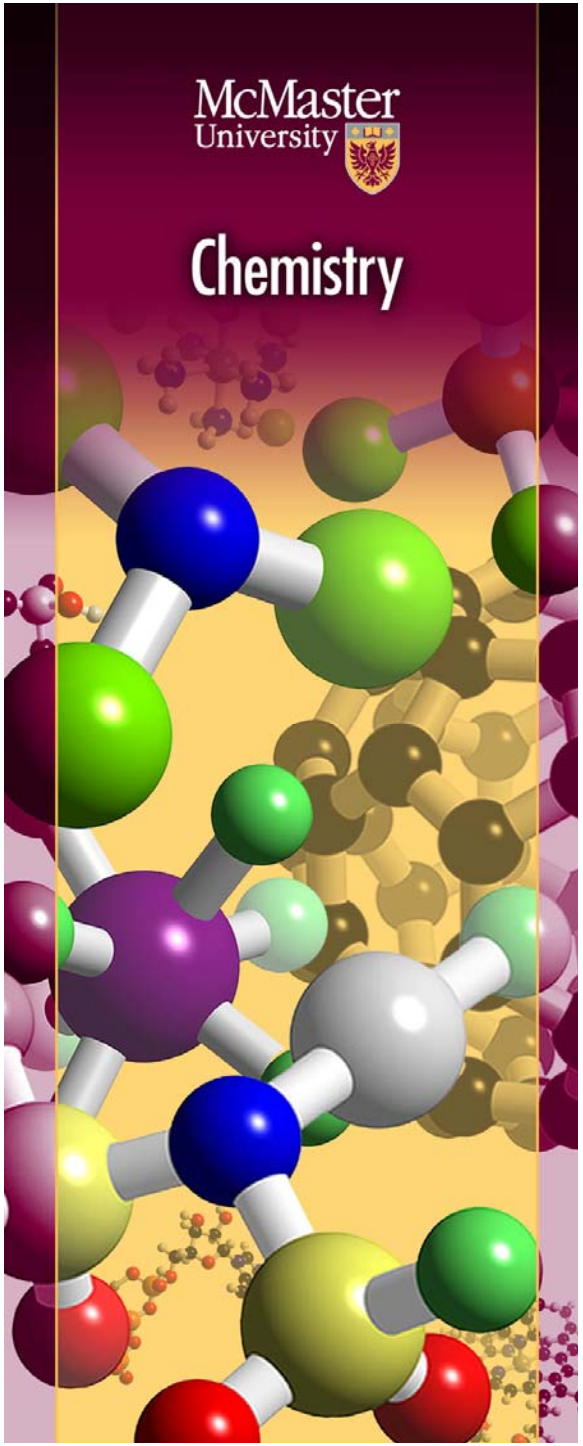
CHEM 1AA3: Intro. Chemistry II

Chapter 14: Chemical Kinetics

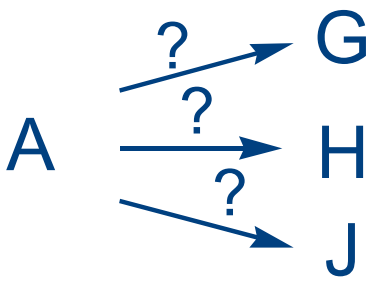


Equations in the slides are identified by **bold** numbers. If the same equation appears in the text, the text's chapter and equation number is given as well (e.g., (**7**, 14.2)).

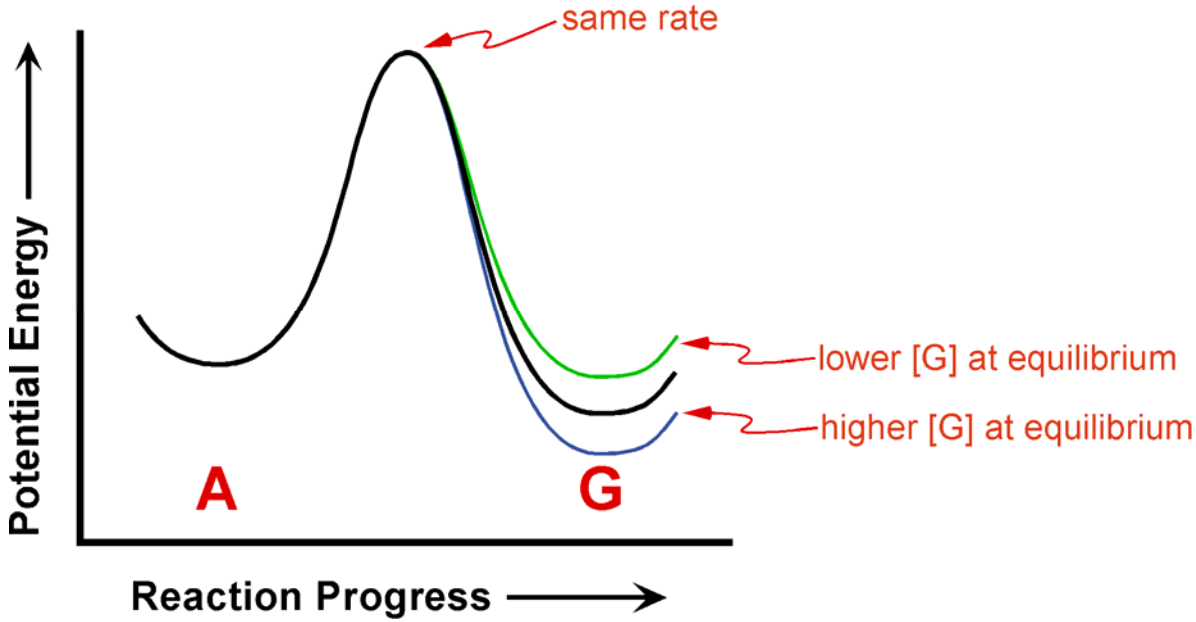
Preface

The 3 big questions in any chemical reaction:

(1) What are the products?

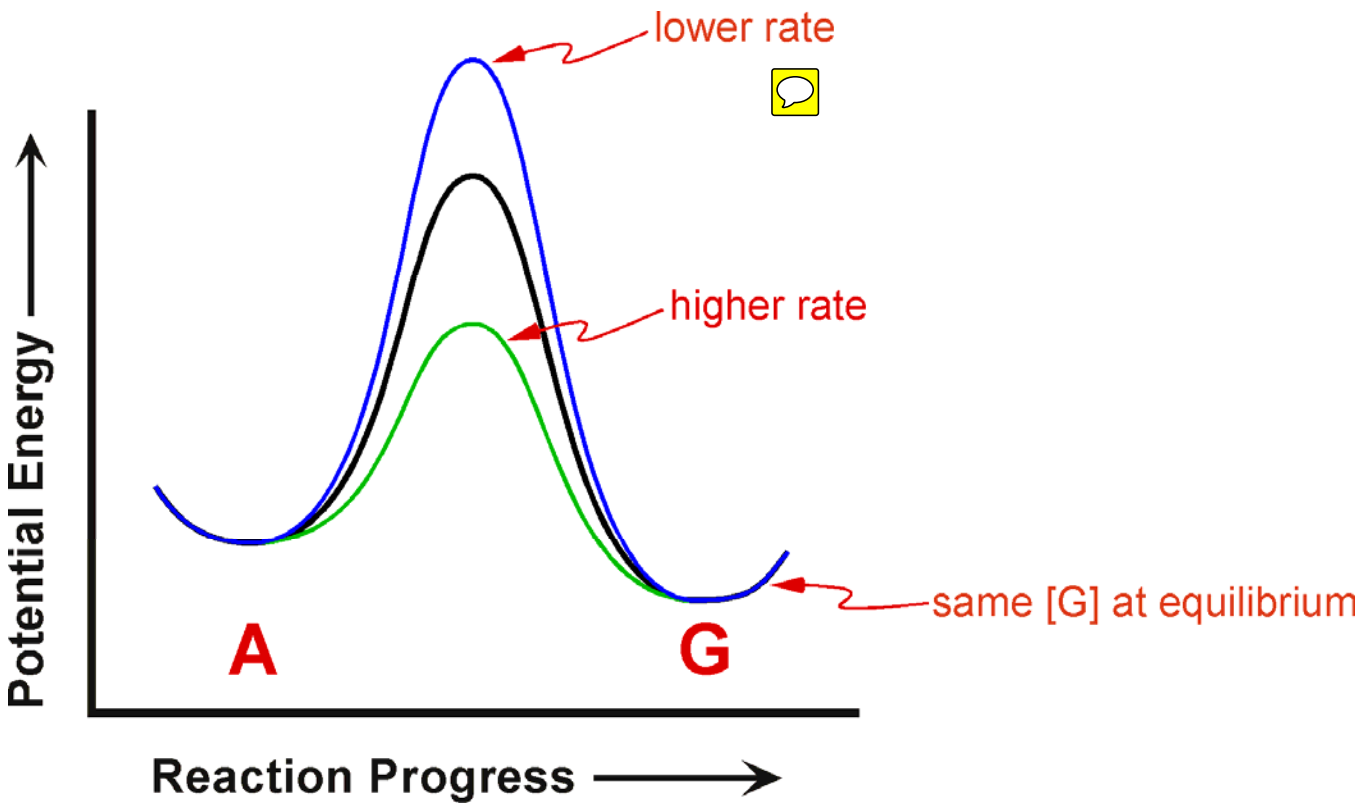


(2) What is the equilibrium position?



Preface

(3) How fast is the reaction?



Preface

Why we measure rates:

(1) predict/control reactions:
- industrial syntheses
- environmental reactions (e.g., smog formation, ozone layer breakdown)

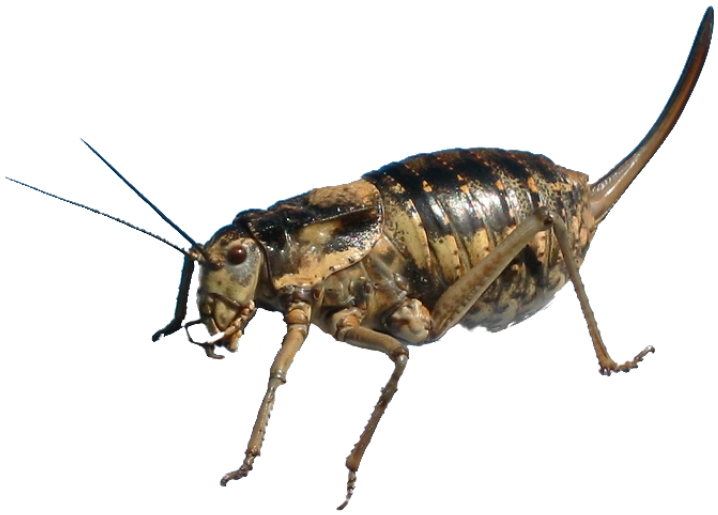
(2) monitor biological or chemical systems:
- clinical diagnostics (e.g. liver damage)
- polymerization (e.g. length and composition of polymers)

Preface

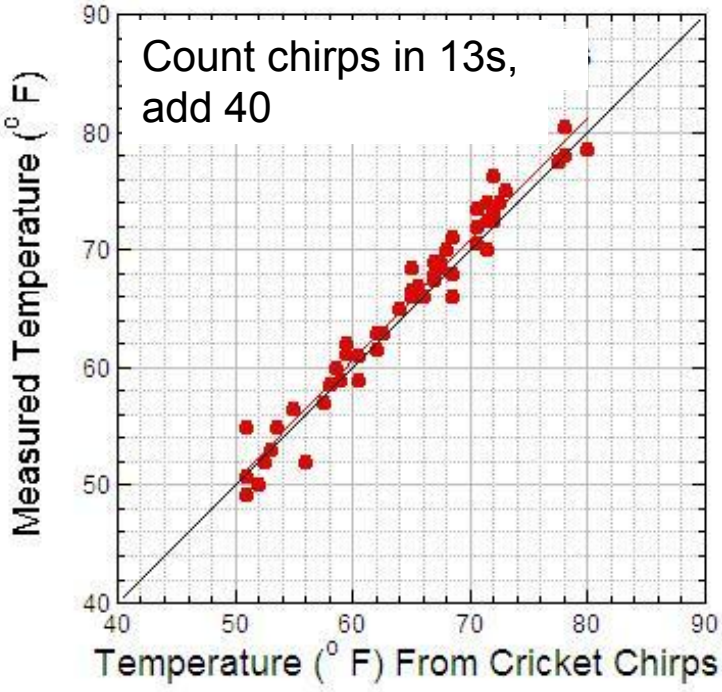
(3) understand reaction mechanisms:

- reaction order shows if a reaction is S_N1 or S_N2
- build general structure/function relationships, such as rate vs. leaving group ability in S_N2 reactions.

(4) tell the temperature by measuring the rate of crickets chirping:



http://www.snopes.com/science/cricket.asp



14-1. The rate of a chemical reaction

- **Rate** = change in concentration of reactants and products over time

- e.g.,

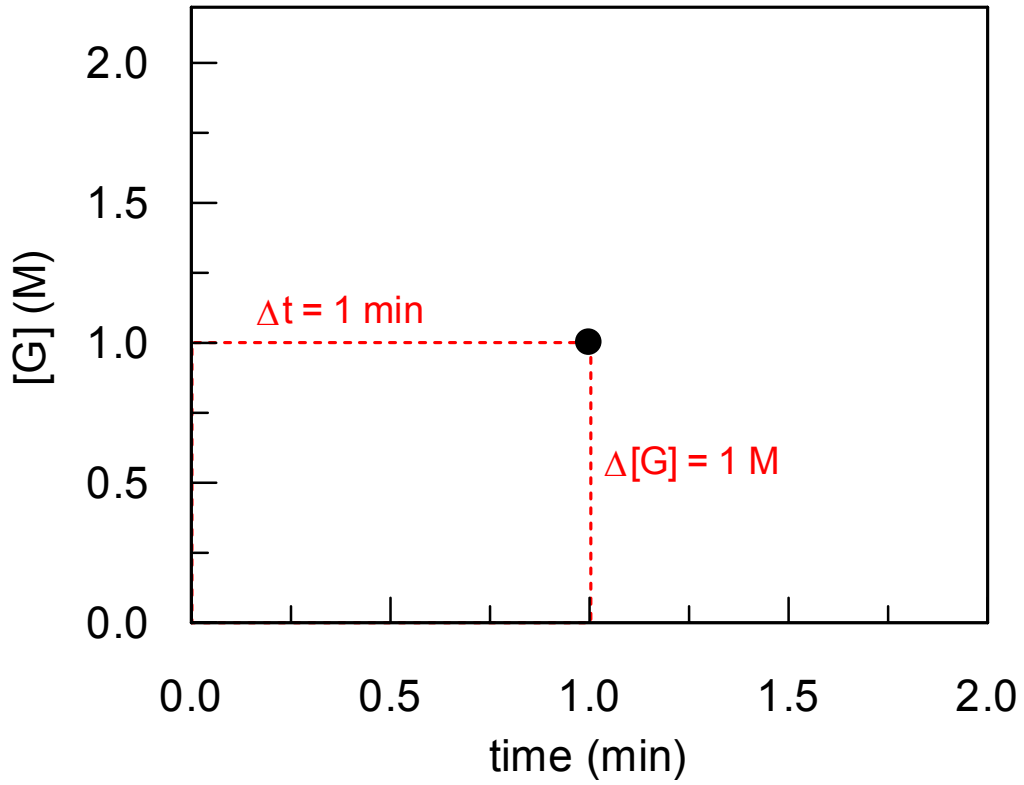
(**1**)

- 1 min after starting reaction, [G] = 1 M

- What is the rate of the reaction over 1 min?

