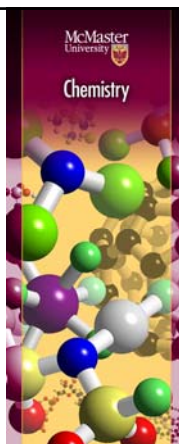


## Chapter 14: Chemical Kinetics

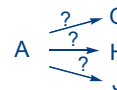
Equations in the slides are identified by **bold** numbers. If the same equation appears in the text, the text's chapter and equation number is given as well (e.g., (7, 14.2)).



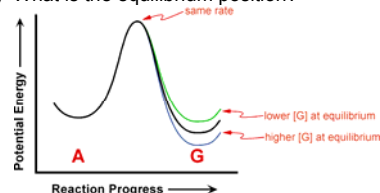
### Preface

The 3 big questions in any chemical reaction:

(1) What are the products?



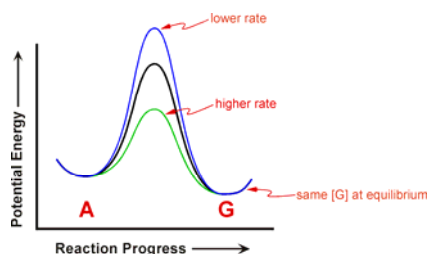
(2) What is the equilibrium position?



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### Preface

(3) How fast is the reaction?



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### 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)

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### Preface

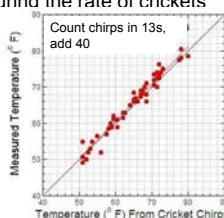
(3) understand reaction mechanisms:

- 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>



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## 14-1. The rate of a chemical reaction

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

• e.g.,

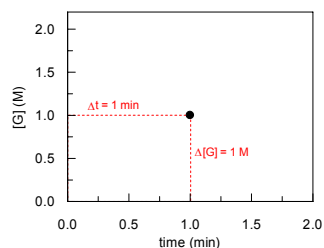


(1)

- 1 min after starting reaction,  $[G] = 1 \text{ M}$
- What is the rate of the reaction over 1 min?

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#### 14-1. The rate of a chemical reaction



- **average rate** =  $\Delta[G]/\Delta t = 1 \text{ M} / 1 \text{ min}$ .

#### 14-1. The rate of a chemical reaction

- For  $A \rightarrow G$   
average rate =  $\frac{\Delta[G]}{\Delta t}$  (2)

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

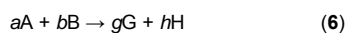
$$\text{average rate} = -\frac{\Delta[A]}{\Delta t} \quad (3)$$

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

$$\text{average rate} = -\frac{\Delta[A]}{\Delta t} = \frac{1}{2} \frac{\Delta[G]}{\Delta t} \quad (5)$$

#### 14-1. The rate of a chemical reaction

- In general:



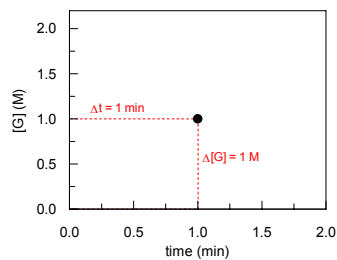
$$\text{average rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{g} \frac{\Delta[G]}{\Delta t} = \frac{1}{h} \frac{\Delta[H]}{\Delta t} \quad (7, 14.2)$$

- **Key concepts:**

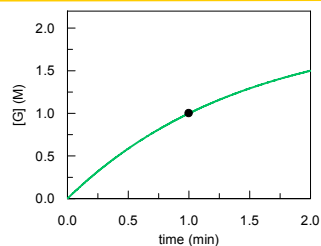
- rate is change in concentration over time
- rates are always positive
- stoichiometry matters

#### 14-2. Measuring reaction rates

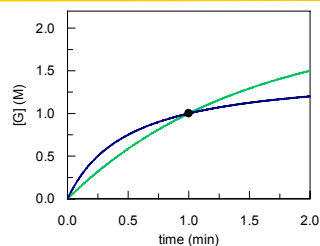
- Rates can change during a reaction
- Many reactions may give an *average rate* of 1 M/min for 1 min.



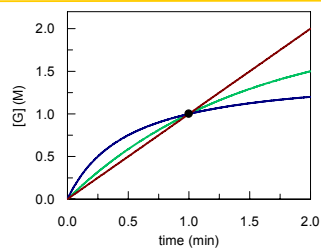
#### 14-2. Measuring reaction rates



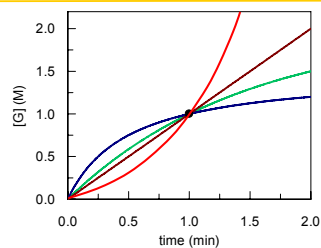
#### 14-2. Measuring reaction rates



#### 14-2. Measuring reaction rates



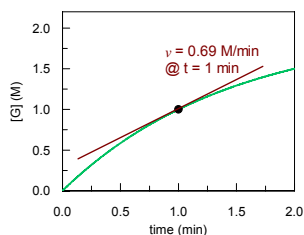
#### 14-2. Measuring reaction rates



- 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 ( $v$ )**: the rate at a specific time  $t$
- $v$  = the slope of the **tangent** to the **curve** of **[G] vs. time**



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  $\Delta[A]$  or  $\Delta[G]$  over a finite time interval,  $\Delta t$ , 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.

