

# CHEM 116

## Collision Theory and Reaction Mechanisms

Lecture 13  
Prof. Sevian

Note: If there is anything we do not finish about reaction mechanisms today, that is where we will start on Tuesday with Lecture 14.



## Today's agenda

Kinetics: the study of the rates of chemical reactions

- Using data that can be experimentally obtained to determine rate laws
  - Finish example of a table of initial reaction rates to determine the order of reaction for different species involved in a reaction, and the value and units for rate constant ( $k$ )
  - The special case of first-order rate laws
- Modeling kinetics at the particle level
  - Collision theory for explaining/predicting why different factors (e.g., concentration, temperature) affect rate
  - Arrhenius equation for explaining/predicting temperature dependence of rate constant ( $k$ )
  - Reaction mechanisms

## Method 2: Determining rate law by measuring initial rate at various concentrations

### Example

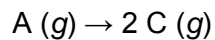
Given the following measurements of initial rate of reaction under various conditions of initial concentrations of reactants, determine:

- the rate law
- the value of the rate law constant,  $k$
- the units of  $k$

Experiment	Initial Concentration (M)		Initial rate (M/s)
	[NO]	[O <sub>2</sub> ]	
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

## A clicker question about material we covered at the last lecture

The rate of appearance of C is  $6.2 \times 10^{-2}$  mol/L·s in the chemical reaction below.



What is the rate of disappearance of A?

- (A)  $-6.2 \times 10^{-2}$  mol/L·s
- (B)  $-1.2 \times 10^{-1}$  mol/L·s
- (C)  $-3.1 \times 10^{-2}$  mol/L·s
- (D) There is not enough information to tell.

## Half-life

The amount of time it takes for half of the reactant to react (disappear)

Mathematical definition

Need to find time at which concentration of the reactant is equal to half the initial concentration

$[A]_t$  is a function of  $t$

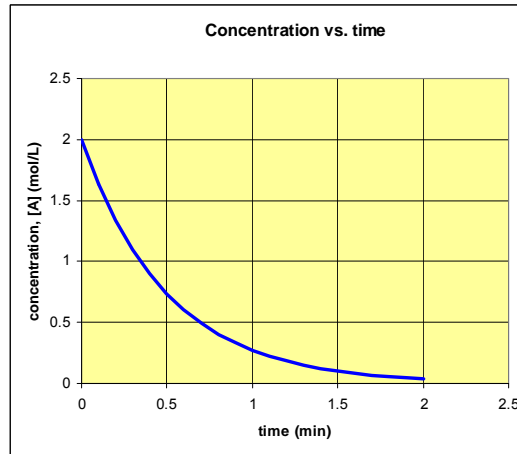
For first - order,  $[A]_t$  given by

$$\ln[A]_t = \ln[A]_0 - kt$$

Half - life is the value of  $t$  when

$$[A]_t = \frac{1}{2}[A]_0$$

Graphical representation



What does  $t_{1/2}$  equal in this example?

## General equation for half-life

If the reaction is first-order, meaning  $\left\{ \begin{array}{l} \text{Rate} = \frac{\Delta[A]}{\Delta t} = k[A] \\ \ln[A]_t = \ln[A]_0 - kt \end{array} \right.$

differential  
rate law

integrated  
rate law

and if you know the value of the rate law constant  $k$ ,  
then you can determine the half-life algebraically

Looking for value of  $t$  when  $[A]_t = \frac{1}{2}[A]_0$ , or  $\frac{[A]_0}{[A]_t} = 2$

$$\ln[A]_t = \ln[A]_0 - kt$$

Rearranging,

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

So at the time where half the reactant is gone :

$$\ln(2) = k t_{\text{half-life}}$$

$$t_{\text{half-life}} = \frac{\ln(2)}{k}$$

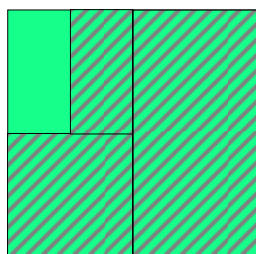
$$t_{\text{half-life}} = \frac{0.693}{k}$$

or

$$k = \frac{0.693}{t_{\text{half-life}}}$$

## Sometimes it is easier to work with the half-life

Example: If a given reaction is first-order and the half-life is 2.5 minutes, how much reactant remains after 5.0 minutes have passed if the initial amount of reactant is 100. grams?