14-1. The rate of a chemical reaction

A → G



- **average rate =**

14-1. The rate of a chemical reaction

- For A → G

$$\text{average rate} = \frac{\Delta[\text{G}]}{\Delta t} \qquad (2)$$

- rates are always positive, so add a negative sign if using decrease of starting material to describe rate:

$$\text{average rate} = \qquad (3)$$

- stoichiometry is important: if $\text{A} \rightarrow 2\text{G}$ (4)

$$\text{average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = \qquad (5)$$

14-1. The rate of a chemical reaction

- In general:

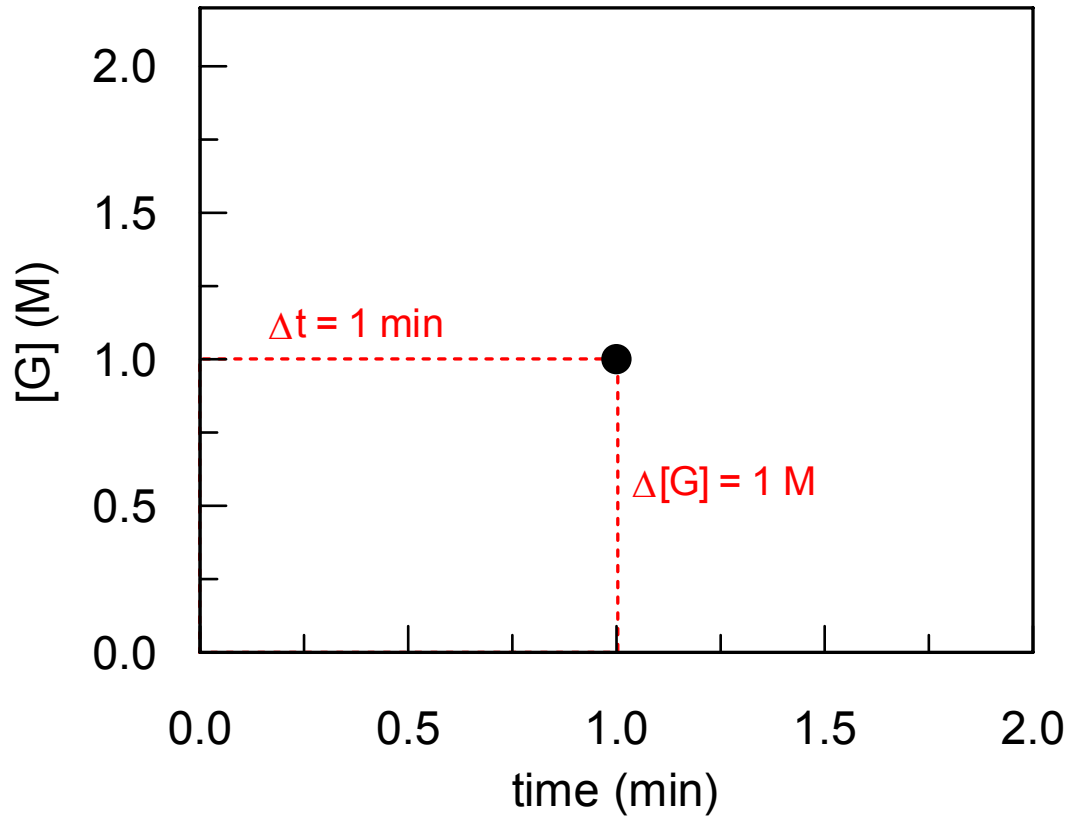
$$aA + bB \rightarrow gG + hH \qquad (\mathbf{6})$$

$$\text{average rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = \qquad (\mathbf{7}, 14.2)$$

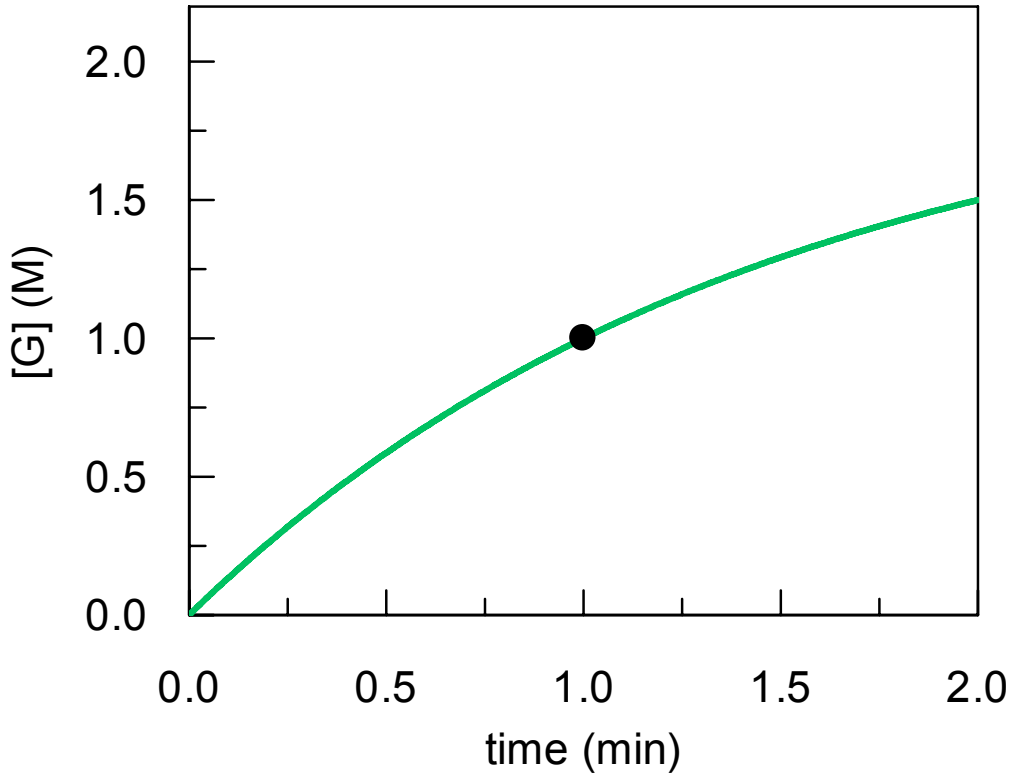
- **Key concepts:**
  - rate is change in
  - rates are always
  - stoichiometry

14-2. Measuring reaction rates

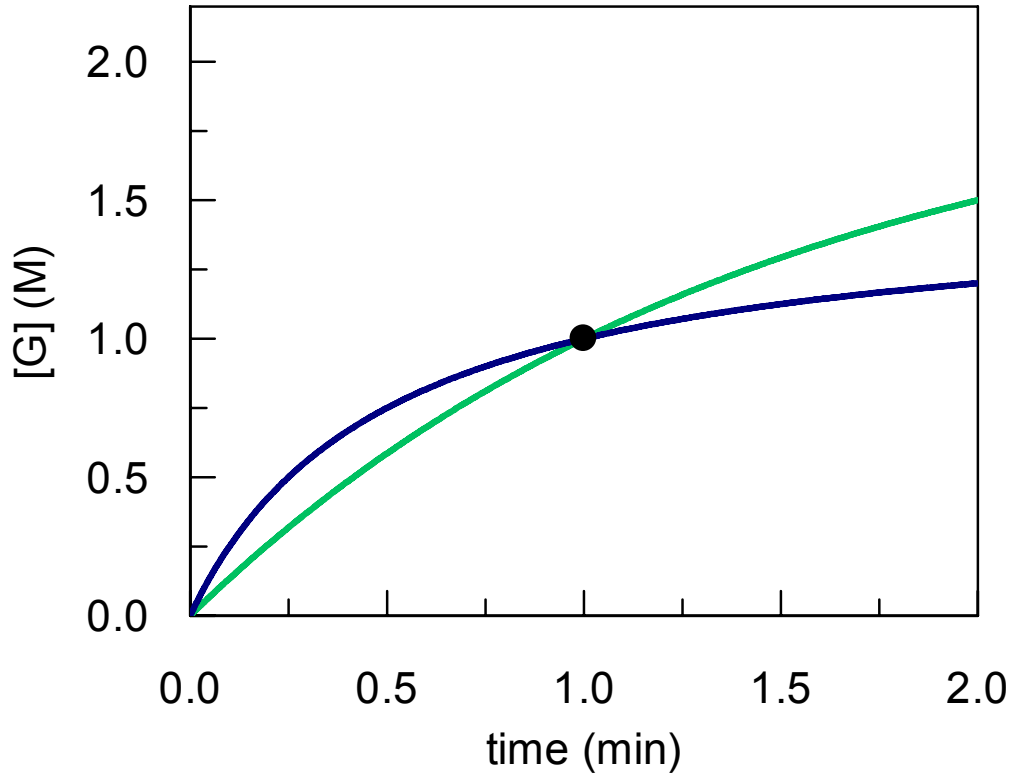
- Rates can change during a reaction
- Many reactions may give an *average rate* of 1 M/min for 1 min.



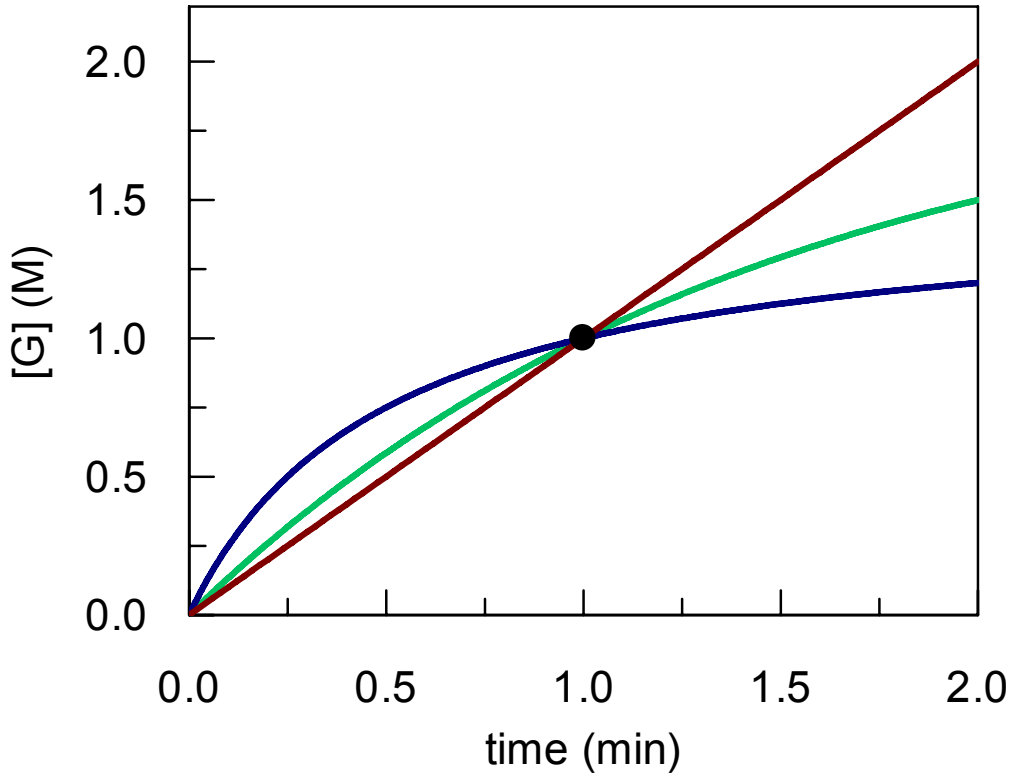
14-2. Measuring reaction rates



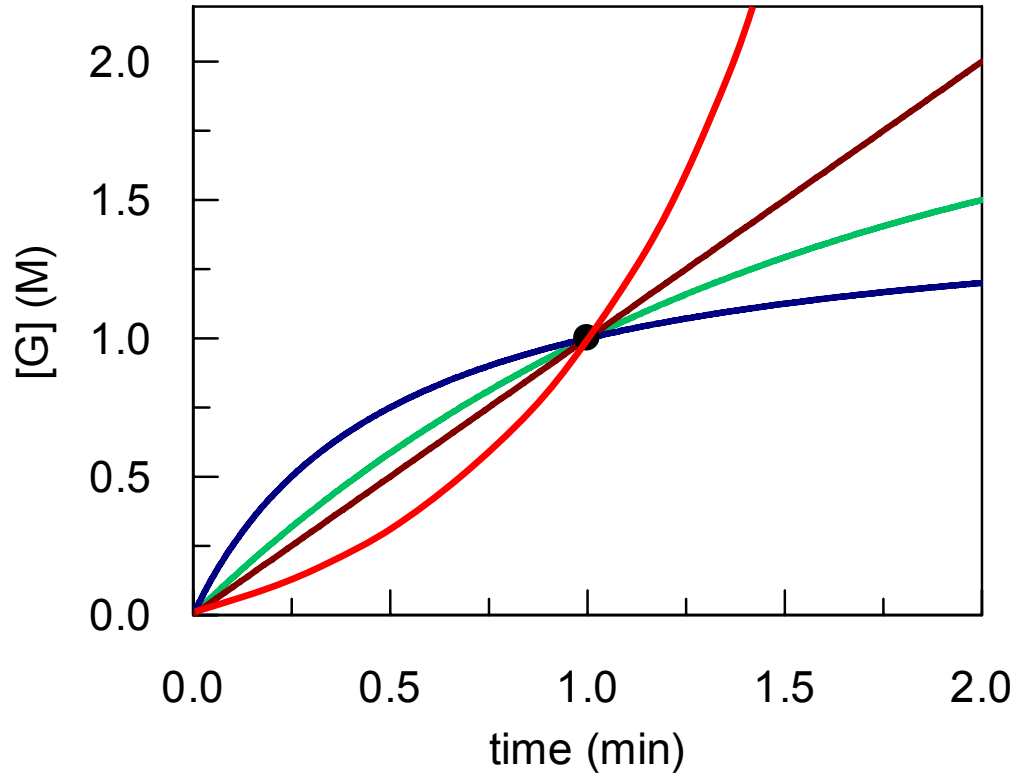
14-2. Measuring reaction rates



14-2. Measuring reaction rates



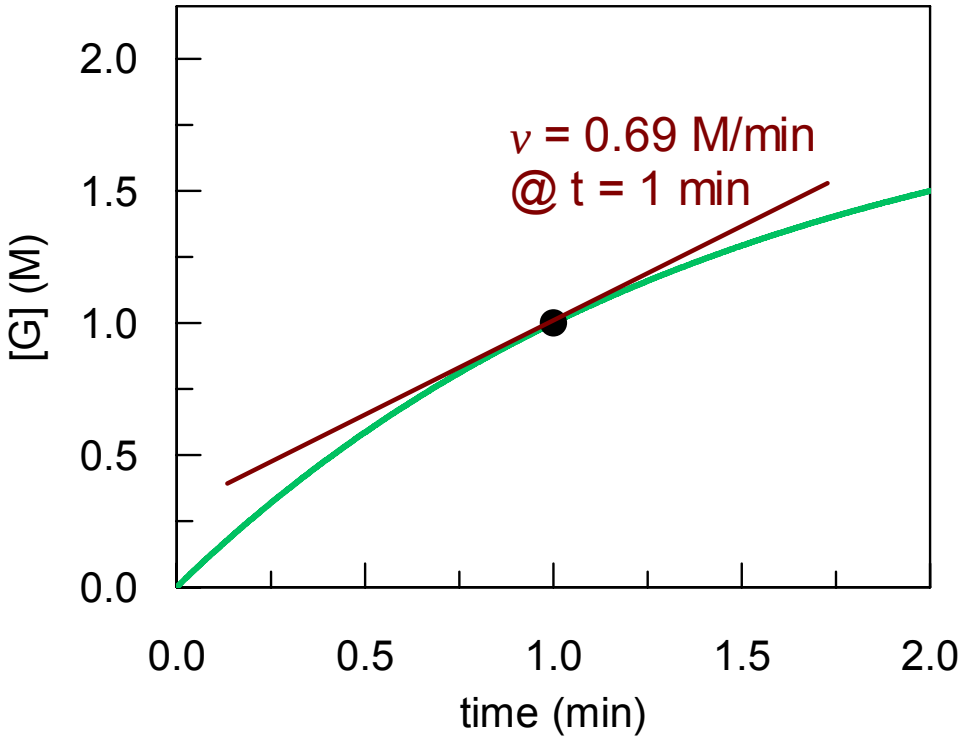
14-2. Measuring reaction rates



- average rate = 1 M/min over first min for *all* 4 curves
- average rates are of limited use - prefer instantaneous rates

14-2. Measuring reaction rates

- **instantaneous rate (*v*)*:***
- ***v*** = the slope of the



note that "*v*" is the italicized letter *vee*, not the Greek letter nu. "*v*" comes from *velocity*, another common term for rate. Petrucci writes out "rate of reaction".

14-2. Measuring reaction rates

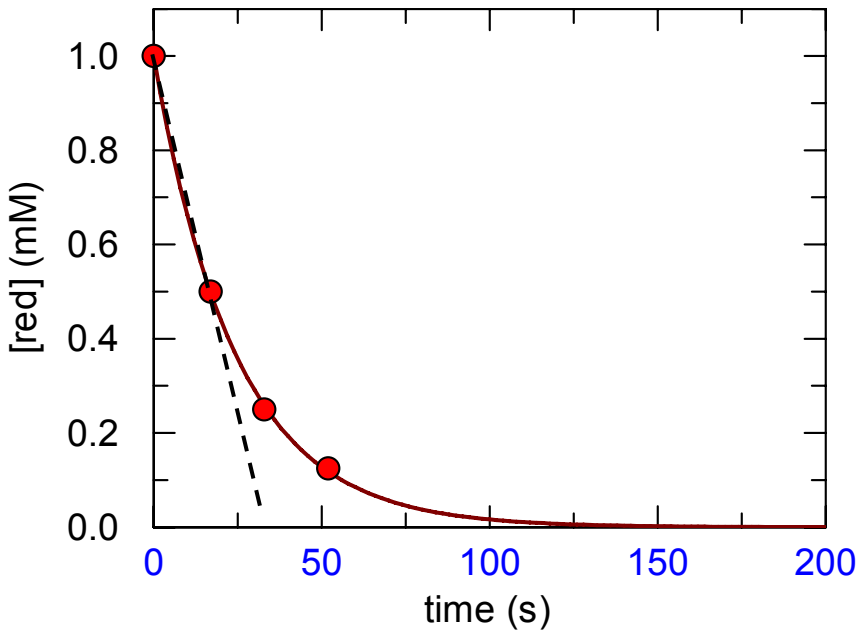
- measuring Δ[A] or Δ[G] over a finite time interval, Δt, gives the *average rate* for that interval (e.g., 1 M/min)
- we would prefer the *instantaneous rate*, v, at time = t. This is equivalent to the average rate over an infinitely short time interval about t (e.g., 0.69 M/min).
- taking an infinitely short time interval is the same as differentiating an equation in calculus.
- $$\text{average rate} = \frac{1}{g}\frac{\Delta[\text{G}]}{\Delta \text{t}} \qquad (\mathbf{7}, 14.2)$$
- $v =$  (8)