$$\text{average rate} = \frac{1}{g} \frac{\Delta[G]}{\Delta t} \quad (7, 14.2)$$

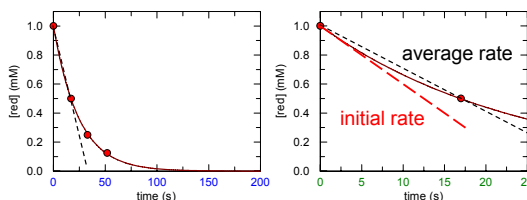
$$v = \lim_{\Delta t \rightarrow 0} \frac{1}{g} \frac{\Delta[G]}{\Delta t} = \frac{1}{g} \frac{d[G]}{dt} \quad (8)$$

#### Average vs instantaneous and initial rates

- Experimentally measured rates are always average rates
- To best approximate instantaneous rates, we measure  $\Delta[A]$  or  $\Delta[G]$  over the smallest possible  $\Delta t$
- We ideally get instantaneous rates at  $t = 0$ . To get such *initial rates*, we have to measure  $\Delta[G]$  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*,  $v_0$  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 initial rates
- experimental rates are average rates
- to approach initial rates experimentally, use short measurement times  $\Delta t$  & measure rates near  $t = 0$

## iClicker Question #1

For the following reaction, which statement is incorrect?



- (a) avg. rate =  $-\Delta[\text{O}_2]/\Delta t$
- (b)  $v = -\frac{1}{2} \times d[\text{NO}]/dt$
- (c)  $v = \frac{1}{2} \times d[\text{NO}_2]/dt$
- (d) avg. rate =  $-\frac{1}{2} \times \Delta[\text{O}_2]/\Delta t$

## iClicker Question #2

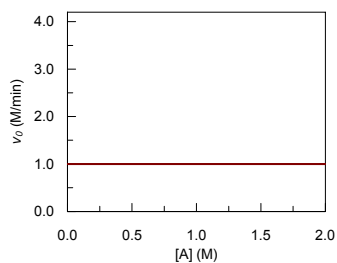
For the following reaction, which statement is correct?



- (a)  $-\frac{1}{2} \Delta[\text{NO}]/\Delta t = \Delta[\text{O}_2]/\Delta t$
- (b)  $-d[\text{NO}]/dt = -d[\text{NO}_2]/dt$
- (c)  $\Delta[\text{NO}]/\Delta t = 2\Delta[\text{O}_2]/\Delta t$
- (d)  $-\Delta[\text{O}_2]/\Delta t = \Delta[\text{NO}_2]/\Delta t$
- (e) All of the above are correct

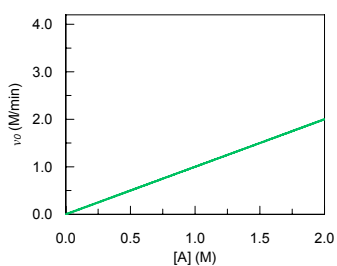
## 14-3. Effect of concentration on reaction rates: The rate law

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



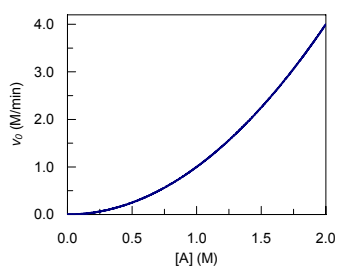
## 14-3. Effect of concentration on reaction rates: The rate law

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



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

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



#### 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:

$$v_0 = k[A]^m[B]^n \quad (9, 14.6)$$

$m$  &  $n$  = 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

$$v_0 = k[A]^m[B]^n \quad (9, 14.6)$$

- $m$  &  $n$ 
  - determined experimentally
  - usually small, positive integers (0, 1 or 2)
  - may be negative, fractions
- 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:  $2A + B \rightarrow C + D$

$$v_0 = k[A]^m[B]^n \rightarrow \text{what are } m \text{ and } n?$$

- Set up three reactions:
 

exp	$[A]_0$	$[B]_0$	$v_0$
1	1	1	0.01
2	2	1	0.04
3	1	2	0.01

ratios of  $v_0(\text{exp 2}) / v_0(\text{exp 1})$ :

- $v_0(2)/v_0(1) = k(2M)^m(1M)^n / k(1M)^m(1M)^n = 2^m = 4 \rightarrow m = 2$
- $v_0(3)/v_0(1) = k(1M)^m(2M)^n / k(1M)^m(1M)^n = 2^n = 1 \rightarrow n = 0$
- Overall reaction order =  $m + n = 2$

#### 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  $\neq$  stoichiometry
- order is determined experimentally
- order = number of species involved at transition state of the rate-limiting step

#### iClicker Question #3

Which of the following rate equations is not third order overall?

- (a)  $v_0 = k[A]^3[B]^{-1}[C]$
- (b)  $v_0 = k[B]^3[C]^0[D]$
- (c)  $v_0 = k[A]^3[B]^0$
- (d)  $v_0 = k[A]^1[B]^2$

#### 14-4. Zero-order reactions

- $v_0$  is independent of  $[A]$

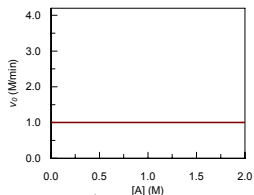
$$v_0 = k [A]^0 = k = \text{constant} \quad (13, 14.9)$$

##### 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  $\text{M}\cdot\text{s}^{-1}$ )

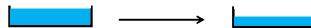
→ Units of  $k$  for zero-order reactions are concentration/time, e.g.,  $\text{M}\cdot\text{s}^{-1}$