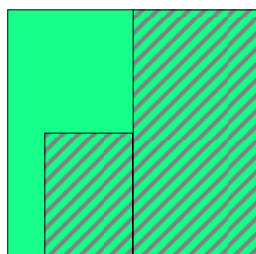
Amount of reactant	# of half-lives
All (100%)	0
Half (50%)	1
One-fourth (25%)	2
One-eighth (12.5%)	3

Amount of reactant remaining :

$$[A] = \left(\frac{1}{2}\right)^{\# \text{ of half-lives}} [A]_0$$

## Example of working with the half-life

Example: If a given reaction is first-order and the half-life is 2.5 minutes, how much reactant remains after 4.0 minutes have passed if the initial amount of reactant is 100. grams?



Amount of reactant	# of half-lives
All (100%)	0
Half (50%)	1
One-fourth (25%)	2

$$[A] = \left(\frac{1}{2}\right)^{\# \text{ of half-lives}} [A]_0$$

$$\# \text{ of half-lives} = \frac{\text{time}}{t_{\text{half-life}}} = \frac{4.0 \text{ min}}{2.5 \text{ min}} = 1.6$$

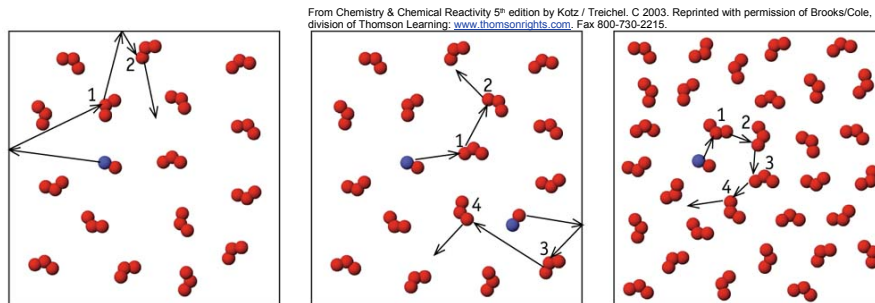
$$[A] = \left(\frac{1}{2}\right)^{1.6} [A]_0 = 0.3299(100. \text{g}) = 33 \text{ g}$$

## All nuclear decay processes are first-order

### Example

Radioactive iodine-125, which is used for studies of thyroid functioning, has a rate constant for decay of  $0.011 \text{ day}^{-1}$ . If you begin a treatment with iodine-125, and start with  $1.6 \times 10^{15}$  atoms, how many atoms remain after 2.0 days?

## Reaction rates: what's happening at the particle level?



(a) 1 NO: 16 O<sub>3</sub> – 2 hits/second

(b) 2 NO: 16 O<sub>3</sub> – 4 hits/second

(c) 1 NO: 32 O<sub>3</sub> – 4 hits/second

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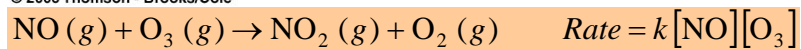
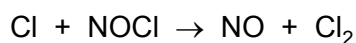


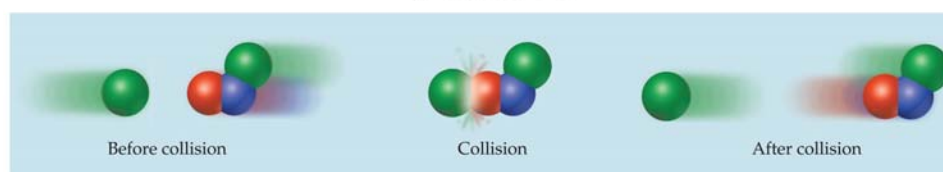
Figure	Ratio of NO:O <sub>3</sub>	# of collisions per sec
(a)	1/16	2
(b)	2/16	4
(c)	1/32	4