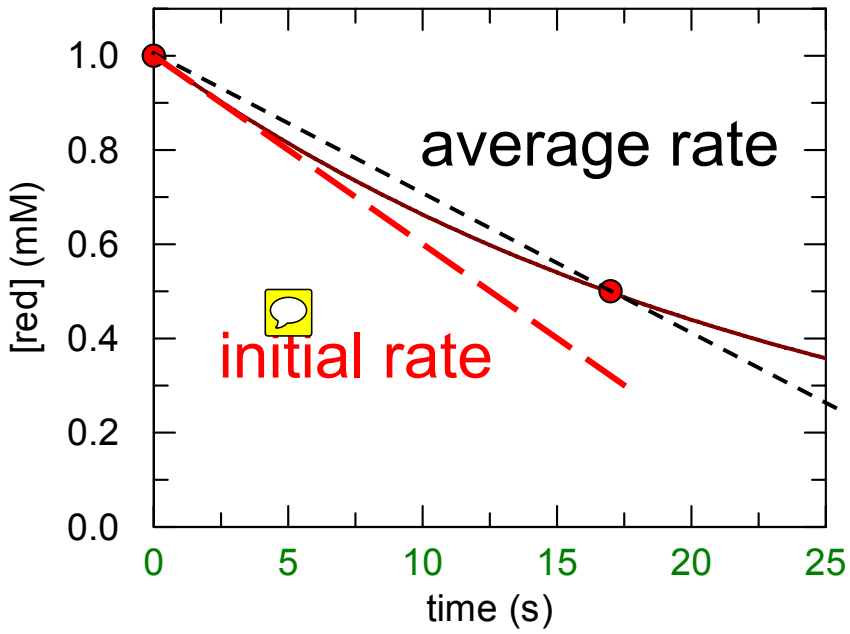
Average vs instantaneous and initial rates

- Experimentally measured rates are <u>always</u> average rates
- To best approximate instantaneous rates, we measure Δ[A] or Δ[G] over the smallest possible Δt
- We ideally get instantaneous rates at t = 0. To get such *initial rates*, we have to measure Δ[G] very close to t = 0
- At t = 0 reactions are uni-directional and do not suffer from product inhibition – best place to study their mechanism
- The resulting *initial rate*, $\boldsymbol{v_0}$ can reveal much about the reaction mechanism

Average vs. initial rate

- Sample experiment – decay of red coloured reactant:





14-2. Measuring reaction rates

Key concepts:

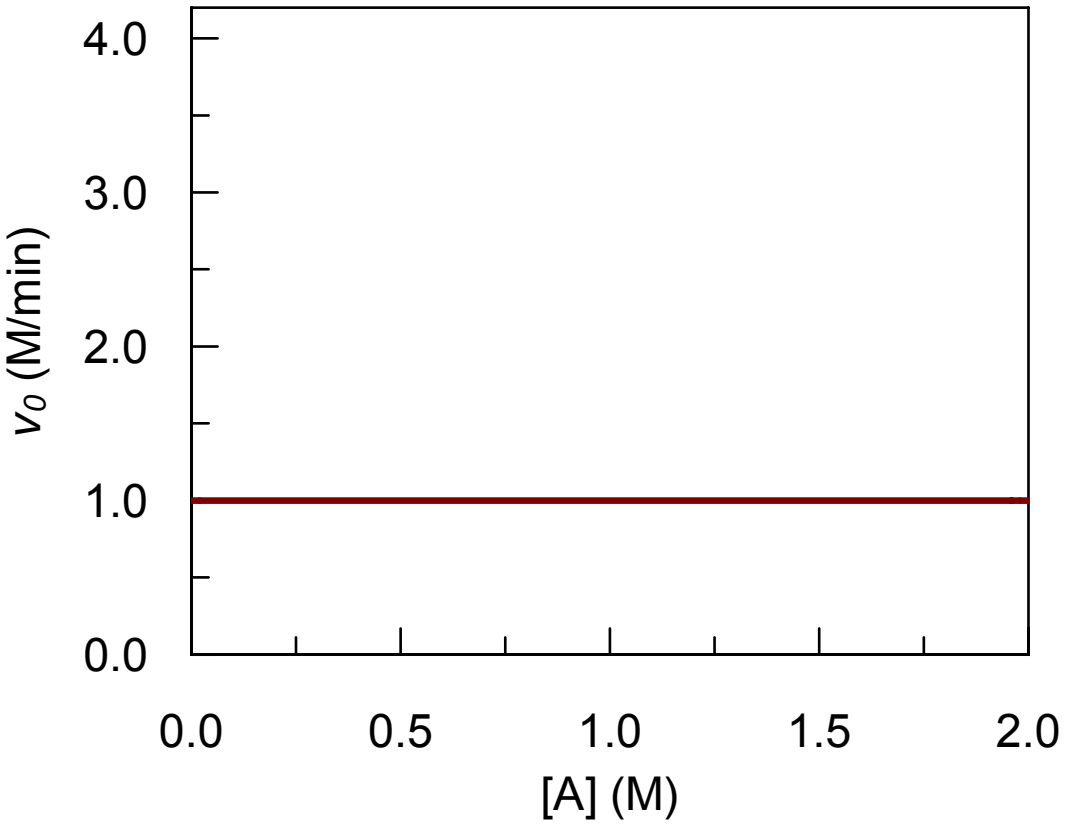
- want to know
- experimental rates are
- to approach initial rates experimentally, use short

iClicker Question #1

iClicker Question #2

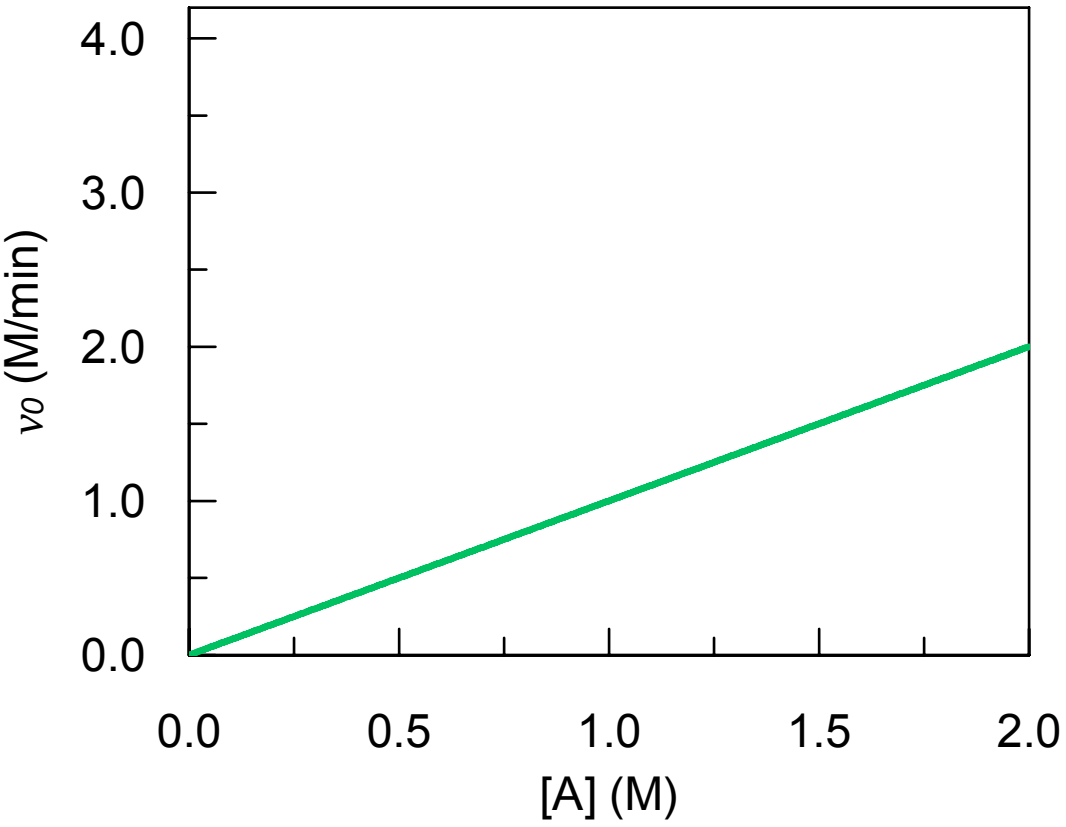
14-3. Effect of concentration on reaction rates: The rate law

- v_0 may be independent of [A]: $v_0 \propto [A]^0$



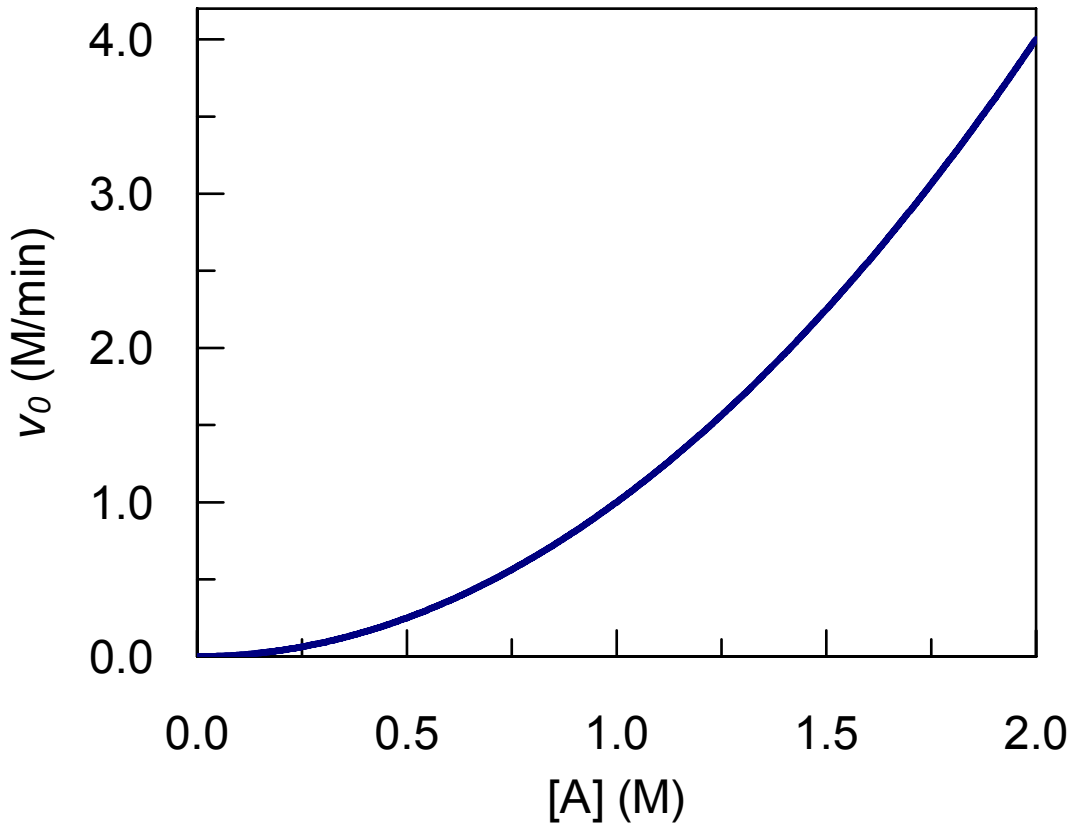
14-3. Effect of concentration on reaction rates: The rate law

- v_0 may increase linearly with [A]: $v_0 \propto$ [A]



14-3. Effect of concentration on reaction rates: The rate law

- v_0 may increase with the square of [A]: $v_0 \propto$ [A]^2



14-3. Effect of concentration on reaction rates: The rate law

- For any given reaction $aA + bB \rightarrow gG + hH$ (**6**, 14.5)

  the dependence of v_0 on [A] and [B] reflects its mechanism.

- The **rate law,** or **rate equation,** describes this relationship between rate and concentration for each reaction:

  $$v_0 = k[A]^m[B]^n \qquad (\mathbf{9}, 14.6)$$

  m & n = reaction orders with regard to A and B.

  m & n are not necessarily equal to a and b, the stoichiometric coefficients.

14-3. Effect of concentration on reaction rates: The rate law

$$v_0 = k[\mathrm{A}]^m[\mathrm{B}]^n \qquad (\mathbf{9}, 14.6)$$

- *m* & *n*
  - determined
  - usually small, positive integers
  - *may be*
- overall order of a reaction is (*m* + *n*), while
  - *m* is the order of the reaction with regard to A, and
  - *n* is the order of the reaction with regard to B.

14-3. Effect of concentration on reaction rates: The rate law

- We determine *m* and *n* through the method of initial rates: measure v_0 at different $[A]_0$ and $[B]_0$, and extract *m* and *n*.

  Reactions may be:

  Zero-order $m, n = 0$, no effect of [A] or [B]

  First-order $m = 1$, $v_0 \propto [A]$

  Second-order $(m + n) = 2$, $v_0 \propto [A]^2$ or [A][B]

- once *m* & *n* are known, you can solve from the rate law v_0 for the **rate constant, *k***

- ***k*** is a fundamental property of each reaction. It depends on temperature, catalyst, solvent, but not on [A] and [B].

Method of Initial Rates

- For a reaction: 2A + B → C + D

  $v_0 = k[A]^m[B]^n$ → what are m and n?

- Set up three reactions:

exp	$[A]_0$	$[B]_0$	v_0
1			
2			
3			

- Extract m and n from ratios of $v_{0(\text{exp 2})}$ / $v_{0\ (\text{exp 1})}$:

- $v_o(2)/v_o(1) = k(2M)^m(1M)^n / k(1M)^m(1M)^n = 2^m = 4$ → m = 2
- $v_o(3)/v_o(1) = k(1M)^m(2M)^n / k(1M)^m(1M)^n = 2^n = 1$ → n = 0
- Overall reaction order =

14-3. Effect of concentration on reaction rates: The rate law

- The order of the reaction tells us how many species are present in the rate-limiting step of the reaction

- This information helps us determine reaction mechanisms

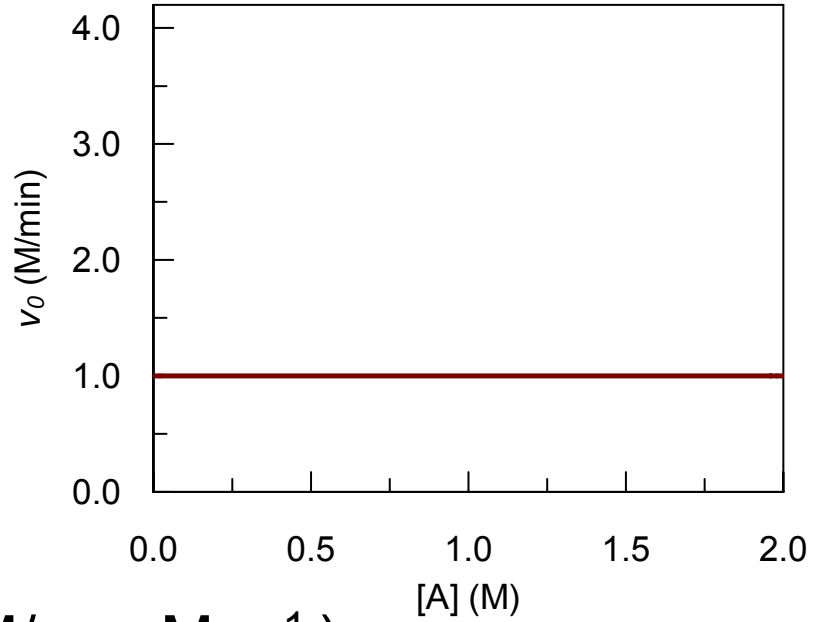
- **Key concepts:**
  - order
  - order is determined
  - order = number of species

iClicker Question #3

14-4. Zero-order reactions

- v_0 is independent of [A]

$$v_0 = k\,[\mathrm{A}]^0 \;=\; k \;=\; \text{constant} \qquad (\mathbf{13},14.9)$$



Concept check:

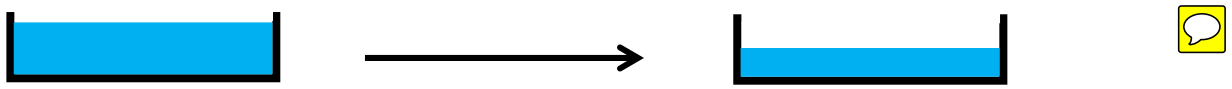
What are the units of k for a zero-order reaction?