#### 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:

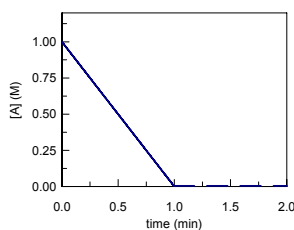
- rate = rate constant ( $k$ )
- true zero-order reactions are rare

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

- $v_0 = k$  or  $-d[A]/dt = k$

- the integrated version of this rate law is:

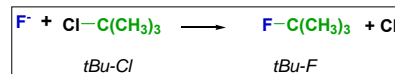
$$[A]_t = [A]_0 - kt \quad (14, 14.10)$$



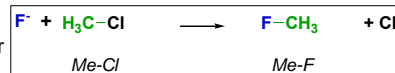
#### Reaction orders in nucleophilic substitutions

- 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.:

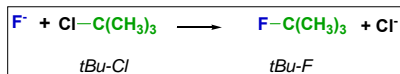
- First order



- Second Order



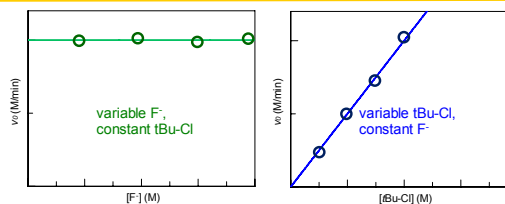
#### 14-5. First-order reactions



- Experiments have shown that the above reaction of  $\text{F}^-$  with *t*Bu-Cl is first order in *t*Bu-Cl, i.e. that  $v_0 \propto [\textit{t}\text{Bu-Cl}]$
- What were these experiments?
- Measurement of  $v_0$  at different  $[\textit{t}\text{Bu-Cl}]$ ,  $[\text{F}^-]$  (method of initial rates), and checking the dependence of  $v_0$  on  $[A]$ ,  $[B]$ :

exp	$[\text{F}^-]$	$[\text{Cl}-\text{C}(\text{CH}_3)_3]$	initial rate, M/s
1	0.1	0.1	$1.2 \times 10^{-4}$
2	0.2	0.1	$1.2 \times 10^{-4}$
3	0.1	0.2	$2.4 \times 10^{-4}$

#### 14-5. First-order reactions



- reaction order w.r.t. *t*Bu-Cl?

$\text{F}^-$ ?

- overall reaction order?
- rate equation?

**1<sup>st</sup>-order**

**0<sup>th</sup>-order**

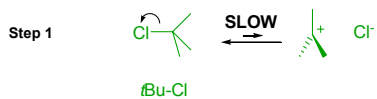
**1<sup>st</sup>-order**

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

$$= k[\textit{t}\text{Bu-Cl}]^1[\text{F}^-]^0$$

#### 14-5. First-order reactions

##### Why first order?



- Step 1: slow C-Cl bond cleavage to form carbocation
- Step 2: fast attack of  $\text{F}^-$  on carbocation
- overall rate controlled by Step 1: C-Cl bond cleavage

#### 14-5. First-order reactions

- $\text{F}^-$  does not enter until after the rate-limiting step, hence no effect from  $[\text{F}^-]$

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

$$v_0 = k[\text{A}] \quad (10, 14.12)$$

- reaction is called **S<sub>N</sub>1**:
  - S = substitution
  - N = nucleophilic
  - 1 = one species in the rate-limiting step

#### 14-5. First-order reactions

##### Concept check:

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

- units for  $k$  are 1/time (e.g.,  $\text{s}^{-1}$ )

Recall the characteristics of  $k$ :

- (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  $[\text{A}]$  consumed (or  $[\text{G}]$  formed)
  - integrate  $d[\text{A}]/dt$  with respect to time:

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

- $\ln[\text{A}]$  is unitless, so  $kt$  is unitless

- rearrange eq. 11 (apply exponential):

$$[\text{A}]_t = [\text{A}]_0 \cdot e^{-kt} \quad (11a)$$

(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?

Solution:  $\ln \frac{[\text{A}]_t}{[\text{A}]_0} = -kt$

If the reaction is 75% complete, then 25% of the initial reactant remains after 25 s.

$$\ln \frac{[0.25]}{[1]} = -k(25 \text{ s})$$

$$\text{and } k = -\ln(0.25) / 25 \text{ s} = 0.055 \text{ s}^{-1}$$

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

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

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

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

to obtain:  $\frac{1}{2}[\text{A}]_0 = [\text{A}]_0 \cdot e^{-kt_{1/2}}$

Apply  $\ln$  and rearrange to get:

$$\ln \left( \frac{\frac{1}{2}[\text{A}]_0}{[\text{A}]_0} \right) = -k \cdot t_{1/2} \quad \text{and} \quad \ln \left( \frac{1}{2} \right) = -k \cdot t_{1/2}$$

$$t_{1/2} = - \left( \frac{\ln \frac{1}{2}}{k} \right) = \frac{\ln 2}{k} = \frac{0.693}{k} \quad (12, 14.14)$$

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

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- 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)

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### Take-Home Practice Problem


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

Solution:

$$t_{1/2} = \ln 2 / k$$
$$t_{1/2} = \ln 2 / 0.0138 \text{ s}^{-1}$$
$$t_{1/2} = 50.2_3 \text{ s}$$

and convert units:

$$t_{1/2} = 50.2_3 \text{ s} \times (1 \text{ min} / 60 \text{ s}) \times (1 \text{ hour} / 60 \text{ min})$$
$$t_{1/2} = 0.0140 \text{ h}$$

