

From Last Time



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

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**

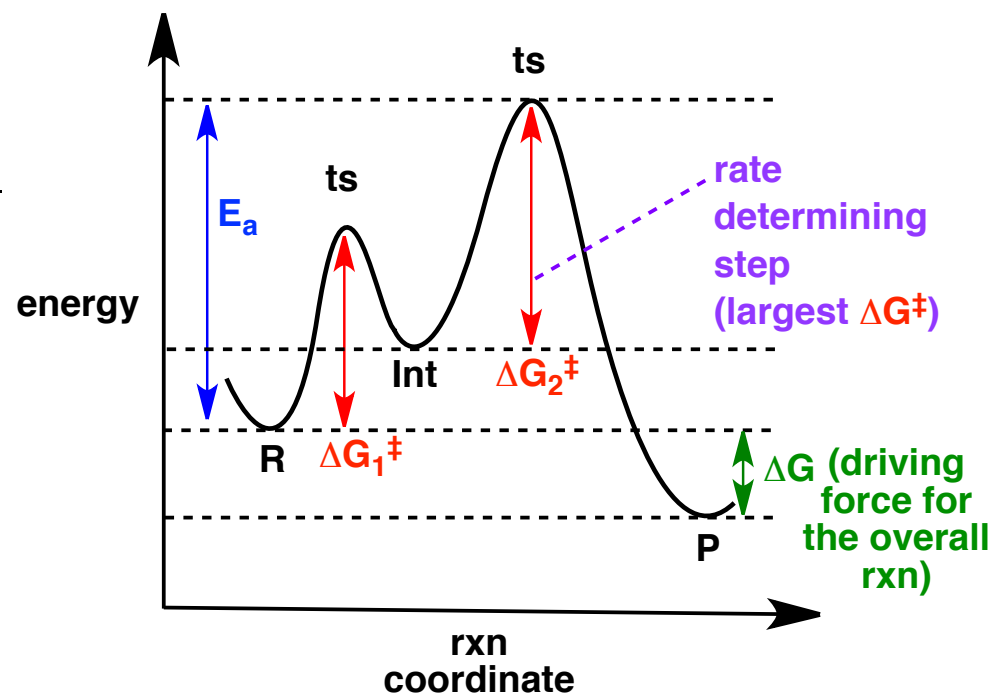
Eyring equation: used to determine the activation parameters (ΔG^\ddagger , ΔS^\ddagger , ΔH^\ddagger) for each elementary step of a reaction.

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

Experimentally useful expression of the Eyring equation:

$$\ln \left(\frac{k}{T} \right) = \frac{-\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \ln \left(\frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R}$$

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



Arrhenius equation: used to experimentally determine the energy for a reaction barrier. Is macroscopic treatment; does not consider mechanism.

$$k = Ae^{(-E_a/RT)}$$

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Experimental methods to determine the orders of a reaction:

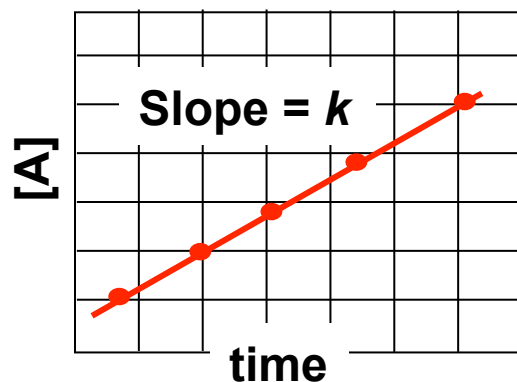
- the method of **isolation** puts all but one reactant in such a large excess that their concentration change over the course of the reaction is essentially zero.
- the method of **initial rates** measures the rate at the beginning of the reaction (<10% conversion) for several initial concentrations of the reactant .

Zero order rates: (no reaction can be zero order in **all** reagents/catalysts)

Consider a reaction that consumes A, but shows no rate dependence on A.

$$\text{rate law: } -\frac{d[A]}{dt} = k[A]^0 = k$$

$$\text{integrated rate law: } -[A] = kt$$

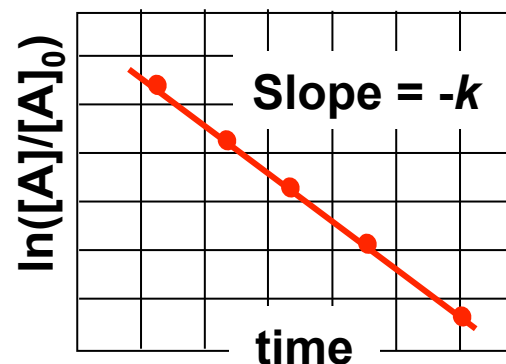


First order rates:



$$\text{rate law: } \frac{d[P]}{dt} = k[A]$$

$$\text{integrated rate law: } \ln\left(\frac{[A]}{[A]_0}\right) = -kt$$



(plot is straight line when 1st order in A)