Recall that units for v are always concentration/time (e.g., M/s or M•s^{-1})

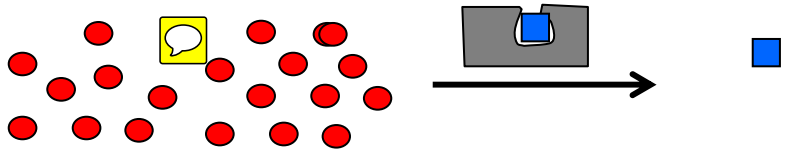
→

14-4. Zero-order reactions: Examples

- Zero-order processes:
  - evaporation / sublimation with constant surface area



- Pseudo zero-order reactions:
  - reactions where catalyst or enzyme is saturated with reactants (e.g., drug/alcohol metabolism)



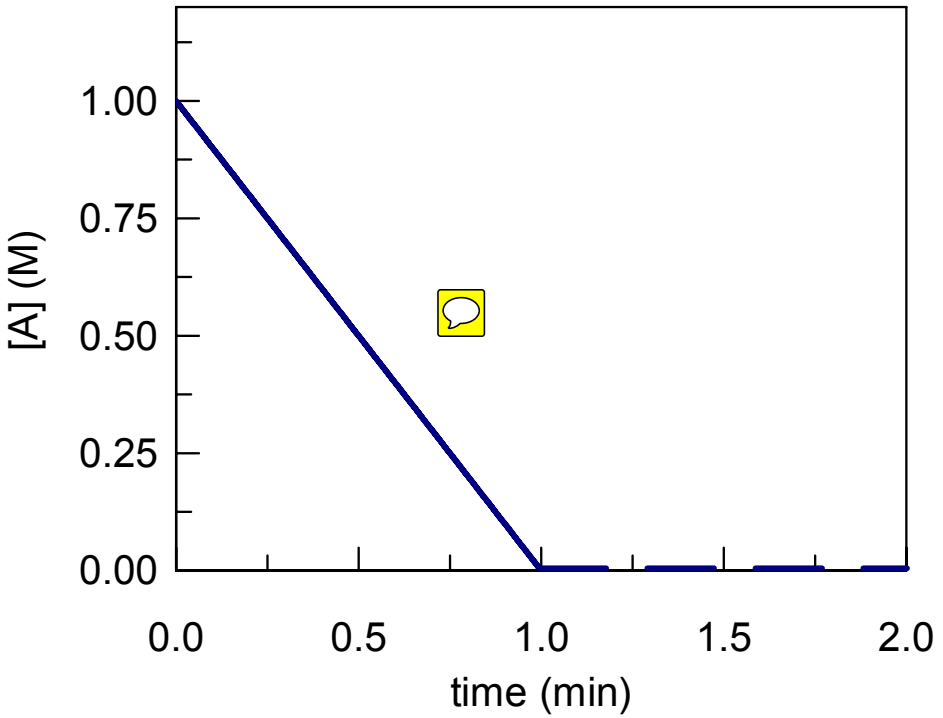
Key concepts:

- rate =
- true zero-order reactions are

14-4. Zero-order reactions: Integrated rate law

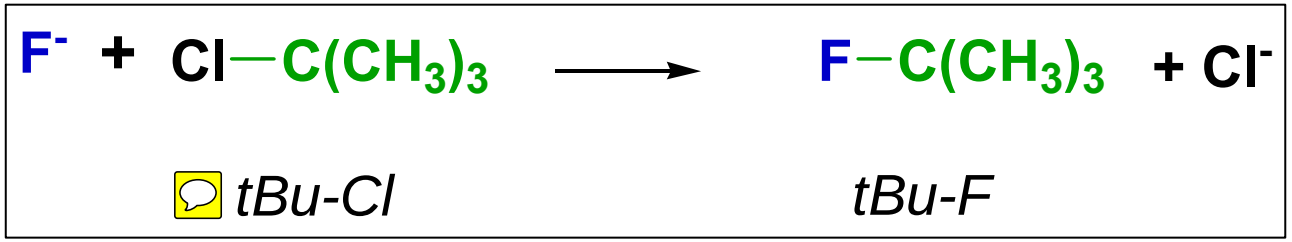
- $v_0 = k$ or $-d[\mathrm{A}]/dt = k$
- the integrated version of this rate law is:

$[\mathrm{A}]_t =$ (**14**, 14.10)

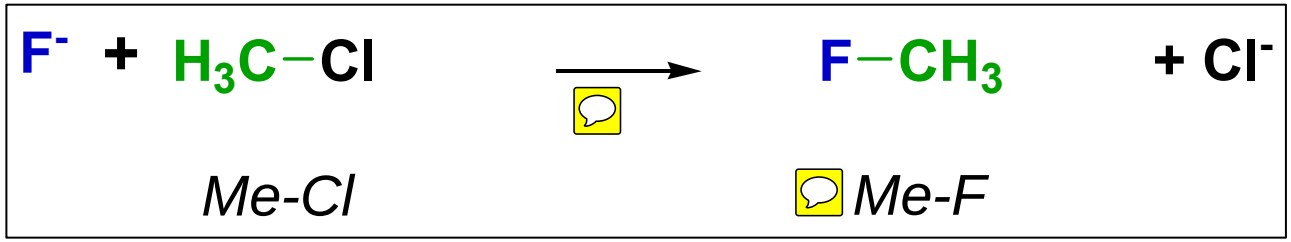


Reaction orders in nucleophilic substitutions

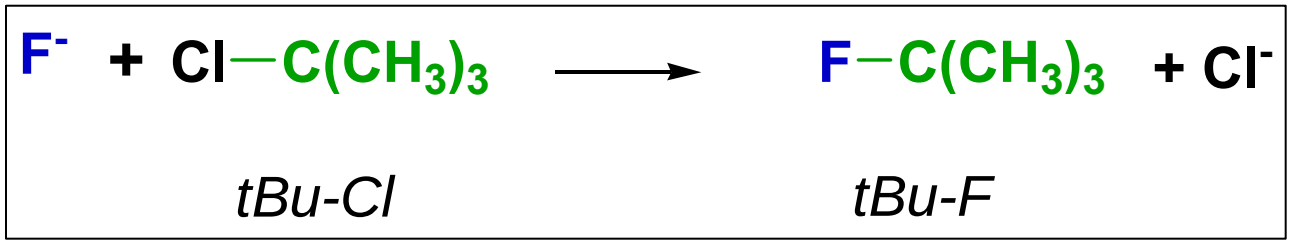
- nucleophilic substitution: an electronegative atom or group bonded to a carbon atom is replaced by another. (see more in the Organic Chemistry unit)
- nucleophilic substitutions can be first order or second order overall, depending on chemical structure.
- e.g.:
- First order



- Second Order



14-5. First-order reactions

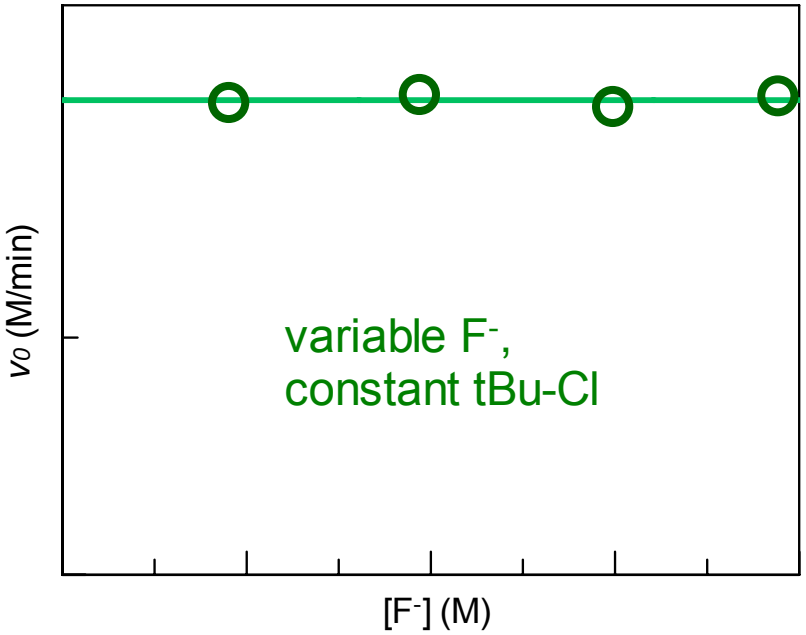


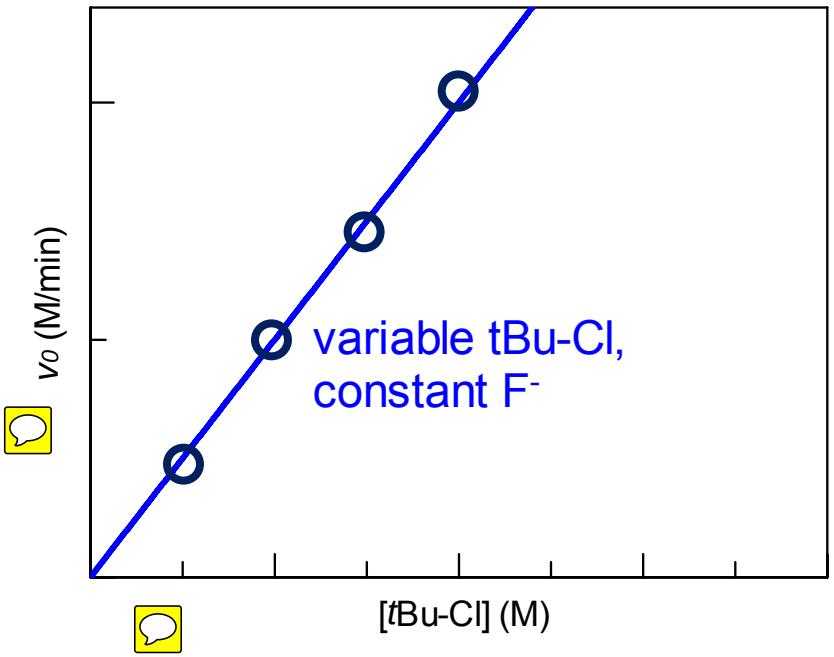
- Experiments have shown that the above reaction of F^- with *t*Bu-Cl is first order in *t*Bu-Cl, i.e. that $v_0 \propto$ [*t*Bu-Cl]

- What were these experiments?
- Measurement of v_0 at different [*t*Bu-Cl], [F^-] (method of initial rates), and checking the dependence of v_0 on [A], [B]:

exp	[F^-]	[Cl-$C(CH_3)_3$)]	initial rate, M/s
1			
2			
3			

14-5. First-order reactions

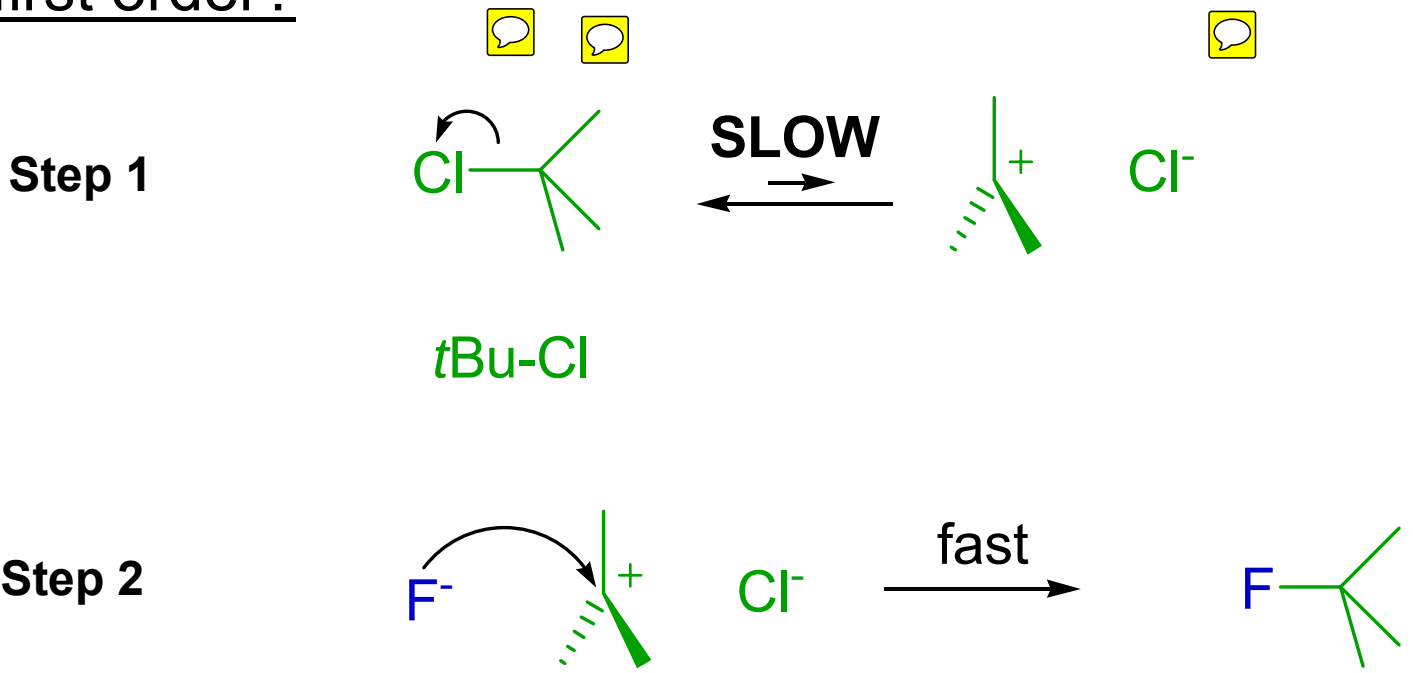




- reaction order w.r.t. *t*Bu-Cl?
  F^-?
- overall reaction order?
- rate equation?

14-5. First-order reactions

Why first order?



- Step 1: slow C-Cl bond cleavage to form carbocation
- Step 2: fast attack of F^- on carbocation

  → overall rate controlled by Step 1: C-Cl bond cleavage

14-5. First-order reactions

- F^- does not enter until <u>after</u> the rate-limiting step, hence no effect from $[F^-]$

- <u>one</u> molecule in the rate-limiting step, hence 1st-order

$$v_0 = k[A] \qquad (\mathbf{10}, 14.12)$$

- reaction is called $\mathbf{S_N1}$:
  - **S** =
  - **N** =
  - **1** =

Concept check:

What are the units of k for a first-order reaction?

– units for k are

Recall the characteristics of $\boldsymbol{k}$:

(1) constant regardless of concentration

(2) depends on the identity of the reactants, temperature, catalyst, solvent

14-5. First-order reactions

- Integrated rate law for first-order reactions
  - rate equation gives v at every instant
  - integrating v *vs.* time gives [A] consumed (or [G] formed)
  - integrate $d[\mathrm{A}]/dt$ with respect to time:

$$ln\frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad \ln[A]_t = \qquad (\mathbf{11}, 14.13)$$

  - ln[A] is unitless, so kt is unitless

- rearrange eq. **11** (apply exponential):

$$[A]_t = \qquad (\mathbf{11a})$$

(integration is shown on p. 613 of the text)

Practice Problem

- A reaction is 75% complete in 25 s. What is the rate constant for this reaction?

14-5. First-order reactions: Half-Lives $t_{1/2}$

First order reactions have constant half-lives, or $t_{1/2}$

this means: $[A]_t = ½ \bullet [A]_0$ at $t_{1/2}$

substitute this into $[A]_t = [A]_0 \bullet e^{-kt}$ (11a)

to obtain:

Apply *ln* and rearrange to get:

and

$$t_{1/2} = = \frac{\ln 2}{k} = \frac{0.693}{k}$$ (**12**, 14.14)

14-5. First-order reactions: Half-Lives $t_{1/2}$

- Reactions involving gases
  - same as solution reactions, but use partial pressures (P_A) in place of [A], e.g.:

$$ln\frac{(P_A)_t}{(P_A)_0} = -kt$$

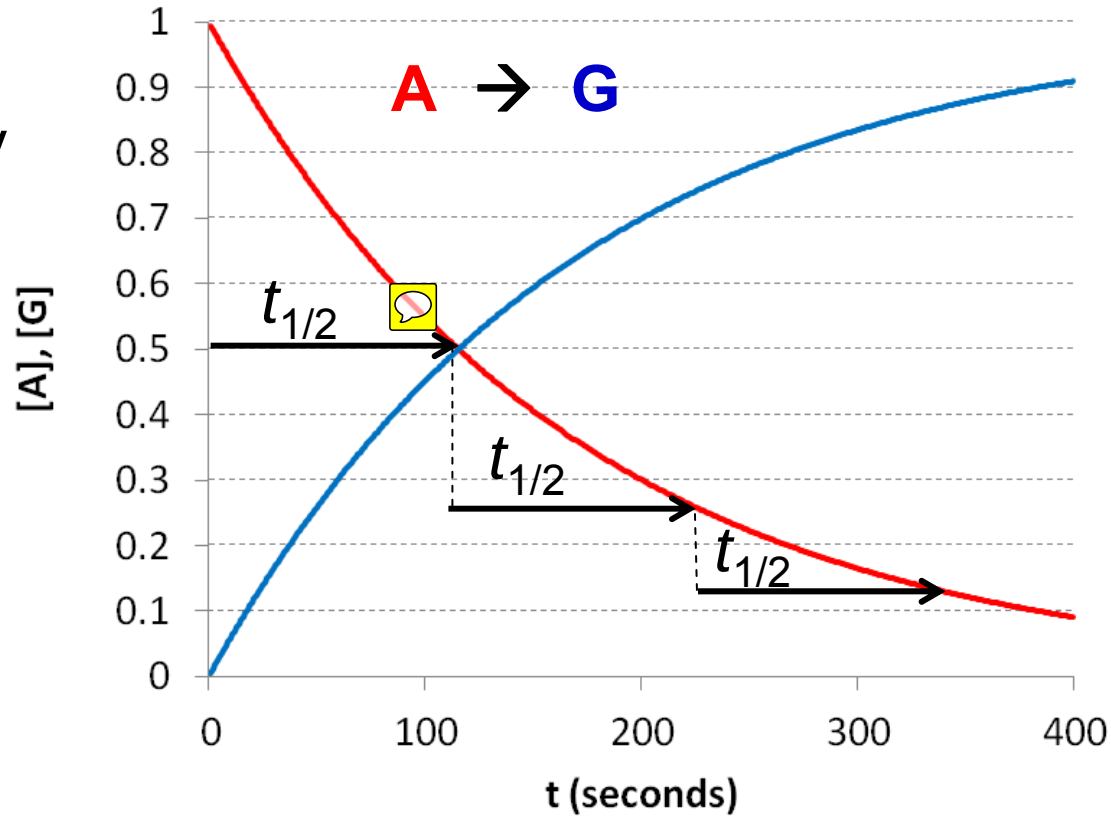
(**11b**, 14.15)

Take-Home Practice Problem

A reaction has a rate constant of $k = 0.0138\ s^{-1}$. What is the reaction's half-life, in hours?