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14-5. First-order reactions

- Examples:
  - (1) radioactive decay
  - (2)  $S_N1$
- Key Concepts:
  - $v_0 \propto [A]$
  - $t_{1/2} = \text{constant}$
  - rate and integrated rate equations

The graph illustrates the concentration of reactant A (red curve) and product B (blue curve) over time for a first-order reaction  $A \rightarrow B$ . The y-axis represents the concentration  $[A]$  in grams, ranging from 0 to 1.0. The x-axis represents time  $t$  in seconds, ranging from 0 to 400. The red curve starts at  $[A] = 1.0$  g at  $t = 0$  and decreases exponentially. The blue curve starts at  $[B] = 0$  g at  $t = 0$  and increases, mirroring the decay of A. The two curves intersect at  $t = 100$  seconds and  $[A] = 0.5$  g. Three half-lives ( $t_{1/2}$ ) are marked: from  $t = 0$  to  $t = 100$ , from  $t = 100$  to  $t = 200$ , and from  $t = 200$  to  $t = 300$ , each corresponding to a halving of the concentration of A.

## 14-6. Second-order reactions


A second-order reaction:

- $S_N2$  nucleophilic substitution

$$\text{F}^- + \text{H}_3\text{C}-\text{Cl} \longrightarrow \text{F}-\text{CH}_3 + \text{Cl}^-$$

*Me-Cl* *Me-F*

- $S_N2$ :  
S = substitution  
N = nucleophilic  
2 = two species in the rate-limiting step

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14-6. Second-order reactions

• reaction order w.r.t. Me-Cl? **1<sup>st</sup>-order**

• overall reaction order? **1<sup>st</sup>-order**

• rate equation? **2<sup>nd</sup>-order**

$$v = k[\text{Me-Cl}][\text{F}^-]$$

$$= k[\text{Me-Cl}]^1[\text{F}^-]^1$$

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

Me-Cl                      transition state                      MeF

- rate depends on the presence of *both* reactants

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

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#### 14-6. Second-order reactions

$$v_0 = k[F^-][Me-Cl] \quad (15)$$

- 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  $1/(\text{concentration} \cdot \text{time})$  (e.g.,  $M^{-1} \cdot s^{-1}$ )

#### 14-6. Second-order reactions

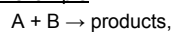
- example from the textbook:



- where:

$$v_0 = k[A]^2 \quad (17, 14.17)$$

- S<sub>N</sub>2 example:

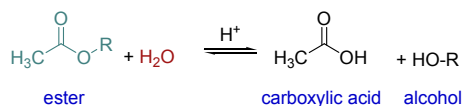


- where:

$$v_0 = k[A][B] \quad (17a)$$

#### Preview: ester hydrolysis

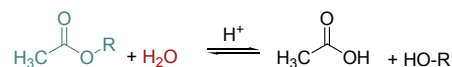
- Esters are synthesized from carboxylic acids and alcohols (see more in Organic Chemistry unit)
- Esters are broken down by hydrolysis
- Reversible reaction; equilibrium position is determined by Le Châtelier's principle:



#### 14-6. Second-order reactions

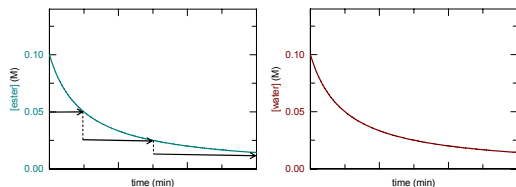
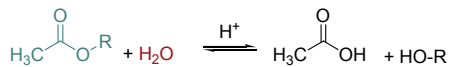
- Stoichiometric ester hydrolysis is a 2<sup>nd</sup>-order reaction which becomes very slow as the reactants are depleted

- e.g.:



#### 14-6. Second-order reactions

- e.g., reaction of 0.1 M ester and 0.1 M H<sub>2</sub>O in acetone:



Note: these calculations consider only the forward reaction

#### 14-6. Second-order reactions

#### Turn 2<sup>nd</sup> Order Reactions into Pseudo 1<sup>st</sup> Order Reactions:

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

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

	[ester]	[H <sub>2</sub> O]	[AcOH]	[HO-R]
initial	0.1 M	55.5 M	0 M	0 M
final	0 M	55.4 M	0.1 M	0.1 M

#### 14-6. Second-order reactions

##### • Key concepts:

- rate depends on both reactants (or  $[A]^2$ )
- make pseudo-1<sup>st</sup> order with one excess reagent

#### iClicker Question #4

What is the rate constant,  $k$ , for a reaction with the following relationship between reactant concentration,  $[A]$ , and initial velocity,  $v_0$ ?