2nd Order Reactions

Consider the process:



Which is 2nd order in A

the differential rate law is:

$$\frac{d[\text{P}]}{dt} = k[\text{A}]^2 \quad \text{or expressed as}$$

$$-\frac{1}{2} \frac{d[\text{A}]}{dt} = k[\text{A}]^2$$

and so:

$$-\frac{d[\text{A}]}{[\text{A}]^2} = 2 \cdot k dt$$

(in many text books, this is wrapped into the rate constant and is not shown)

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the integrated rate law is written as:

$$\frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} = 2 \cdot kt$$

Integrating this equation between $[\text{A}]_0$ and $[\text{A}]$ and between $t=0$ and t , we get the integrated rate law

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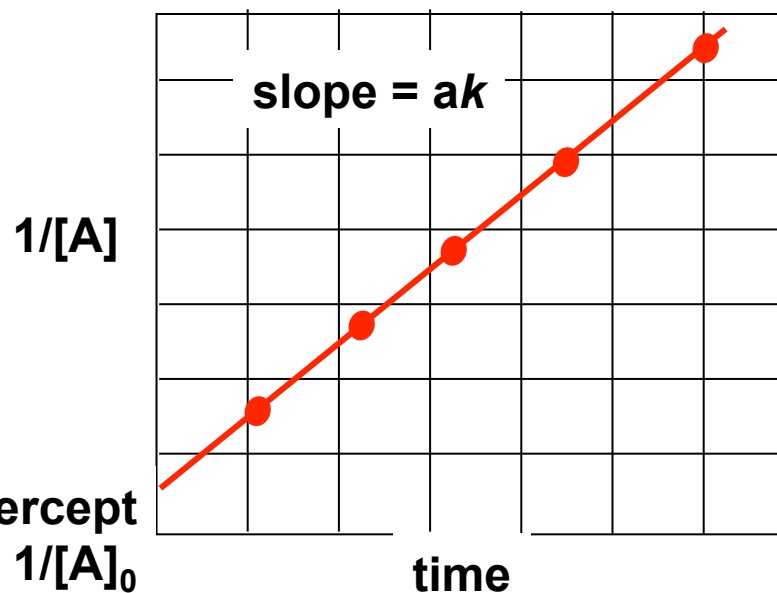
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Plot $1/[\text{A}]$ versus t ; slope is **ak** where **a** is the stoichiometry of $[\text{A}]$

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[A] at any time **t** during
the course of the reaction
can be calculated from

$$[\text{A}] = \frac{[\text{A}]_0}{1 + [\text{A}]_0 \cdot 2 \cdot kt}$$

More on 2nd Order Reactions

For the general process:



there are many ways by which a reaction can be 2nd order overall

2 nd Order in A 0 th order in B	rate = $k[A]^2$
2 nd Order in B 0 th order in A	rate = $k[B]^2$
1 st Order in A 1 st order in B	rate = $k[A][B]$

Let's consider the case of rate = $k[A][B]$

2nd Order Reactions: First Order in Each of Two Species

Consider the process: **A + B → products**

- **2nd order** overall reaction, **1st order** in each **A** and **B**
- **rate = $k[A][B]$**
- Based on the fact that when one molecule of A reacts, one molecule of B is consumed, the following equation results:

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

this is the integrated rate law

this expression is awkward to use, (and not that simple to derive)

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What simplifications can we make here??

2nd Order Reactions: Simplification #1



Consider the case of

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

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

If we set $[A]_0 = [B]_0$, then

$$\text{rate} = 2k[A]^2$$

we've seen this before!

2nd Order Reactions: Simplification #2



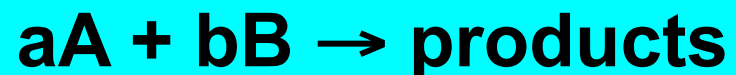
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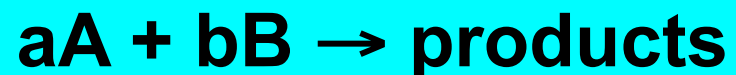
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$$\frac{d[A]}{[A]} \approx -kdt \quad \text{and} \quad \ln \left(\frac{[A]}{[A]_0} \right) \approx -kt$$

This allows us to determine a pseudo-order in **A**.
We can also conduct experiments with a little bit of **B** and a lot of **A**, to determine psuedo-order in **B**.