For a nice review of these concepts, along with animations, see <http://www.sciencepages.co.uk/keystage4/GCSEChemistry/m3ratesofreaction.php>

## Why isn't collision frequency the only factor affecting reaction rate?



(a) Effective collision



(b) Ineffective collision

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Why is (a) effective and (b) is ineffective?

## What affects the reaction rate?

### Macroscopic level

Evidence: use experimental measurements to determine orders and value of  $k$  in rate law

1. When you increase reactant concentrations, rate of reaction increases
2. When you increase temperature, rate of reaction increases
3. Some reactions have very slow rates and some very fast rates – what differs is the value of  $k$

*Assumption: Rate laws always have the mathematical form*

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

### Particle level

What we *believe* is happening at the particle level that explains why reaction rates have the mathematical form they do

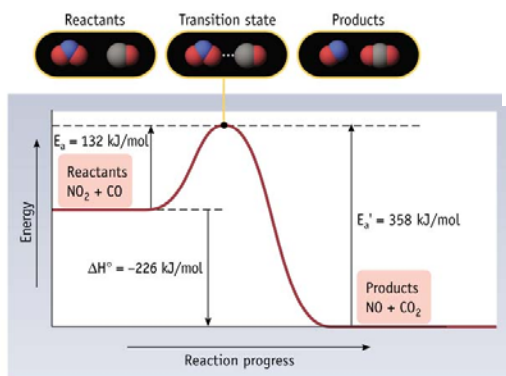
- 1. When there are more reactant particles, they collide more often
- 2. When the average speeds of reactant particles increases, they collide more often
- 3. There must be some reason for this at the particle level...

*Assumption: in order for molecules to react with each other, they must collide*

What is the theoretical basis for the form of the rate law? Must be based on how particles behave.

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

1. Numbers of particles: reflected in concentration
2. Temperature: must be part of  $k$
3. There must be something else that is part of  $k$  that explains why two reactions at the same  $T$  can have different values of  $k$



### Energy considerations: Activation barrier

Forward:  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$

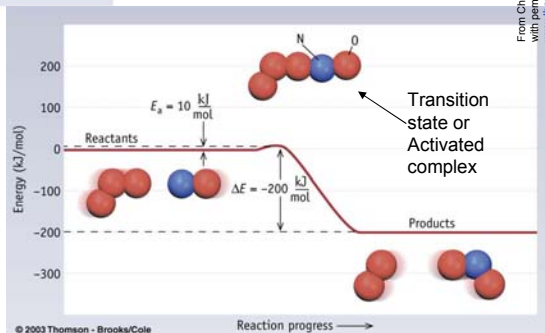
Activation energy: 132 kJ/mol  
Heat of reaction is exothermic

Reverse:  $\text{NO} + \text{CO}_2 \rightarrow \text{NO}_2 + \text{CO}$

Activation energy: 358 kJ/mol  
Heat of reaction is endothermic

Forward:  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$   
Activation energy: 10 kJ/mol  
Heat of reaction is exothermic

Reverse:  $\text{NO}_2 + \text{O}_2 \rightarrow \text{NO} + \text{O}_3$   
Activation energy: 210 kJ/mol  
Heat of reaction is endothermic



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## What does the rate constant depend on?

$$k = A e^{-E_a/RT}$$

**Rate constant that appears in the rate law:**  
*Rate* =  $k [A]^n [B]^m$

(Note - unfortunate coincidence that can confuse: same letter *A* used for this constant and generic reactant name.)