$[A]$	$v_0$
1 M	100 M•s <sup>-1</sup>
3 M	900 M•s <sup>-1</sup>

- (a)  $k = 100 \text{ M}^{-1}\text{s}^{-1}$
- (b)  $k = 100 \text{ M}\cdot\text{s}^{-1}$
- (c)  $k = 300 \text{ M}\cdot\text{s}^{-1}$
- (d)  $k = 300 \text{ s}^{-1}$

#### 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  $\Delta t$
  - (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<sup>st</sup>-order)
  - (iv) integrated rate law which gives a constant  $k$

#### 14-7. Reaction kinetics: A summary

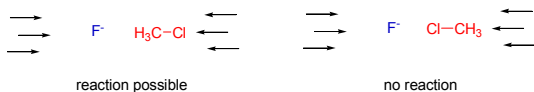
##### Things you can calculate:

- (4)  $k$  from:
  - (i) slope of line in an appropriate graph
  - (ii) the appropriate integrated rate law
  - (iii)  $t_{1/2}$  (1<sup>st</sup>-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 ( $\sim 10^{30}/\text{s}$ ),
- only very few ( $\sim 10^{-4} \text{ M}^{-1}\cdot\text{s}^{-1}$ ) 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



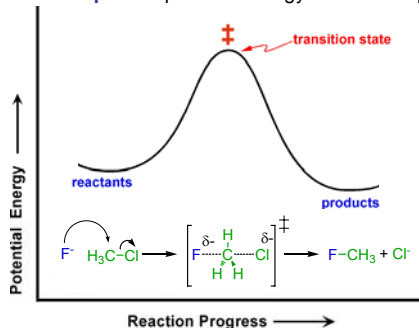
#### 14-8. Theoretical models of chemical kinetics

##### Transition state theory

- the **transition state** is the energy divide between the reactant and the product, i.e. the highest 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



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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?

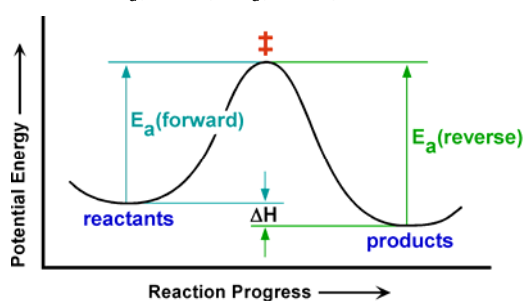
$$\uparrow E_a = \downarrow k, \quad \downarrow E_a = \uparrow k$$

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

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14-8. Theoretical models of chemical kinetics

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



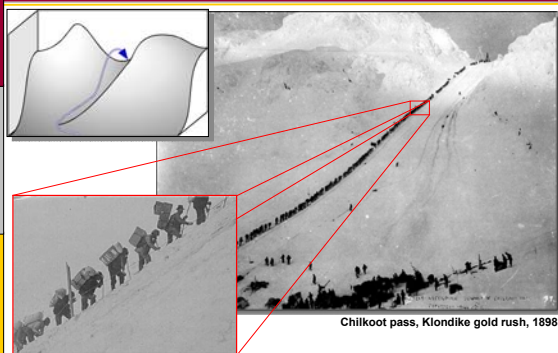
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14-8. Theoretical models of chemical kinetics

- 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

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14-8. Theoretical models of chemical kinetics



Chilkoot pass, Klondike gold rush, 1898

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14-8. Theoretical models of chemical kinetics

**Key concepts of:**

- collision theory:
  - most collisions do not result in a reaction
  - need sufficient energy & correct relative orientation
- transition state theory:
  - hypothetical species, short lifetime
  - highest energy point in reaction
  - $k$  determined by  $E_a$
  - difference in activation energies determines the equilibrium position

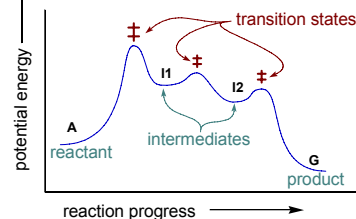
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### 14-10. Reaction mechanism

- ...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 ( $A \rightarrow G$ )

### 14-10. Reaction mechanisms

Multistep reactions consist of two or more elementary steps: from reactant to intermediate 1 ( $A \rightarrow I_1$ ), from intermediate 1 to intermediate 2 ( $I_1 \rightarrow I_2$ ), and from intermediate 2 to product ( $I_2 \rightarrow G$ )



### 14-10. Reaction mechanisms

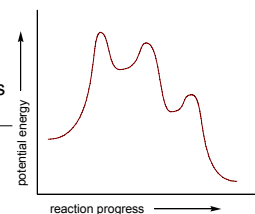
#### Elementary Processes...

- May be unimolecular (dissociation), or bimolecular (association). Termolecular = rare
- Have reaction orders the same as their stoichiometry
- 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 *rate-limiting* (when an elementary process is much slower than all others)

### iClicker Question #5

How many transition states and intermediates are there in this reaction profile?

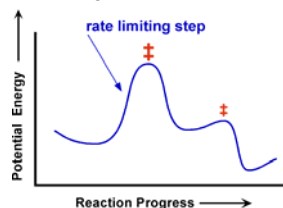
	# of transition states	# of intermediates
A	1	4
B	2	3
C	3	2
D	3	3



### 14-10. Reaction mechanisms

#### Case 1: Slow initial step followed by a fast step

- first step is rate-limiting  $\rightarrow$  rate law determined by first step



- e.g.,  $S_N1$  reaction of  $t\text{Bu-Cl} + \text{F}^-$   
 $v_0 = k[t\text{Bu-Cl}]$

### 14-10. Reaction mechanisms

#### Case 2: Fast equilibrium step followed by a slow step

- Overall reaction:



- Experimentally determined rate law:

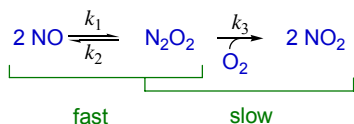
$$v_0 = k[\text{NO}]^2[\text{O}_2] \quad (18)$$

- 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:



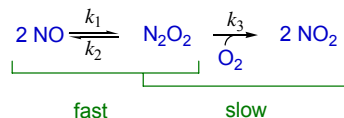
- assume that  $k_3$  is rate-limiting, and hence:

$$v_0 = k_3[\text{N}_2\text{O}_2][\text{O}_2] \quad (19)$$

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#### 14-10. Reaction mechanisms

- $\text{N}_2\text{O}_2$  is an intermediate, and thus **must not** appear in the rate equation  $\rightarrow$  we need to express  $[\text{N}_2\text{O}_2]$  differently:
- $[\text{N}_2\text{O}_2]$  at equilibrium depends on  $[\text{NO}]$ :



$$K_{12} = [\text{N}_2\text{O}_2]/[\text{NO}]^2 \quad (20)$$

or

$$[\text{N}_2\text{O}_2] = K_{12}[\text{NO}]^2 \quad (20a)$$

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#### 14-10. Reaction mechanisms

- combining eq. 19 and 20a:

$$v_0 = k_3 K_{12} [\text{NO}]^2 [\text{O}_2] \quad (18a)$$

or

$$v_0 = k [\text{NO}]^2 [\text{O}_2] \quad \text{where } k = k_3 K_{12} \quad (18)$$

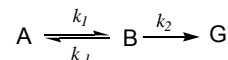
- eq. 18a is consistent with the observed rate law (18), so the proposed mechanism is consistent with the experimental observations

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#### 14-10. Reaction mechanisms

**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  $\rightarrow$  use steady state approximation.

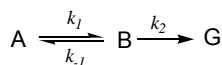


- 1<sup>st</sup> assumption:  $v_0 = k_2 [B]$  (21)  
(always true, whether step 2 is rate-limiting or not)
- As B is an intermediate, [B] must be replaced in the rate law

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#### 14-10. Reaction mechanisms

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



- Production of B:  $v_0 = k_1 [A]$  (22)

$$\text{equals consumption of B: } v_0 = k_{-1} [B] + k_2 [B] \quad (23)$$

- Combine:  $k_1 [A] = k_{-1} [B] + k_2 [B]$  (24)

- Isolate [B]:  $[B] = \frac{k_1 [A]}{k_{-1} + k_2}$  (24a)

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#### 14-10. Reaction mechanisms

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

$$v_0 = \frac{k_2 k_1 [A]}{k_{-1} + k_2} \quad (25)$$

- 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:

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#### 14-10. Reaction mechanisms

- When  $k_{-1} \gg k_2$  (reversible fast first step, slow second step):

- Then 
$$v_o = \frac{k_2 k_1 [A]}{k_{-1} + k_2} \quad (25)$$

- simplifies to 
$$v_o = \frac{k_2 k_1 [A]}{k_{-1}} = k_2 K_{12} [A]$$

- which is like in Case 2

#### 14-10. Reaction mechanisms

- When  $k_2 \gg k_1$ , and  $k_{-1} \approx 0$  (slow first step, fast second step):

- Then (23) simplifies from: 
$$v_o = \frac{k_2 k_1 [A]}{k_{-1} + k_2} \quad (25)$$

- to: 
$$v_o = k_1 [A] \quad (21d)$$

- which is like in Case 1

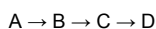
#### 14-10. Reaction mechanisms

##### Key concepts:

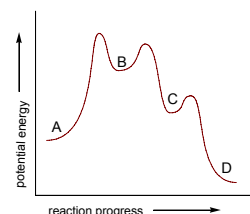
- mechanism is the elementary processes of a reaction
- must be consistent with stoichiometry, rate equation
- slowest step = rate-limiting step

#### iClicker Question #6

Which is the slowest step in this reaction from A to D?



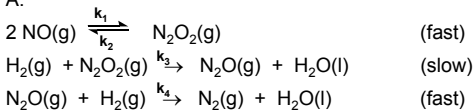
- (a)  $A \rightarrow B$   
 (b)  $B \rightarrow C$   
 (c)  $C \rightarrow D$   
 (d)  $A \rightarrow D$



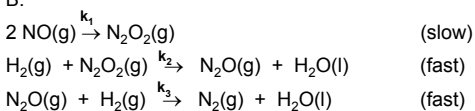
#### Take-Home Practice Problem

The experimentally determined rate law for the reaction:  
 $2 \text{NO(g)} + \text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + \text{H}_2\text{O(l)}$  is  $v = k[\text{H}_2][\text{NO}]^2$ .  
 Which of the following mechanisms is consistent with this rate law?

A:



B:



#### Take-Home Practice Problem – Solution

The rate law for each mechanism is based on the rate-determining, or slow, step.

For mechanism A the rate law is based on the second step:  
 $v = k[\text{H}_2][\text{N}_2\text{O}_2]$ . The  $\text{N}_2\text{O}_2$  is a reactive intermediate, so it must be replaced in the rate law with species that appear in the overall reaction.

From the equilibrium in Step 1, rate forward = rate reverse, and thus  $k_1[\text{NO}]^2 = k_2[\text{N}_2\text{O}_2]$ . Isolate for  $[\text{N}_2\text{O}_2] = k_1[\text{NO}]^2/k_2$  and substitute into the rate law:

$$v = k_3[\text{H}_2]\{k_1[\text{NO}]^2/k_2\} \text{ or } v = k[\text{H}_2][\text{NO}]^2 \text{ with all the constants combined. This is consistent with experiment.}$$

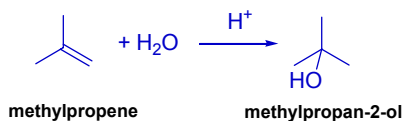
For mechanism B the rate law is based on the first step:  
 $v = k[\text{NO}]^2$ . This is not consistent with experiment.