2nd Order Reactions: Simplification #2



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$$\frac{d[A]}{[A]} \approx -kdt \quad \text{and} \quad \ln \left(\frac{[A]}{[A]_0} \right) \approx -kt$$

total reaction order = order in [A] + order in [B]

Overview of Common Rate Laws

a table of useful reactions, rate laws, and integrated rate laws:

reaction	rate law	integrated rate law
$A \longrightarrow P$	$\frac{d[P]}{dt} = k[A]$	$\ln \left(\frac{[A]}{[A]_0} \right) = -kt$
$2A \longrightarrow P$	$\frac{d[P]}{dt} = k[A]^2$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
$A + B \longrightarrow P$	$\frac{d[P]}{dt} = k[A][B]$	$\ln \left(\frac{[B][A]_0}{[A][B]_0} \right) = ([B]_0 - [A]_0) \cdot kt$

taken from: Anslyn and Dougherty, Physical Organic Chemistry, p 390

Why Do We Care?

Kinetic experiments provide information about the mechanism of a reaction...which can enable the development of improved reaction conditions.

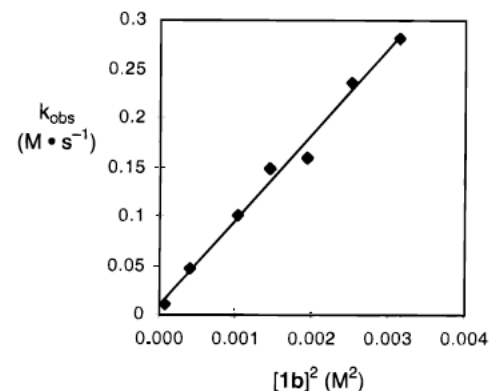
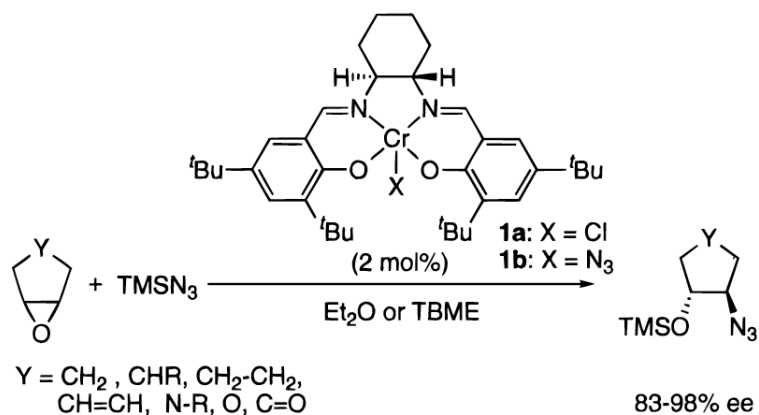


Figure 3. Plot of k_{obs} vs $[1b]^2$ for the catalytic ring opening of cyclohexene oxide with HN₃. Individual runs were monitored for appearance of product by GC using an internal standard. Initial concentrations: [epoxide] = 2.0 M, [HN₃] = 0.2 M in TBME.

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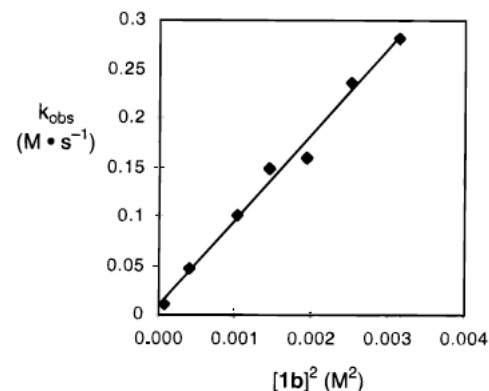
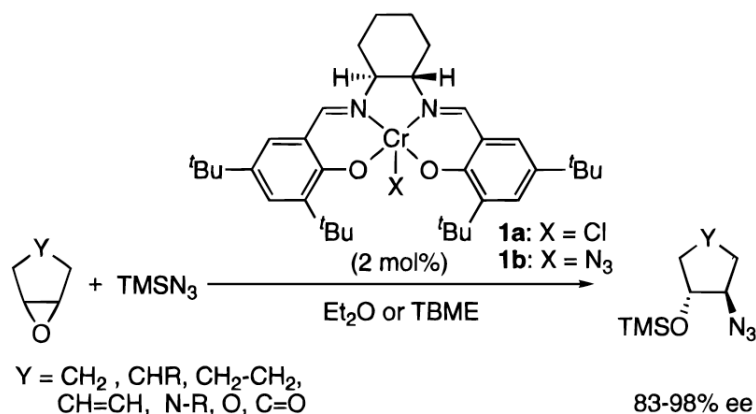
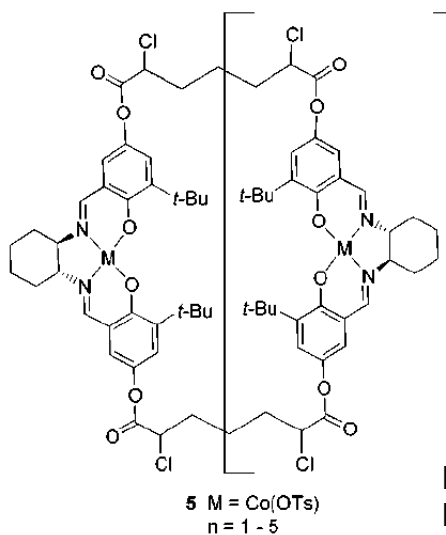