14-5. First-order reactions

- Examples:
  (1) radioactive decay
  (2) S_N1

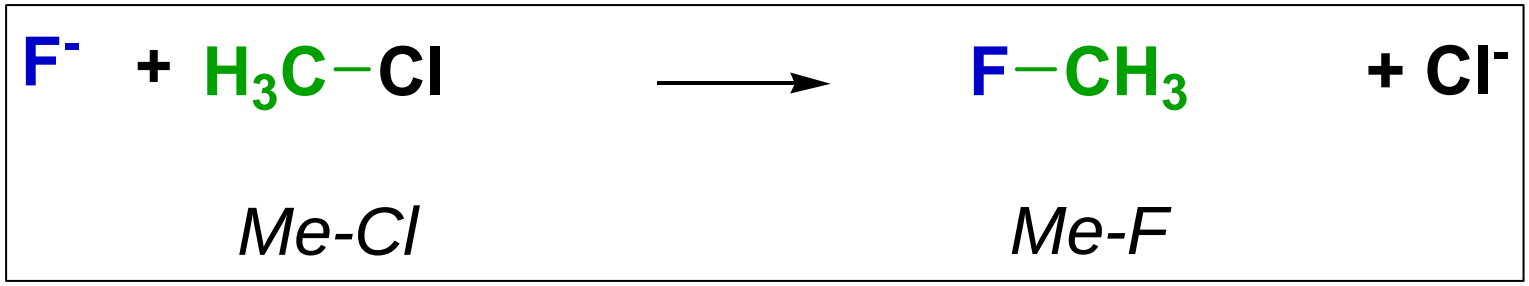


- **Key Concepts:**
  - $v_0 \propto$
  - $t_{1/2}$ =
  - rate and

14-6. Second-order reactions

A second-order reaction:

- S_N2 nucleophilic substitution



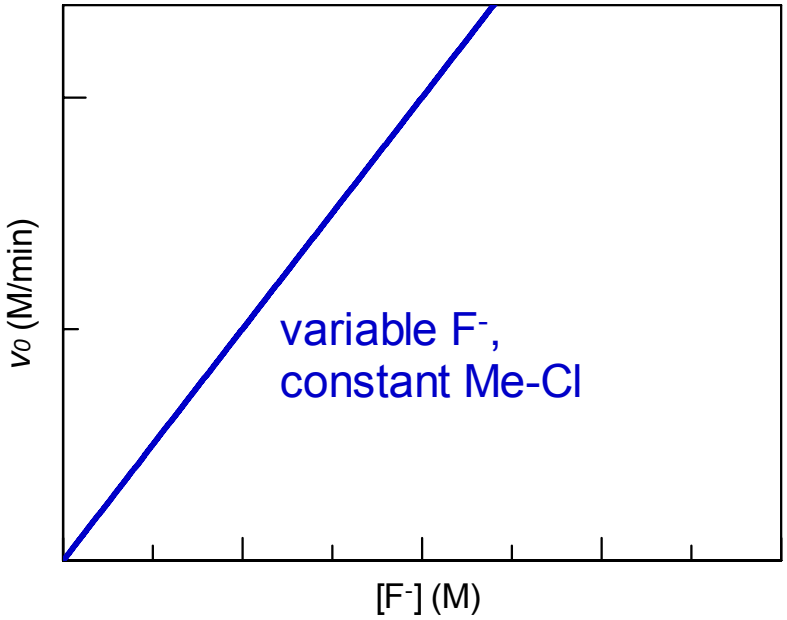
- **S_N2**:

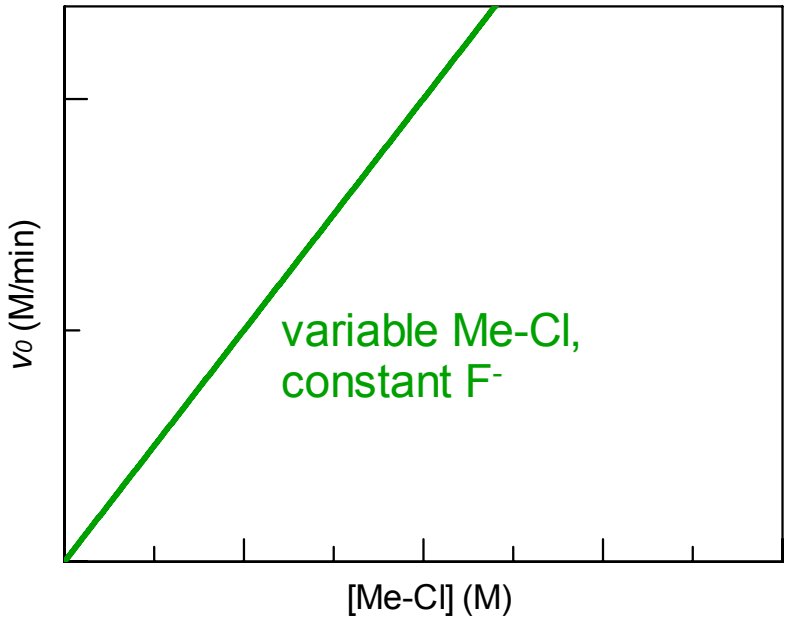
  S =

  N =

  2 =

14-6. Second-order reactions

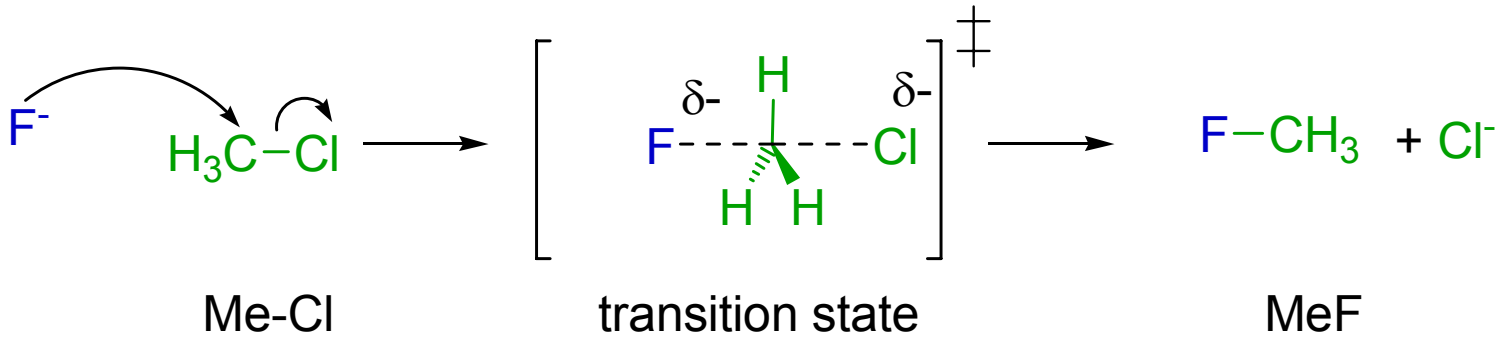




- reaction order w.r.t. Me-Cl?
  F^-?
- overall reaction order?
- rate equation?

14-6. Second-order reactions

- Why second order?
  - *single concerted step* with both reactants present at rate-limiting step



- rate depends on the presence of *both* reactants

$$v_0 = k[F^-][\text{Me-Cl}] \qquad (15)$$

14-6. Second-order reactions

$$v_0 = k[F^-][\text{Me-Cl}] \qquad (\mathbf{15})$$

- units for v are concentration/time (e.g., M/s)
- units of $[F^-]$ and [Me-Cl] are concentration (e.g., M)

Concept check:

What are the units of k for a second-order reaction?

- units for k are

14-6. Second-order reactions

- example from the textbook:

  $2A \rightarrow$ products (**16**)

- where:

  v_0 = (**17**, 14.17)

- S_N2 example:

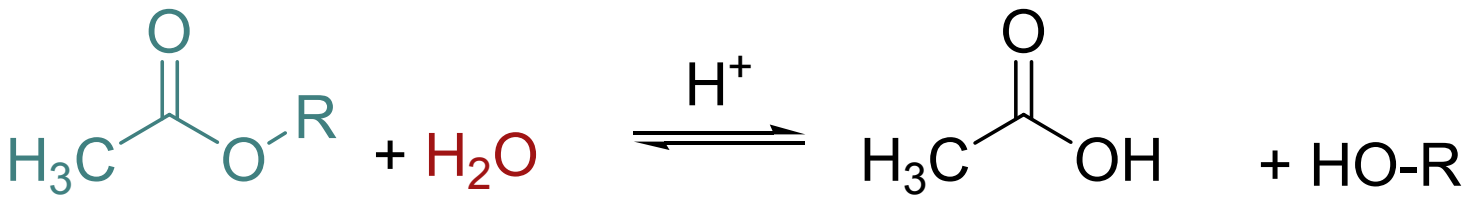
  $A + B \rightarrow$ products,

- where:

  v_0 = (**17a**)

Preview: ester hydrolysis

- Esters are synthesized from carboxylic acids and alcohols (see more in Organic Chemistry unit)
- Esters are broken down by hydrolysis
- Reversible reaction; equilibrium position is determined by Le Châtelier's principle:

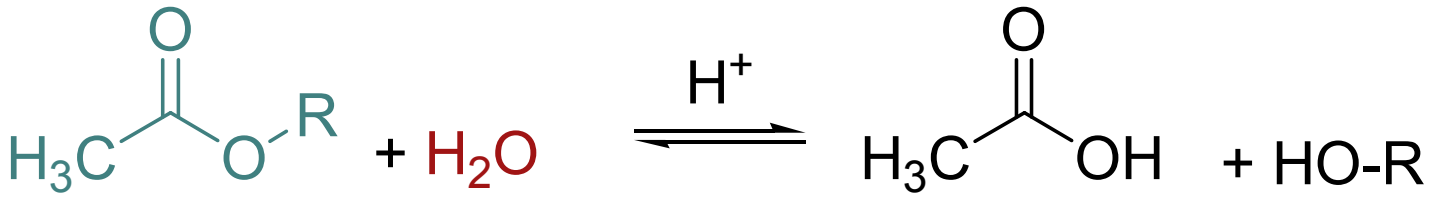


ester carboxylic acid alcohol

14-6. Second-order reactions

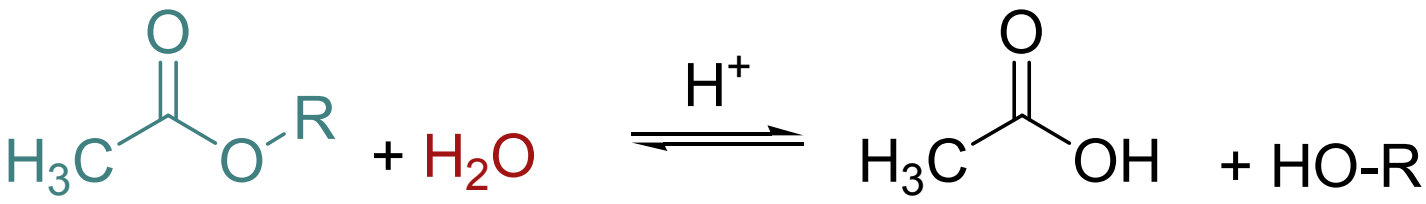
- Stoichiometric ester hydrolysis is a 2nd-order reaction which becomes very slow as the reactants are depleted

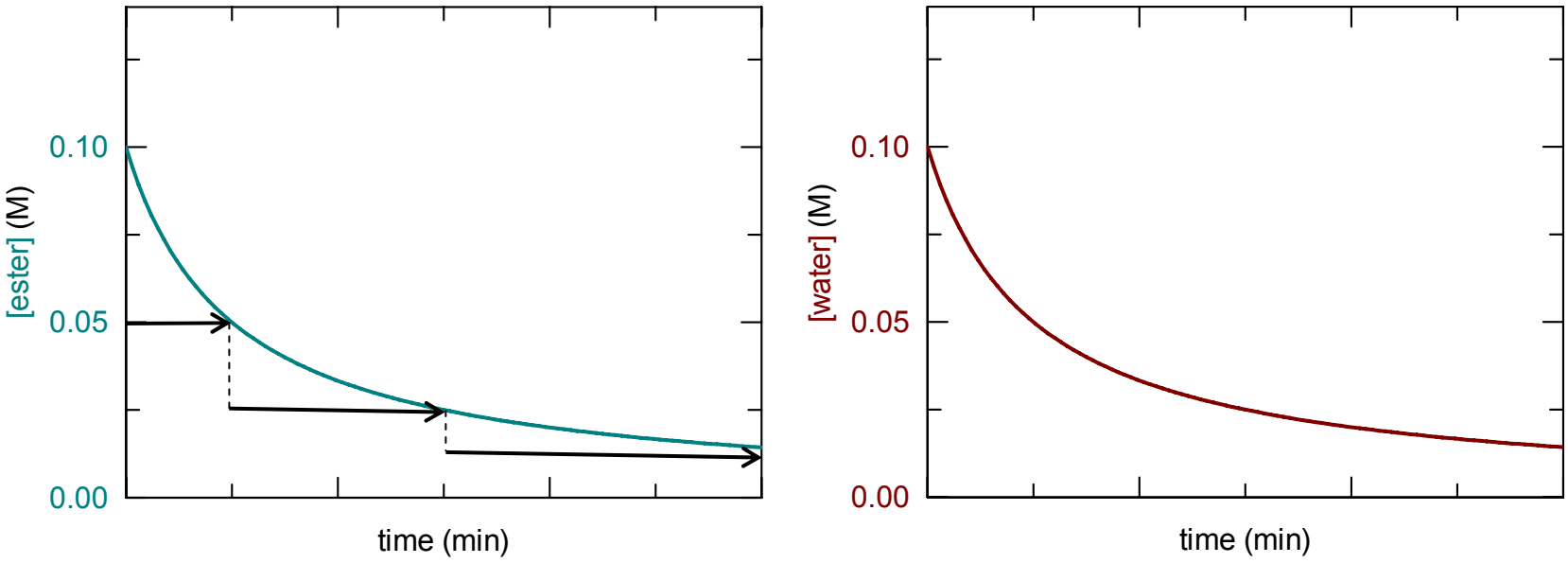
- e.g.:



14-6. Second-order reactions

- e.g., reaction of 0.1 M ester and 0.1 M H_2O in acetone:





Note: these calculations consider only the forward reaction

14-6. Second-order reactions

Turn 2nd Order Reactions into Pseudo 1st Order Reactions:

- Run ester hydrolysis reaction in dilute aqueous acid.
- Now the change in [H_2O] is negligible, and the reaction behaves like a 1st-order irreversible reaction:

$$v = k[\text{ester}]$$

	[ester]	[H_2O]	[AcOH]	[HO-R]
initial	0.1 M	55.5 M	0 M	0 M
final				

14-6. Second-order reactions

- **Key concepts:**
  - rate depends on
  - make pseudo-1st order with

iClicker Question #4

14-7. Reaction kinetics: A summary

Things you can calculate:

(1) v_0 when the rate law is known:

$v_0 = k[A]^m[B]^n...$

(2) Instantaneous rate (v) from:

(*i*) tangent to line in graph of [A] vs. t,

(*ii*) $-\Delta[A]/\Delta t$ (average rate) for short Δt

(*iii*) rate law

(3) Order of reaction from:

(*i*) v_0 vs. concentration

(*ii*) graph that gives a straight line

(*iii*) constant $t_{1/2}$ (1^{st}-order)

(*iv*) integrated rate law which gives a constant k

14-7. Reaction kinetics: A summary

Things you can calculate:

(4) k from:

(*i*) slope of line in an appropriate graph

(*ii*) the appropriate integrated rate law

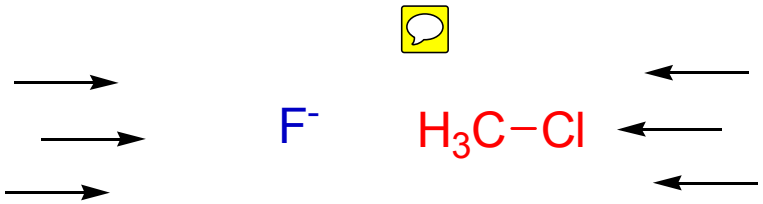
(*iii*) $t_{1/2}$ (1^{st}-order)

(5) $[A]_t$ and $[G]_t$ from k and $[A]_0$, using the integrated rate law

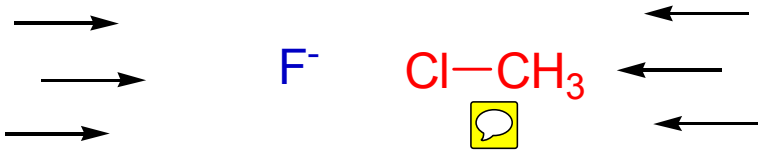
14-8. Theoretical models of chemical kinetics