## 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:

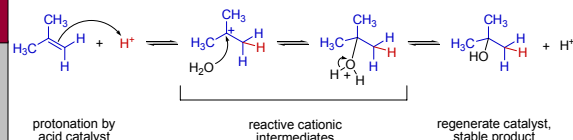


- e.g., acid-catalyzed hydration of an alkene:



## 14-11. Catalysis

- Mechanism:



## 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

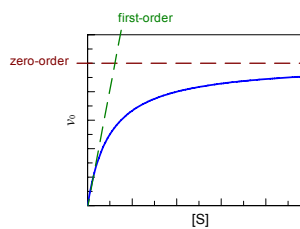
### Key concepts:

- catalysts are unchanged by reaction
- used to lower  $E_a$
- homogeneous vs. heterogeneous

## 14-11. Catalysis

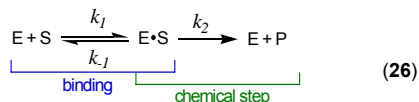
### Enzymes are protein catalysts

- highly specific toward certain reactants (**substrate, S**)
- at low [S], reaction is 1<sup>st</sup>-order in [S]<sub>0</sub>
- at very high [S], reaction is 0<sup>th</sup>-order in [S]<sub>0</sub>



### 14-11. Enzyme catalysis

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

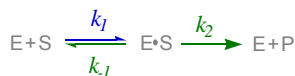


- 1<sup>st</sup> assumption:  $[\text{S}]_0 \gg [\text{E}]_0$  (this is true for most enzymatic reaction, and results in:  $[\text{S}] \gg [\text{E} \cdot \text{S}]$ , and  $[\text{S}] = [\text{S}]_0$ )
- 2<sup>nd</sup> assumption (always true):  $v_0 = k_2[\text{E} \cdot \text{S}]$  (27)
- 3<sup>rd</sup> assumption: steady state approximation:  $\frac{d[\text{E} \cdot \text{S}]}{dt} = 0$  (28)

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### 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  $\text{E} \cdot \text{S}$  formation = rate of  $\text{E} \cdot \text{S}$  breakdown  
 $k_1[\text{S}][\text{E}]_{\text{free}} = (k_{-1} + k_2)[\text{E} \cdot \text{S}]$  (29, 14.35)

- we know the total  $[\text{E}]$  ( $= [\text{E}]_0$ ), but not  $[\text{E}]_{\text{free}}$   
 $\rightarrow$  a bunch of algebra to recast  $[\text{E}]_{\text{free}}$  in terms of  $[\text{E}]_0$ ...

See page 641 of Petrucci, 10<sup>th</sup> ed. for this derivation.

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### 14-11. Catalysis: steady-state approximation

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

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

$$v_0 = \frac{k_2 [\text{E}]_0 [\text{S}]}{(k_{-1} + k_2)/k_1 + [\text{S}]}$$

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

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### 14-11. Catalysis: steady-state approximation

#### Michaelis-Menten equation:

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

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

- therefore:
  - $k_{\text{cat}} = k_2$
  - the rate-limiting step, units of 1/time (e.g., s<sup>-1</sup>)
  - the enzyme's maximal rate, when  $[\text{E} \cdot \text{S}] = [\text{E}]_0$
  - $[\text{E} \cdot \text{S}] = \frac{[\text{E}]_0 [\text{S}]}{K_M + [\text{S}]}$

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### 14-11. Catalysis: steady-state approximation

#### Michaelis-Menten equation:

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

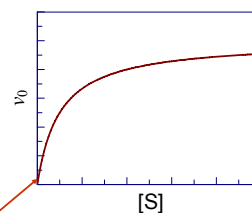
- $K_M$  is the value of  $[\text{S}]$  at which the rate is  $1/2$  maximal
- $K_M$  has units of concentration (e.g., M)
- for example:

	$[\text{E} \cdot \text{S}]$	$v_0$
$[\text{S}] \gg K_M$	$[\text{E}]_0$	$k_{\text{cat}} [\text{E}]_0$
$[\text{S}] = K_M$	$1/2 [\text{E}]_0$	$1/2 k_{\text{cat}} [\text{E}]_0$
$[\text{S}] \ll K_M$	$\approx 0$	low

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### 14-11. Catalysis: steady-state approximation

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



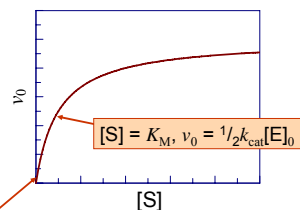
$[\text{S}] \ll K_M, v_0 = k_{\text{cat}} [\text{E}]_0 [\text{S}] / K_M$

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### 14-11. Catalysis: steady-state approximation

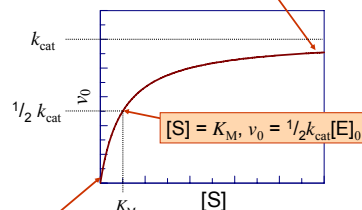
$$v_0 = \frac{k_{\text{cat}}[E]_0[S]}{K_M + [S]}$$



$$[S] \ll K_M, v_0 = k_{\text{cat}}[E]_0[S]/K_M$$

### 14-11. Catalysis: steady-state approximation

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



$$[S] \ll K_M, v_0 = k_{\text{cat}}[E]_0[S]/K_M$$

### 14-11. Catalysis

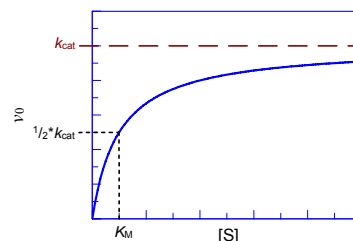
#### Key concepts:

- Michaelis-Menten equation
  - 3 assumptions:
    - $[E]_0 \ll [S]$
    - $k_2$  is rate limiting
    - steady state approximation
  - reaction order changes with  $[S]$

### iClicker Question #7

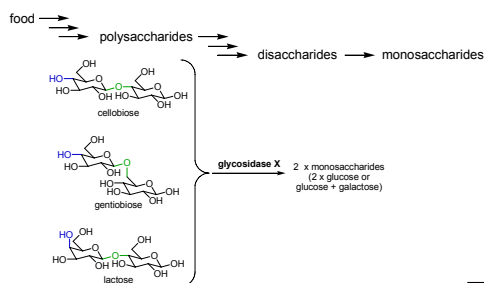
What is the reaction order w.r.t.  $[S]$  when  $[S] \ll K_M$ ?

- A. 2  
B. 1  
C. 0.5  
D. 0



### 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:

$$k_{\text{cat}} = 10 \text{ s}^{-1}$$

$$K_M = 10^{-4} \text{ M.}$$

If:

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

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

what is  $v_0$ ?

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

$$v_0 = (10 \text{ s}^{-1} \times 10^{-7} \text{ M} \times 10^{-5} \text{ M}) / (10^{-4} \text{ M} + 10^{-5} \text{ M})$$

$$= 9 \times 10^{-8} \text{ M/s}$$

### Take-Home Practice: Practical enzyme kinetics

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

$$v_0 = (10 \text{ s}^{-1} \times 10^{-7} \text{ M} \times 2 \times 10^{-5} \text{ M}) / (10^{-4} \text{ M} + 2 \times 10^{-5} \text{ M}) \\ = 1.7 \times 10^{-7} \text{ M/s}$$

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

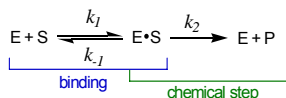
When  $[S] \ll K_m$ , the reaction is first order w.r.t.  $[S]$ , which is the case in this question.

### Take-Home Practice: Practical enzyme kinetics

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

There is almost no change in  $v_0$  when  $[S]$  doubles, so the reaction is roughly zero order w.r.t.  $[S]$ . This occurs when  $[S] \gg K_m$ , so we know that  $K_m$ (cellobiose)  $\ll 2 \times 10^{-4}$  M.

### Enzyme Catalysis: Concept Check



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

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

Yes. Then we end up with

$$k_1[\text{S}][\text{E}]_{\text{free}} = (k_{-1} + k_2)[\text{E} \cdot \text{S}] \quad \text{but } k_{-1} = 0, \text{ so} \\ k_1[\text{S}][\text{E}]_{\text{free}} = k_2[\text{E} \cdot \text{S}]$$

### 14-9. Effect of temperature on reaction rates

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

$$k = Ae^{-E_a/RT} \quad (32, 14.21)$$

- 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

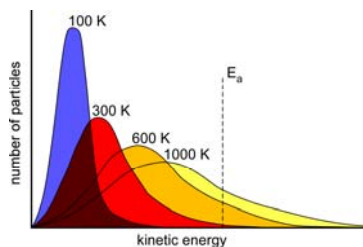
### 14-9. Effect of temperature on reaction rates

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

#### Concept check:

What effect does an increase in  $T$  have on  $k$ ?

$k \approx 0$  at 100 K  
 $k$  small at 300 K  
 $k \uparrow$  at 600 K  
 $k \uparrow$  at  $10^3$  K



### 14-9. Effect of temperature on reaction rates

- rewrite eq. 32:

$$\ln(k) = -E_a/RT + \ln(A) \quad (32a)$$

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

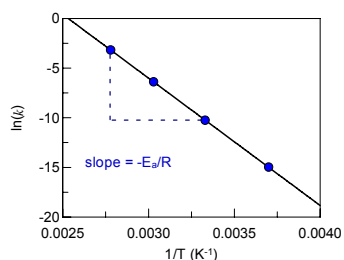
$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (33, 14.22)$$

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

$$\ln \frac{k_2}{k_1} = \frac{1}{RT} (E_{a1} - E_{a2}) \quad (34)$$

#### 14-9. Effect of temperature on reaction rates

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (33, 14.22)$$



#### Take-Home Practice Problem

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

Solution:  $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

$T_1 = 673 \text{ K}$ ,  $T_2 = 703 \text{ K}$  and  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $k_1 = 0.018 \text{ s}^{-1}$  and  $k_2 = \ln 2 / 4.81 \text{ s} = 0.144 \text{ s}^{-1}$

Substitute and solve:

$$\ln \frac{0.144}{0.018} = \frac{E_a}{8.314 \text{ J/Kmol}} \left( \frac{1}{673 \text{ K}} - \frac{1}{703 \text{ K}} \right)$$

$$E_a = 272,650 \text{ J mol}^{-1} = 2.7 \times 10^2 \text{ kJ mol}^{-1}$$

#### 14-9. Effect of temperature on reaction rates

##### Key concepts:

- reactions are faster at higher  $T$
- meaning of  $A$  and  $e^{-E_a/RT}$
- Arrhenius graph

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