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Hansen, K.B.; Leighton, J.L.; Jacobsen, E.N. *J. Am. Chem. Soc.* **1996**, *118*, 10924
Ready, J.M.; Jacobsen, E.N. *J. Am. Chem. Soc.* **2001**, *123*, 2687

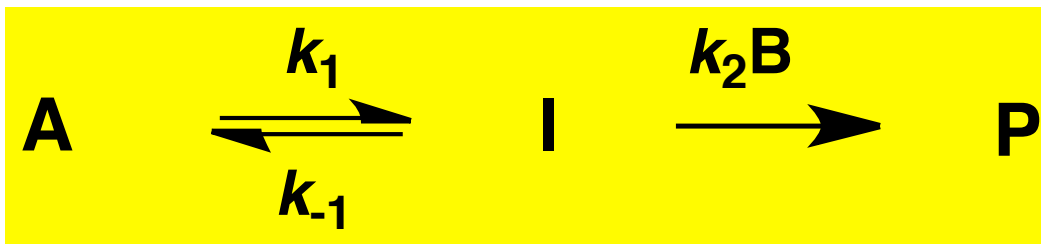


entry	R ¹	R ²	catalyst	Co (mol %) ^b	yield (%) ^c	ee (%) ^d
1	H	CH ₂ Cl	monomer (1c)	4.0 ^e	96	99
			oligomer (5)	0.25	99	99
2	<i>o</i> -O(allyl)	CH ₂ Cl	1c	4.4	48	84
			5	0.25	99	98
3	H	C ₆ H ₅	1c	4.0	^f	n.d.
			5	1.0	60	97
4	H	<i>c</i> -hexyl	1c	8.0	89	94
			5	0.5	99	98

The Steady State Approximation

For a multistep reaction involving a transient intermediate, it is assumed that large concentrations of the intermediate do not accumulate. The **concentration of the reactive intermediate can be assumed to be constant** over the course of the reaction.

One possible
scenario:



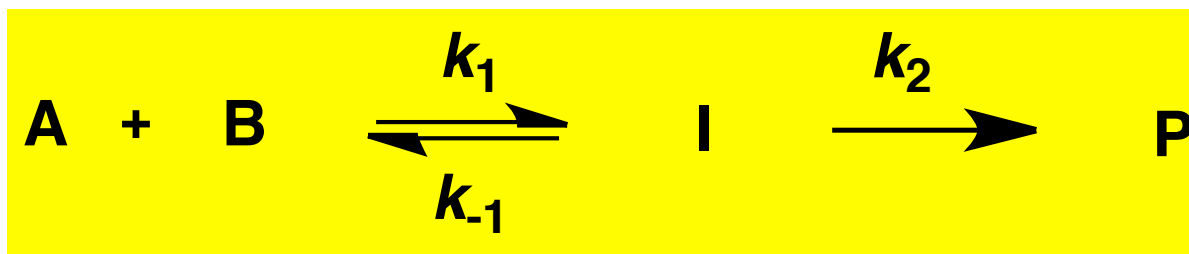
$$\frac{d[P]}{dt} = k_2[I][B]$$

$$\frac{d[I]}{dt} = k_1[A] - k_{-1}[I] - k_2[I][B] = 0$$

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A][B]}{k_{-1} + k_2 [B]}$$

The Steady State Approximation

A second possible scenario:



$$\frac{d[\text{P}]}{dt} = k_2[\text{I}]$$

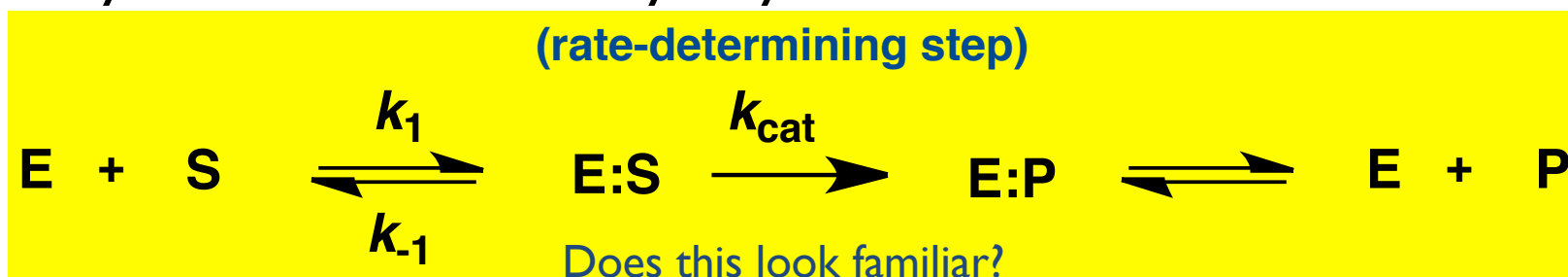
$$\frac{d[\text{I}]}{dt} = k_1[\text{A}][\text{B}] - k_{-1}[\text{I}] - k_2[\text{I}] = 0 \qquad [\text{I}] = \frac{k_1[\text{A}][\text{B}]}{k_{-1} + k_2}$$

$$\frac{d[\text{P}]}{dt} = \frac{k_1 k_2 [\text{A}][\text{B}]}{k_{-1} + k_2} = k_{\text{obs}} [\text{A}][\text{B}] \qquad k_{\text{obs}} = \frac{k_1 k_2}{k_{-1} + k_2}$$

Cannot decipher whether k_{obs} represents a single elementary step, or a combination of several rate constants for individual elementary steps

Michaelis-Menten Equation: Enzyme Kinetics

A model to describe the kinetics of enzyme catalysis, also applicable to many small molecule catalyst systems



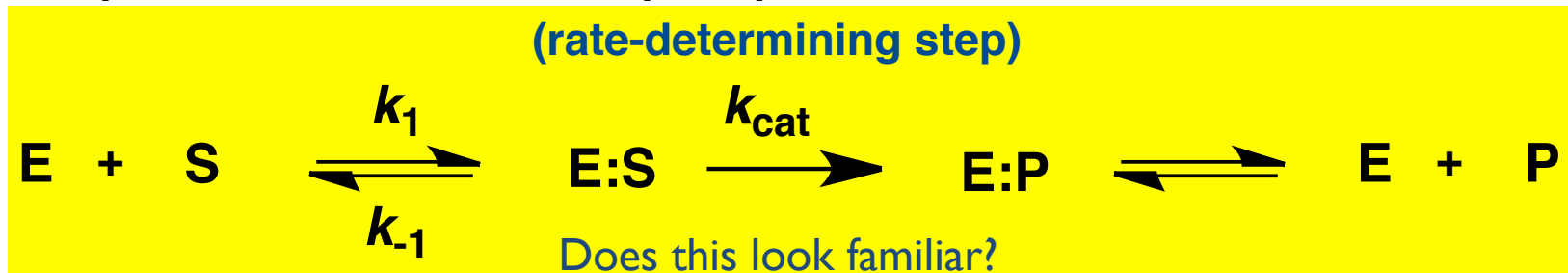
$$\frac{d[P]}{dt} = k_{\text{cat}}[ES]$$

$$\frac{d[E:S]}{dt} = \overbrace{k_1([E]_o - [E:S])}^{[E]}[S] - k_{-1}[E:S] - k_{\text{cat}}[E:S] = 0$$

$$\frac{d[P]}{dt} = \frac{k_1 k_{\text{cat}}[E]_o[S]}{k_{-1} + k_{\text{cat}} + k_1[S]} = \frac{k_{\text{cat}}[E]_o[S]}{[S] + K_M} \quad K_M = \frac{k_{-1} + k_{\text{cat}}}{k_1}$$

Michaelis-Menten Equation: Enzyme Kinetics

A model to describe the kinetics of enzyme catalysis, also applicable to many small molecule catalyst systems



More commonly expressed as:

$$v = \frac{v_{\text{max}}[\text{S}]}{[\text{S}] + K_{\text{M}}}$$