Collision theory

- While molecules can collide at high frequency (~ 10^{30}/s),
- only very few (~10^{-4} M^{-1}•s^{-1}) have enough energy to react.
- reactions are slow because they require transfer of kinetic energy into the reacting bonds, and
- molecules must be correctly oriented to be able to react



reaction possible



no reaction

14-8. Theoretical models of chemical kinetics

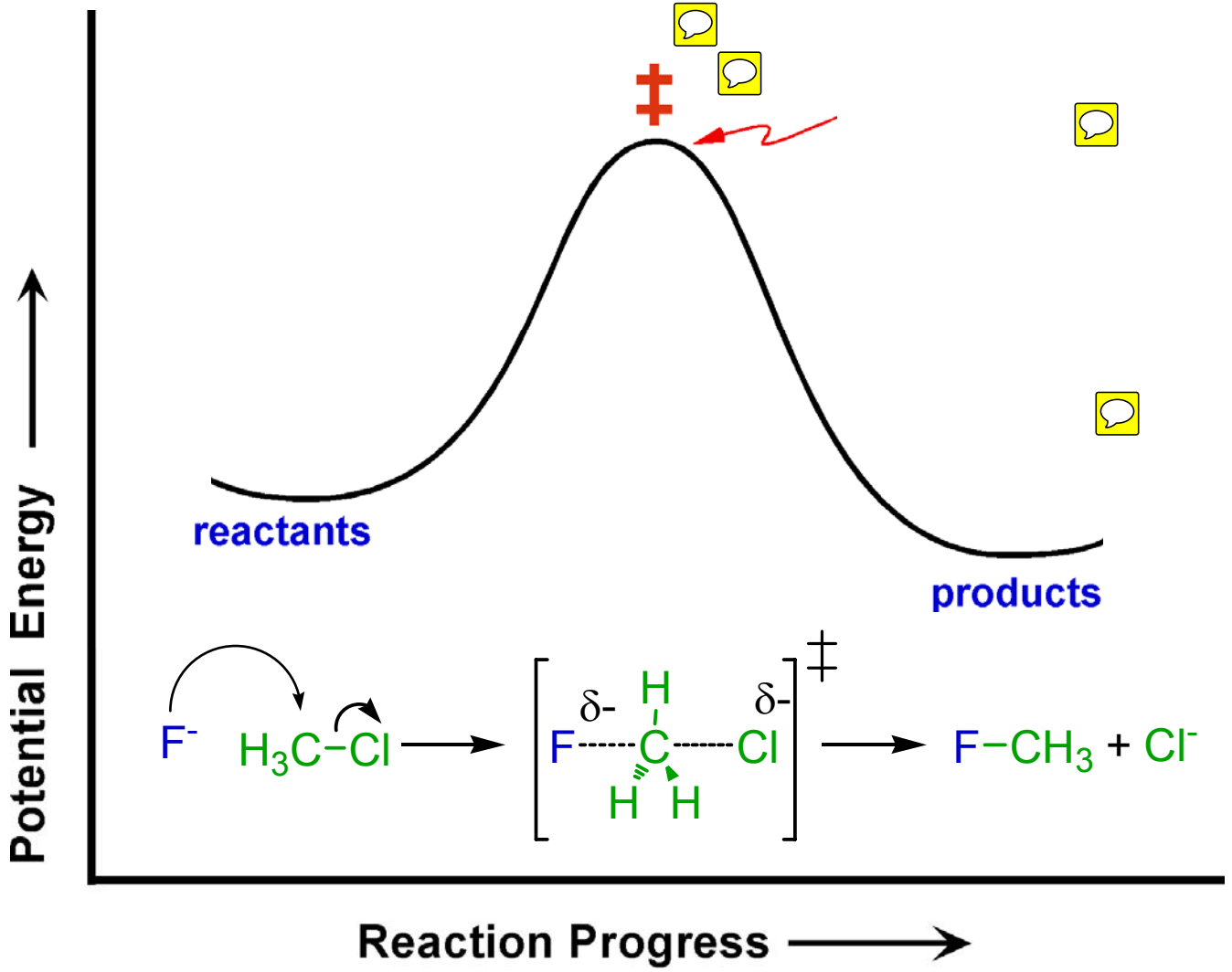
Transition state theory

- the **transition state** is the energy divide between the reactant and the product, i.e. the point along the reaction energy profile

- the species present at this point is called the **transition state species**, or **activated complex**

14-8. Theoretical models of chemical kinetics

- **reaction profile**: potential energy vs. reaction progress



14-8. Theoretical models of chemical kinetics

- k controlled by activation energy (E_a)

Concept check:

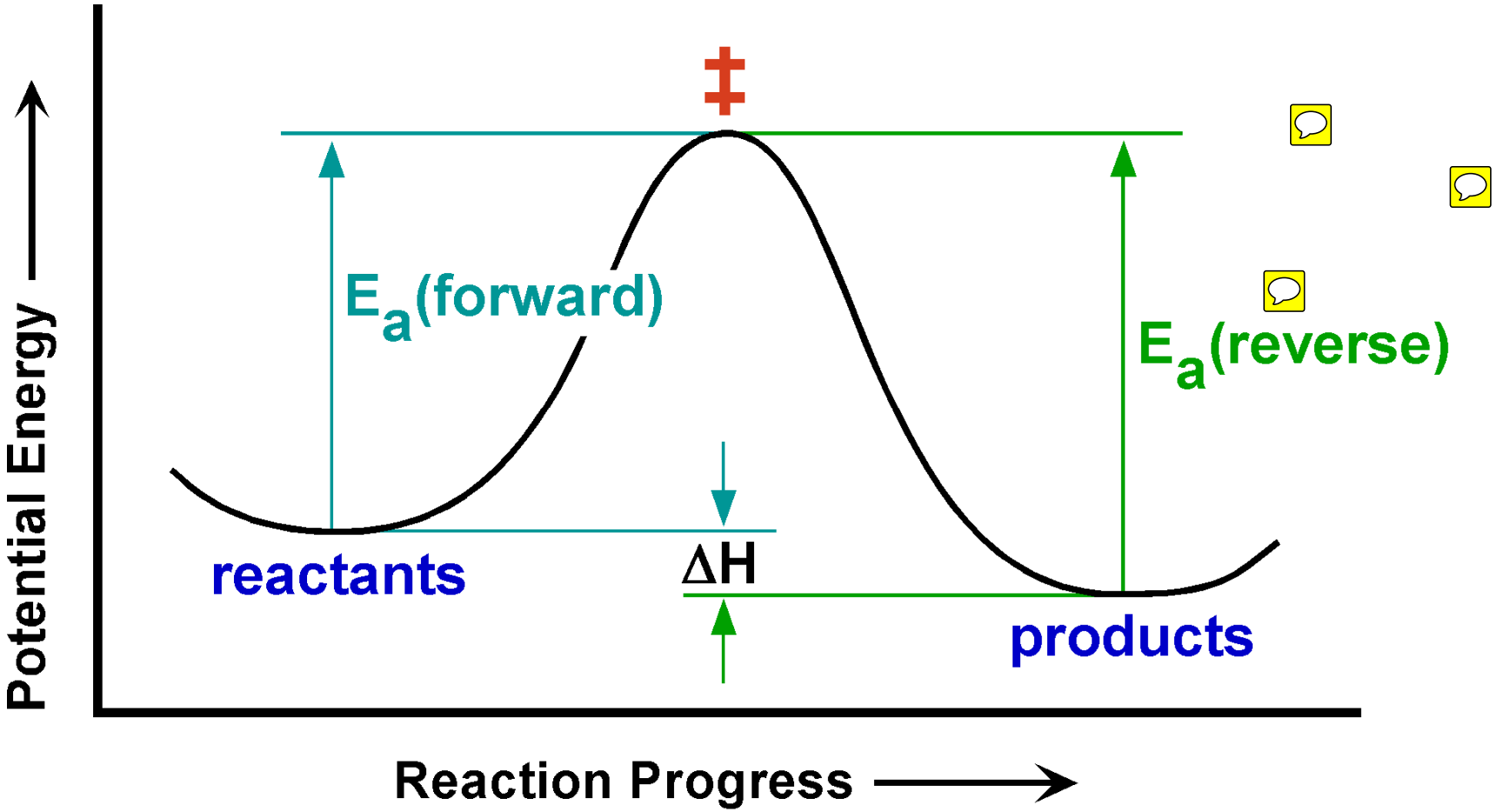
– How do high and low E_a values affect reaction rates?

$\uparrow E_a =$ $\downarrow E_a =$

- all reactions are reversible (in principle), so there are forward and reverse E_a values

14-8. Theoretical models of chemical kinetics

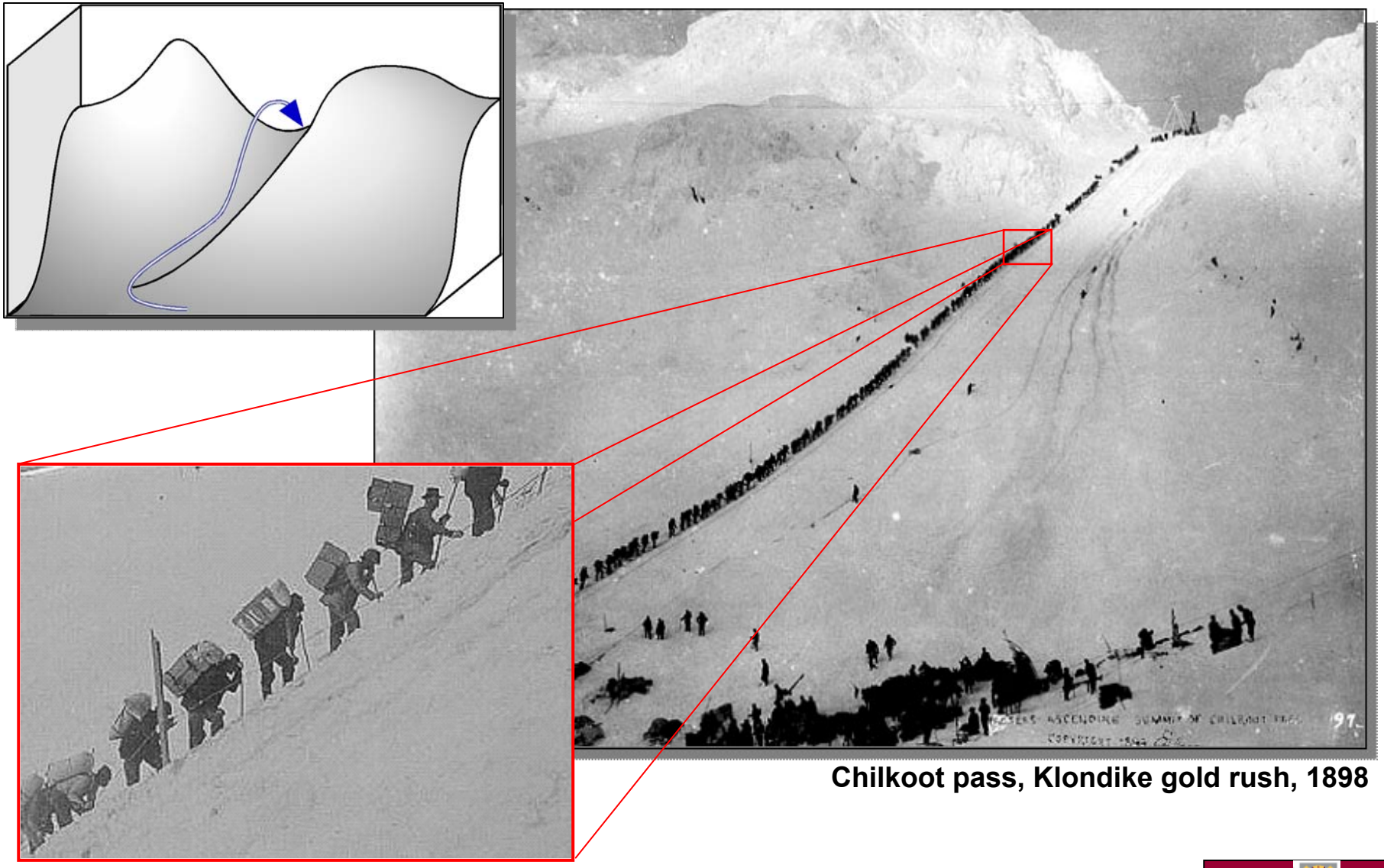
- $\Delta H = E_a(\text{forward}) - E_a(\text{reverse})$



14-8. Theoretical models of chemical kinetics

- activated complexes are unstable, lifetimes < 0.1 ps
- 0.1 ps (pico seconds) = 10^{-13} seconds
- transition state is the highest energy *point* on the lowest energy *path* between reactants and products, like the saddle point on a pass between two valleys

14-8. Theoretical models of chemical kinetics



Chilkoot pass, Klondike gold rush, 1898

14-8. Theoretical models of chemical kinetics

Key concepts of:

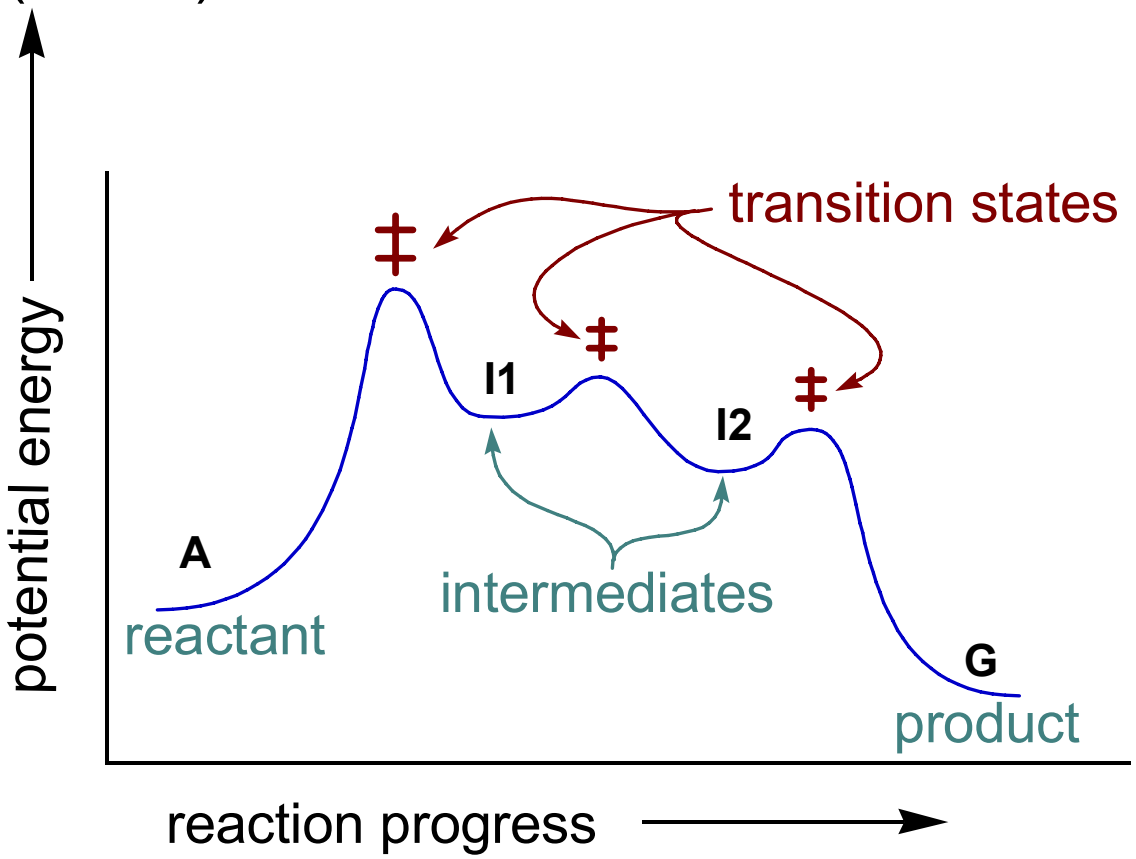
- collision theory:
  -
  -
- transition state theory:
  -
  -
  -
  -

14-10. Reaction mechanism

- …is a step-by-step description of a reaction, with each step representing an **elementary process**
- an elementary process is one step of a reaction, passing through one transition state
  - for a one step reaction, it is the whole reaction from reactant to product (**A**→**G**)

14-10. Reaction mechanisms

Multistep reactions consist of two or more elementary steps: from reactant to intermediate 1 (**A**→**I1**), from intermediate 1 to intermediate 2 (**I1**→**I2**), and from intermediate 2 to product (**I2**→**G**)



14-10. Reaction mechanisms

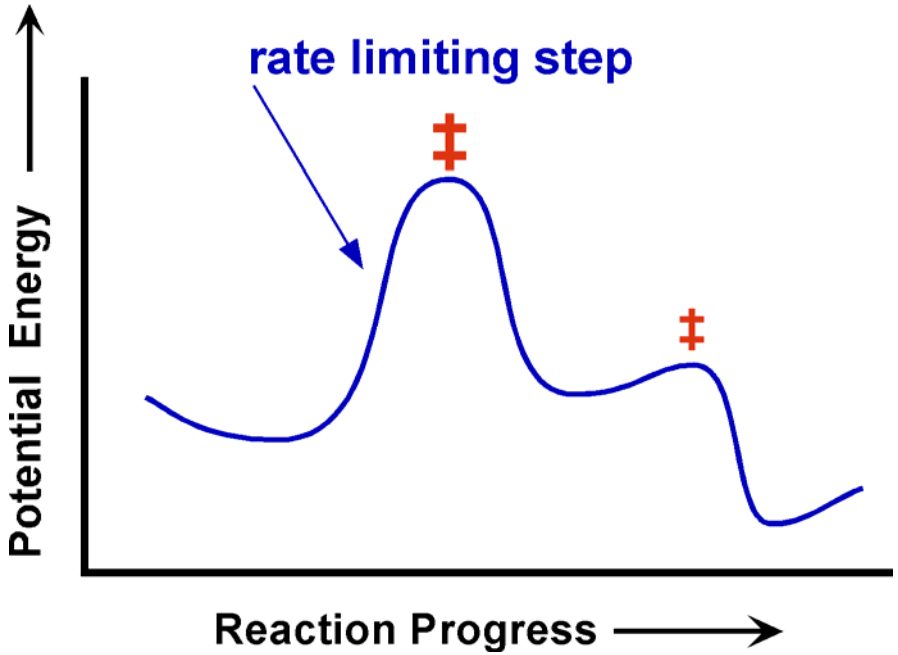
Elementary Processes…

- May be unimolecular (dissociation), or bimolecular (association). Termolecular =
- Have reaction orders the same as their
- Are reversible. May not reach equilibrium in each reaction
- May produce intermediates (species produced in one elementary process and consumed in another. These do not appear in overall reaction, or overall rate law
- are called (when an elementary process is much slower than all others)

iClicker Question #5

Case 1: Slow initial step followed by a fast step

- first step is rate-limiting → rate law determined by first step



- e.g., S_N1 reaction of *t*Bu-Cl + F^-

  $v_0 = k[t\text{Bu-Cl}]$

Case 2: Fast equilibrium step followed by a slow step

- Overall reaction:

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

- Experimentally determined rate law:

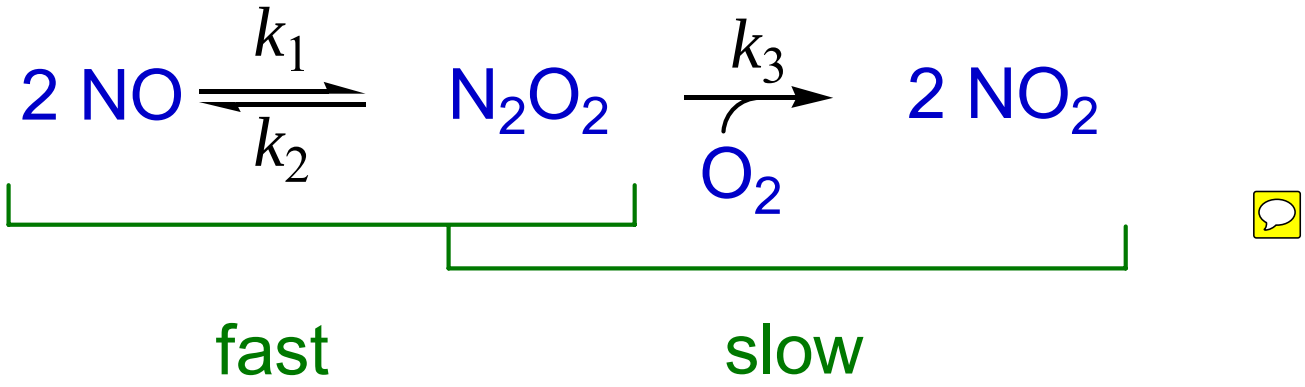
$$v_0 = k\,[NO]^2[O_2] \qquad (18)$$

- What reaction mechanism could account for the observed rate law?

14-10. Reaction mechanisms

Assume a fast reversible step followed by a slow step

- Possible mechanism:



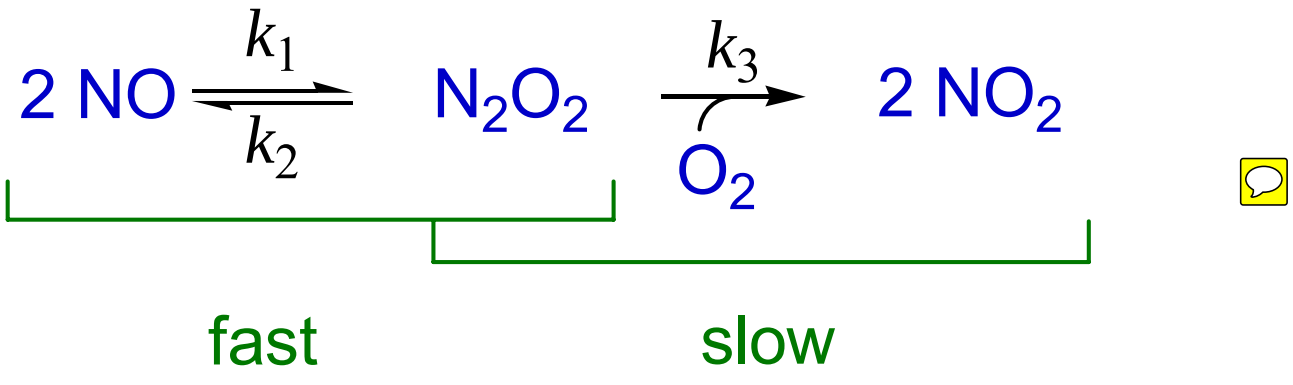
- assume that k_3 is rate-limiting, and hence:

$$v_0 = \qquad (19)$$

14-10. Reaction mechanisms

- N_2O_2 is an intermediate, and thus **must not** appear in the rate equation → we need to express $[N_2O_2]$ differently:

- $[N_2O_2]$ at equilibrium depends on [NO]:



$$K_{12} = \qquad (20)$$

or

$$[N_2O_2] = \qquad (20a)$$

14-10. Reaction mechanisms

- combining eq. **19** and **20a**:

$$v_0 = k_3 K_{12} [NO]^2[O_2] \qquad (\textbf{18a})$$

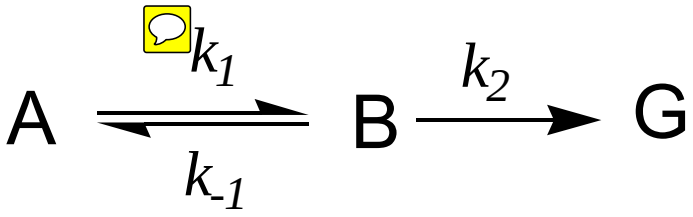
or

$$v_0 = \qquad \text{where } k = k_3 K_{12} \qquad (\textbf{18})$$

- eq. **18a** is consistent with the observed rate law (**18**), so the proposed mechanism is consistent with the experimental observations

Case 3: the steady state approximation – independent of which is the rate-limiting step

- Cases 1 and 2 require that either step 1 or step 2 is rate-limiting. Sometimes we don't know which one, and sometimes they have similar rates → use steady state approximation.



- 1st assumption: $v_0 = k_2$[B] (**21**)
  (always true, whether step 2 is rate-limiting or not)

- As B is an intermediate, [B] must be replaced in the rate law

14-10. Reaction mechanisms

- 2nd assumption: [B] reaches a *steady state* (produced and consumed at equal rates), and thus d[B]/dt = 0 throughout

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} G$$

- Production of B: $v_0 =$ (**22**)
  equals consumption of B: $v_0 =$ (**23**)

- Combine: $k_1[A] =$ (**24**)

- Isolate [B]: $[B] =$ (**24a**)

14-10. Reaction mechanisms

- Substitute (**24a**) into (**21**) ($v_0 = k_2$[B]) to remove [B] from rate law:

$$v_o = \frac{k_2 k_1 [\mathrm{A}]}{k_{-1} + k_2} \qquad (\mathbf{25})$$

- This general form of the rate law is more complicated, but works even when we do not know which step is rate-limiting!

- Cases 1 and 2 are used when we know which step is rate-limiting. The more general steady state equation **25** also works in those cases, and is simplified accordingly:

14-10. Reaction mechanisms

- When $k_{-1} >> k_2$ (reversible fast first step, slow second step):
- Then $$v_o = \frac{k_2 k_1 [\mathrm{A}]}{k_{-1} + k_2} \qquad (\mathbf{25})$$
- simplifies to $v_o =$ $=$
- which is like in Case 2

14-10. Reaction mechanisms

- When k_2 >> k_1, and k_{-1} ≈ 0 (slow first step, fast second step):
- Then (**23**) simplifies from: $$v_o = \frac{k_2 k_1 [\mathrm{A}]}{k_{-1} + k_2} \qquad (\mathbf{25})$$
- to: $$v_o = \square \qquad (\mathbf{21d})$$
- which is like in Case 1

14-10. Reaction mechanisms

Key concepts:

- mechanism is the
- must be consistent with
- slowest step =

iClicker Question #6

Take-Home Practice Problem

The experimentally determined rate law for the reaction: $2\ NO(g) + H_2(g) \rightarrow N_2(g) + H_2O(l)$ is $v = k[H_2][NO_2]$. Which of the following mechanisms is consistent with this rate law?

A:

$2\ NO(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$ (fast)

$H_2(g) + N_2O_2(g) \xrightarrow{k_3} N_2O(g) + H_2O(l)$ (slow)

$N_2O(g) + H_2(g) \xrightarrow{k_4} N_2(g) + H_2O(l)$ (fast)

B:

$2\ NO(g) \xrightarrow{k_1} N_2O_2(g)$ (slow)

$H_2(g) + N_2O_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(l)$ (fast)

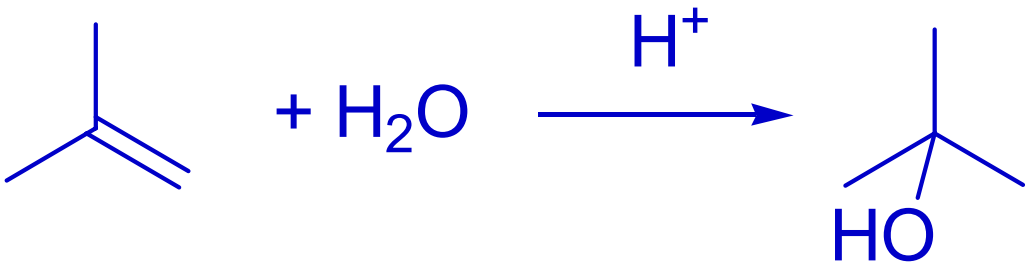
$N_2O(g) + H_2(g) \xrightarrow{k_3} N_2(g) + H_2O(l)$ (fast)

Take-Home Practice Problem – Solution

14-11. Catalysis

- catalysts accelerate reactions without being altered
- catalysts lower the E_a
- catalyst is neither reagent or product, and is hence written *over* the reaction arrow:

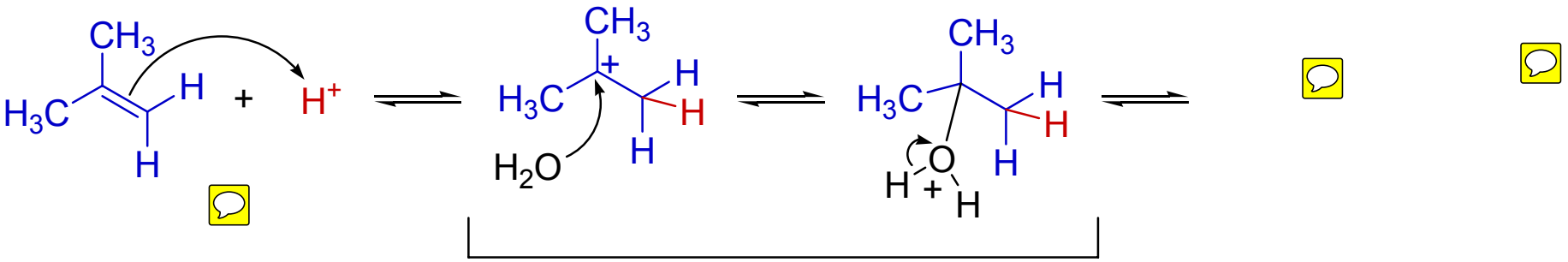
- e.g., acid-catalyzed hydration of an alkene:



methylpropene **methylpropan-2-ol**

14-11. Catalysis

- Mechanism:



protonation by acid catalyst

reactive cationic intermediates

regenerate catalyst, stable product

14-11. Catalysis

Homogeneous Catalysis

- reactants, products & catalyst all in the same phase (solution or gas)
- catalytic activity proportional to its concentration

14-11. Catalysis

Heterogeneous catalysis

- reactants & products in the same phase
- catalyst is a solid, reaction occurs on its surface
- steps in heterogeneous catalysis:
  - reactant adsorption and activation
  - reaction
  - product desorption
- catalyst "concentration" now means the number of active sites (~surface area), not the molar amount of catalyst

14-11. Catalysis

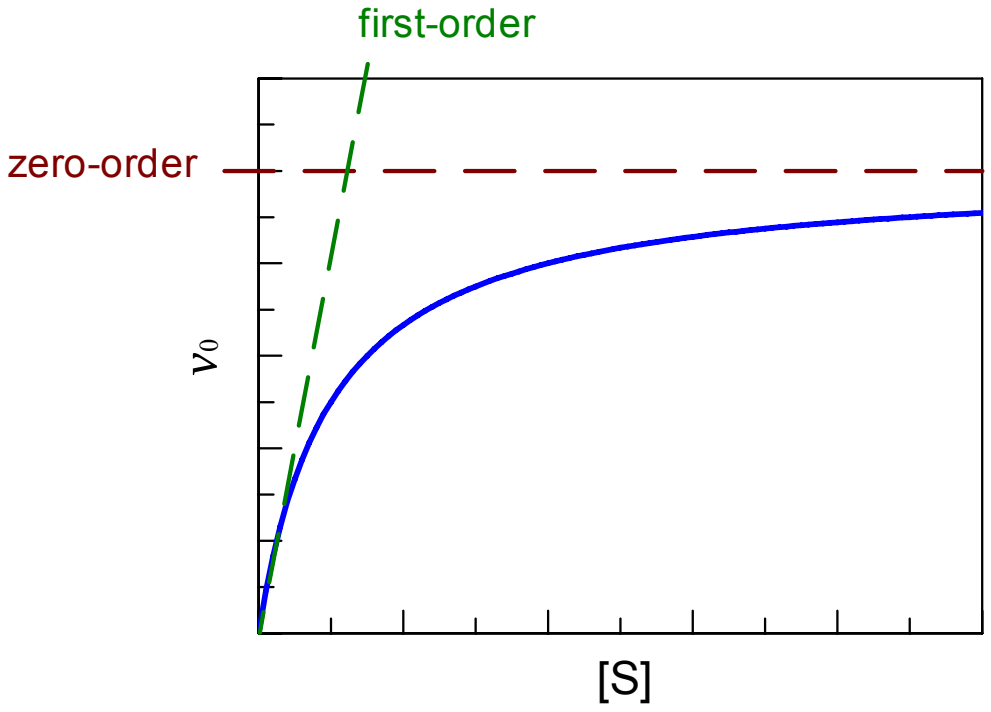
Key concepts:

- catalysts are
- used to
-

14-11. Catalysis

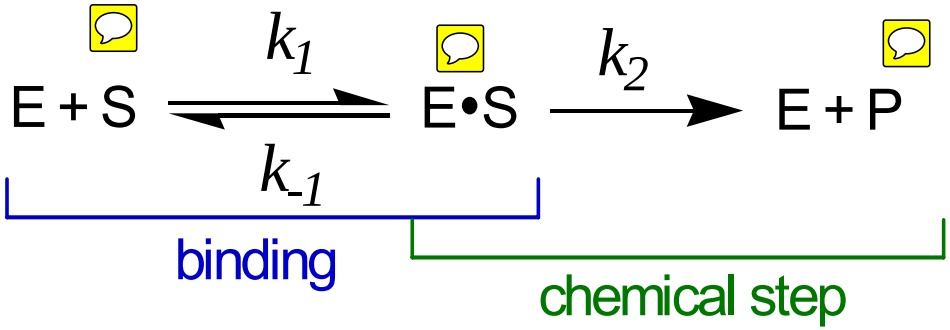
Enzymes are protein catalysts

- highly specific toward certain reactants (**substrate, S**)
- at low [S], reaction is 1st-order in $[S]_0$
- at very high [S], reaction is 0th-order in $[S]_0$



14-11. Enzyme catalysis

- catalysis involves association of enzyme + substrate, followed by the chemical step to form products:



(26)

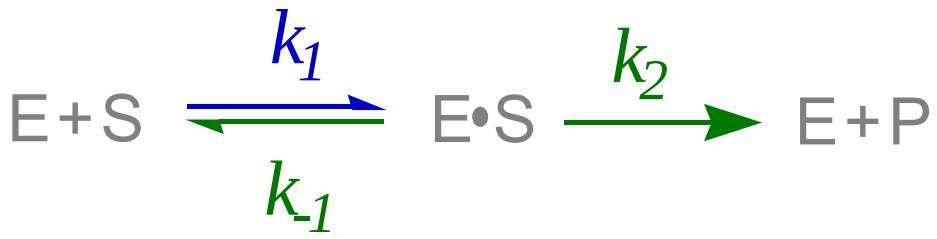
- 1st assumption: $[S]_0 >> [E]_0$ (this is true for most enzymatic reaction, and results in: $[S] >> [E \cdot S]$, and $[S] = [S]_0$)

- 2nd assumption (always true): $v_0 =$ _ **(27)**

- 3rd assumption: steady state approximation: **(28)**

14-11. Catalysis: steady-state approximation

- we use the steady state approximation because we do not know how fast binding (k_1) and dissociation (k_{-1}) are relative to the chemical step (k_2),



- thus: rate of E•S formation = rate of E•S breakdown

(**29**, 14.35)

- we know the total [E] (= $[E]_0$), but not $[E]_{free}$

  → a bunch of algebra to recast $[E]_{free}$ in terms of $[E]_0$…

14-11. Catalysis: steady-state approximation

$$v_0 = \frac{k_1 k_2 [\mathrm{E}]_0 [\mathrm{S}]}{(k_{-1} + k_2) + k_1 [\mathrm{S}]} \qquad (\mathbf{30})$$