**A constant that depends on the fraction of collisions in which molecules collide with an orientation that a reaction will result from**

**Temperature (in Kelvin): as temperature gets higher, *k* gets larger**

**Activation energy barrier: as  $E_a$  gets larger, *k* gets smaller**

## Experimental determination of activation energy

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\underbrace{(\ln k)}_y = \underbrace{(\ln A)}_a - \underbrace{\frac{E_a}{R}}_b \underbrace{\left(\frac{1}{T}\right)}_x$$

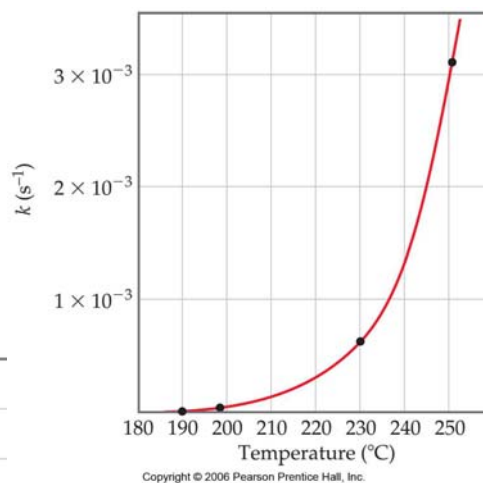
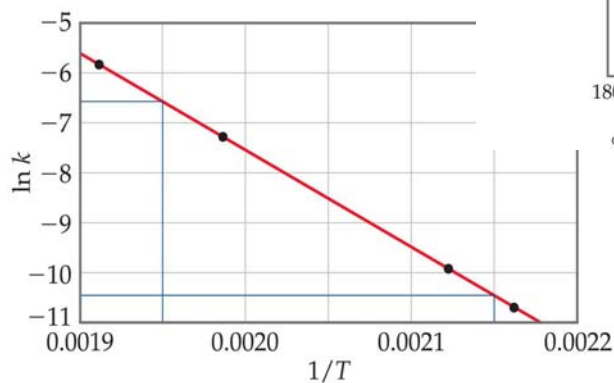
Experimental scenario:

1. Determine form of rate law
2. Form should remain the same at different temperatures
3. Run experiments at many temperatures and experimentally determine  $k$  vs.  $T$



## Which is easier to interpret?

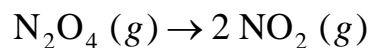
Data correspond to Sample Exercise 14.11 on p. 598



## Calculating activation energy from rate constant vs. temperature data

### Example

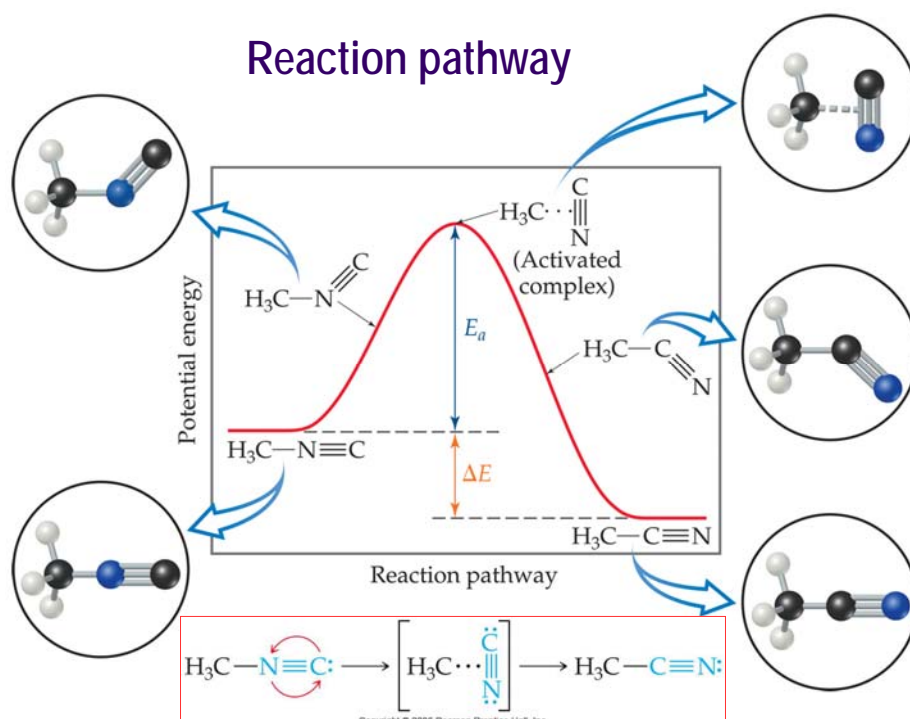
The decomposition of  $\text{N}_2\text{O}_4$  gas is first order.



