O_5]$ (M)	0.110	0.073	0.048	0.032	0.014

Show that the reaction is first order in N_2O_5 and determine the rate constant.

How to start? Use the "litmus test" for 1st order reactions:

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k \cdot t$$

An Example

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Show that the reaction is first order in N_2O_5 and determine the rate constant.

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k \cdot t$$

	Coefficients
Intercept	0
Slope	-0.00206

k = 2.1 x 10⁻³ s⁻¹

$\ln([A]/[A]_0)$

slope = –*k*

Yes – reaction is first order in [N_2O_5]

time