- this resembles the steady state eq. **25** from Case 3, except for "+ k_1[S]" that arises from using $[\mathrm{E}]_0$ instead of $[\mathrm{E}]_{\mathrm{free}}$
- simplify equation **30** by dividing by k_1:

v_0 =

- substitute $K_M = (k_{-1} + k_2)/k_1$ and $k_{cat} = k_2$:

14-11. Catalysis: steady-state approximation

Michaelis-Menten equation:

$v_0 =$ 💬 (**31**, 14.36)

recall: $v_0 = k_2[\text{E•S}]$ (**27**)

- therefore:
  - $k_{cat} = k_2$
  - 💬
  - 💬
  - [E•S] = 💬

14-11. Catalysis: steady-state approximation

Michaelis-Menten equation:

$$v_0 = \frac{k_{cat}[E]_0[S]}{K_M + [S]} \qquad (\mathbf{31}, 14.36)$$

- K_M is the value of [S] at which the rate is $^1/_2$ maximal
- K_M has units of concentration (e.g., M)

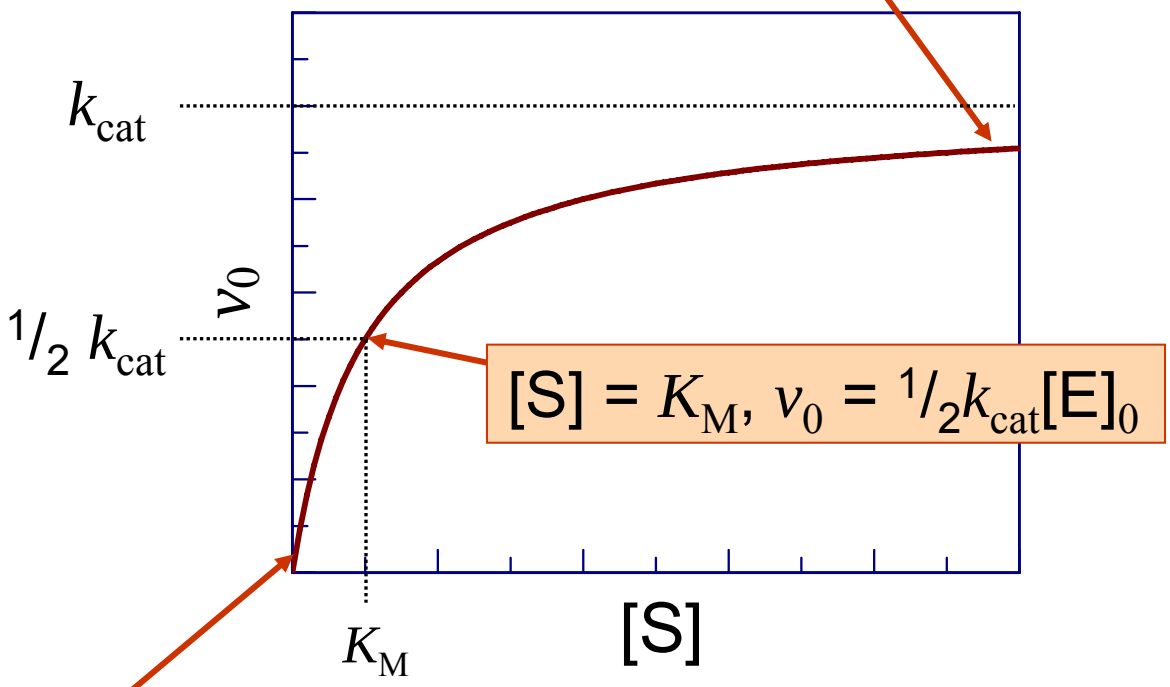
- for example:

	[E•S]	v_0
[S] >> K_M	💬 💬	💬
[S] = K_M	💬	💬
[S] << K_M	💬	💬

14-11. Catalysis: steady-state approximation

$$v_0 = \frac{k_{cat}[E]_0[S]}{K_M + [S]}$$

[S] >> K_M, v_0 = $k_{cat}[E]_0$



[S] = K_M, v_0 = $^1/_2 k_{cat}[E]_0$

[S]<< K_M, v_0 = $k_{cat}[E]_0[S]/K_M$

14-11. Catalysis

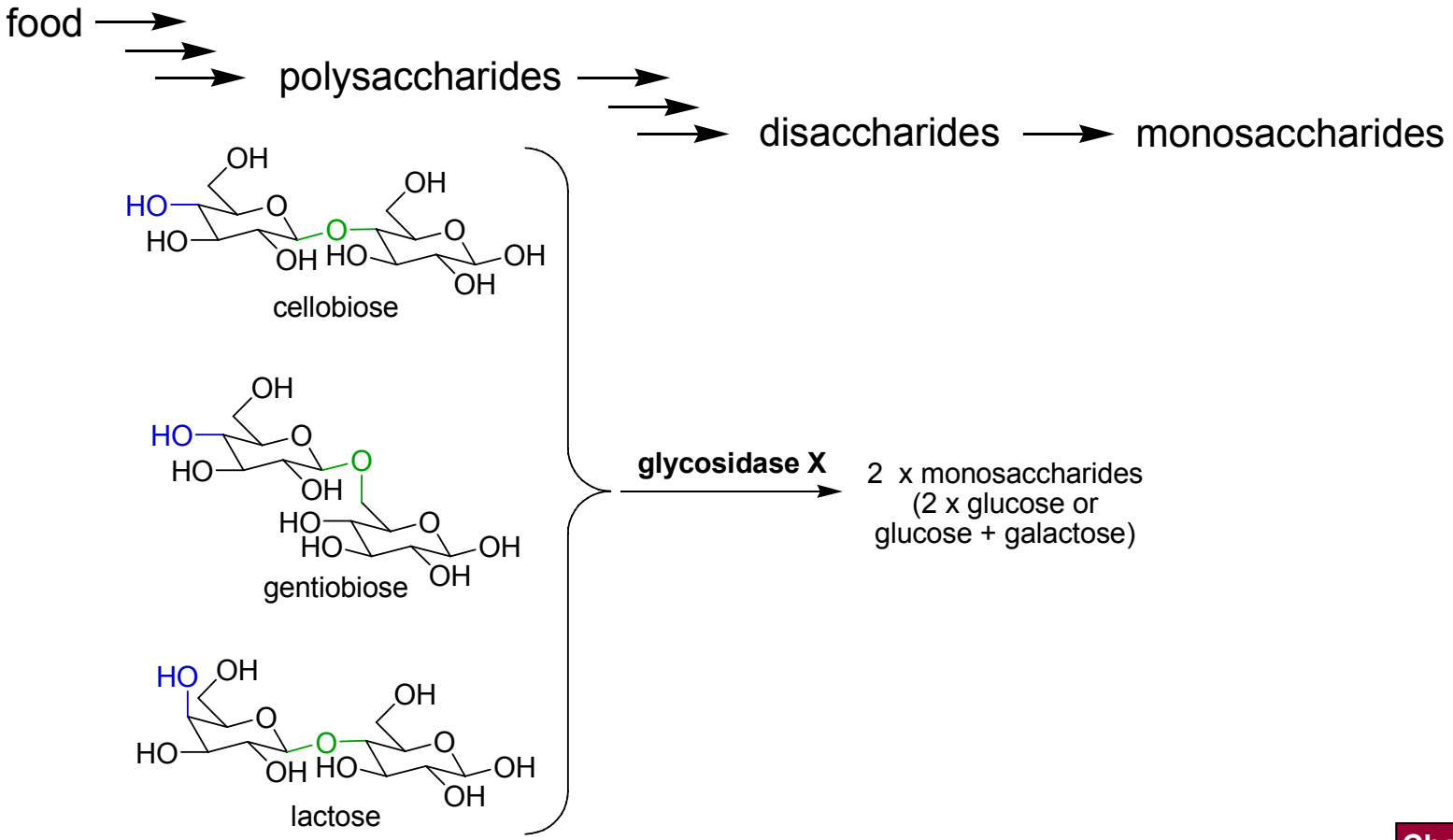
Key concepts:

- Michaelis-Menten equation
  - 3 assumptions:
    -
    -
    -
  - reaction order

iClicker Question #7

Practical enzyme kinetics

- **our bodies need to convert complex carbohydrates (polysaccharides) into simple monosaccharides in order to use them for energy and as building blocks**



Take-Home Practice: Practical enzyme kinetics

With gentiobiose:

k_{cat} = 10 s^{-1}

K_M = 10^{-4} M.

If:

[gX] = 10^{-7} M, and

[gentiobiose] = 10^{-5} M,

what is v_0?

$$v_0 = \frac{k_{cat}[E]_0[S]}{K_M + [S]}$$

Take-Home Practice: Practical enzyme kinetics

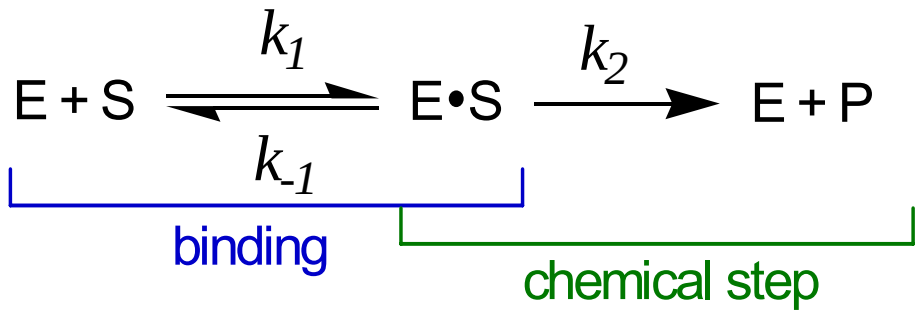
If [gentiobiose] increases to 2×10^{-5} M, what is the new v_0?

Why does the rate roughly double when [gentiobiose] doubles?

Take-Home Practice: Practical enzyme kinetics

If $v_0 = 2 \times 10^{-6}$ M/s with 4×10^{-4} M cellobiose,
and 1.8×10^{-6} M/s with 2×10^{-4} M cellobiose,
what can we conclude about K_M(cellobiose)?

Enzyme Catalysis: Concept Check



If $k_{-1} = 0$, is it possible to make the steady-state approximation?

$$\frac{d[E \bullet S]}{dt} = 0$$

14-9. Effect of temperature on reaction rates

- expect reactions to be faster at higher temperature
- Arrhenius found a relationship between k and T:

$$k = \qquad \text{(32, 14.21)}$$

- where:

  A = pre-exponential term (assume A is constant)

  (A contains information about collision frequency and geometry)

  E_a = activation energy

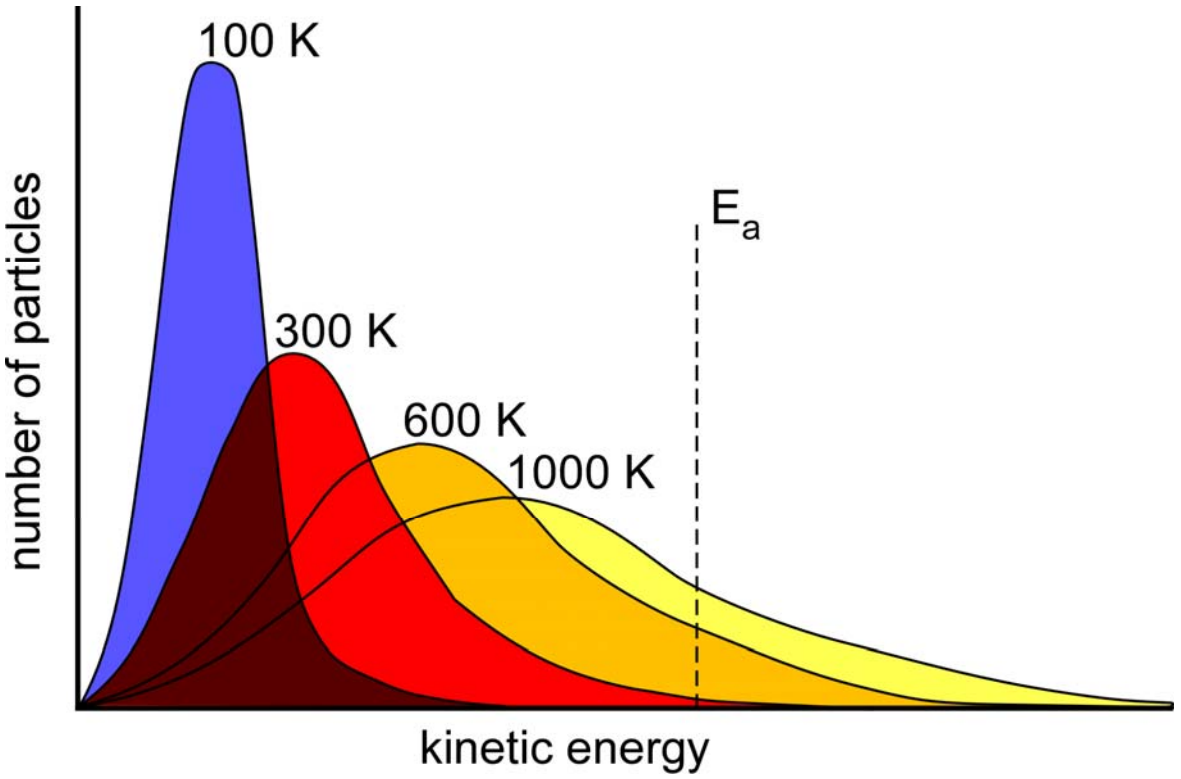
  R = gas constant

  T = temperature

14-9. Effect of temperature on reaction rates

- A = k at infinite T
- $e^{-Ea/RT}$ = fraction of molecules with enough energy to react at a given T

Concept check:
What effect does an increase in T have on k?



14-9. Effect of temperature on reaction rates

- rewrite eq. **32**:

$$\ln(k) = \quad \text{(32a)}$$

- A is hard to define experimentally – so eliminate A
  → determine E_a from k at two different temperatures:

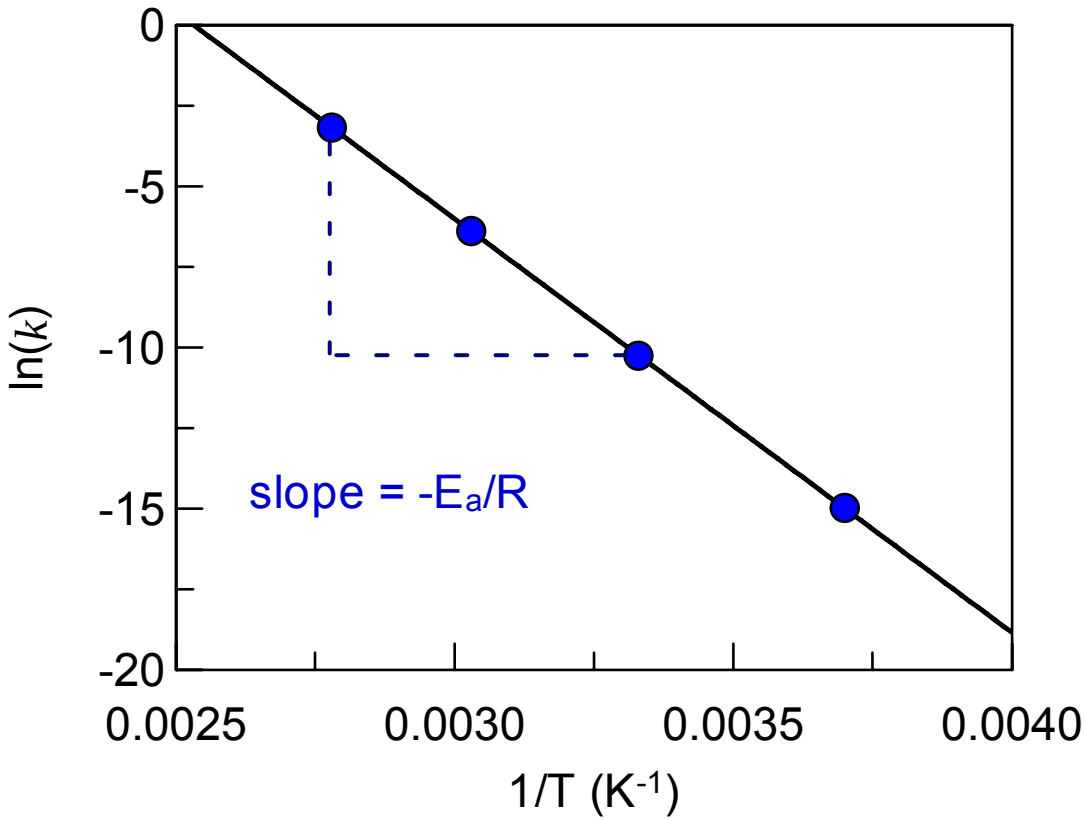
(**33**, 14.22)

- Or determine T from k with two different E_a values:

14-9. Effect of temperature on reaction rates

$$ln\frac{k_2}{k_1} =$$

(**33**, 14.22)



Take-Home Practice Problem

A reaction has k = 0.018 s^{-1} at 400.°C and a half-life of 4.81 s at 430.°C. What is the E_a of this reaction?

14-9. Effect of temperature on reaction rates

Key concepts:

- reactions are
- meaning of
- Arrhenius

Note: More practice examples on the Arrhenius equation and other kinetics questions are in the tutorial sets. These questions are highly recommended!

Postscript

Kinetics doesn't just apply to chemical reactions:

- Physical processes
  - e.g., sublimation, dissolution, heat transfer
- Pharmacokinetics
  - drug absorption, distribution metabolism, excretion (ADME)
- Radioactive decay