The rate constant  $k = 4.5 \times 10^3 \text{ s}^{-1}$  at  $1.0 \text{ }^\circ\text{C}$  and  $1.00 \times 10^4 \text{ s}^{-1}$  at  $10.0 \text{ }^\circ\text{C}$ .  
What is the activation energy?

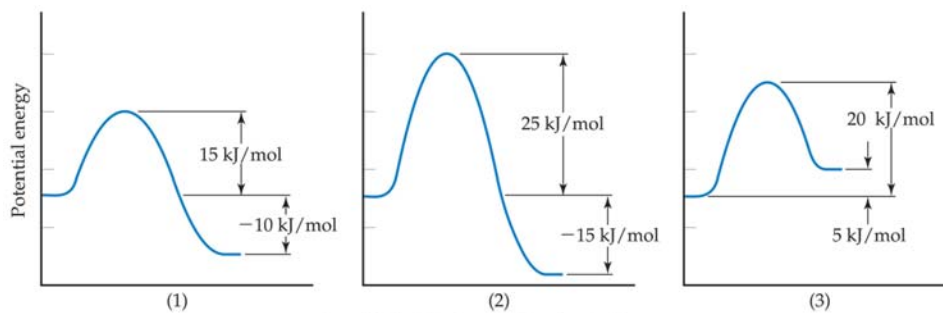
## Key points about kinetics so far

- There are two ways to determine a rate law experimentally
  1. Data needed: concentration vs. time as a single experiment progresses  
Process: graph versions of  $[A]$  vs.  $t$  to determine value of  $n$  in  $d[A]/dt = -k[A]^n$
  2. Data needed: multiple experiments varying initial concentration, measure initial rate for a chemical in the rxn  
Process: compare experiments to determine values of  $n$  (and  $m$ ) for each reactant in rate =  $k[A]^n[B]^m$
- In a first-order reaction, it is often easier to work with half-life to predict amount of reactant remaining
- Rate law constant,  $k$ , depends on temperature and activation energy,  $E_a$ , as well as other factors (e.g., % of collisions that are properly oriented). Value of  $E_a$  can be determined by measuring  $k$  vs.  $T$  and using Arrhenius equation to interpret results.



## Relating energy profiles, activation energies, and speeds of reaction

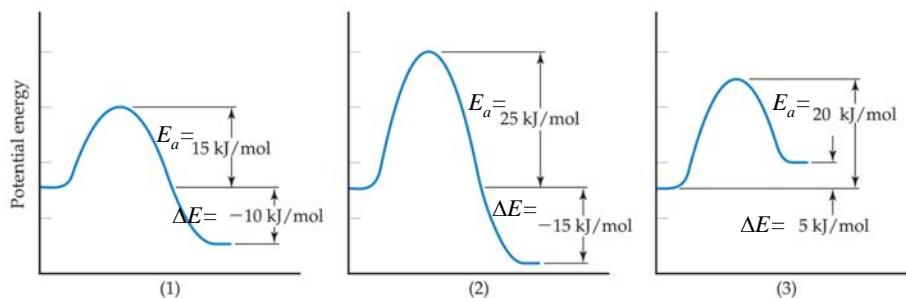
Rank these three reactions from slowest to fastest, assuming they have the same value for  $A$  (in Arrhenius equation,  $k = Ae^{-E_a/RT}$ ).



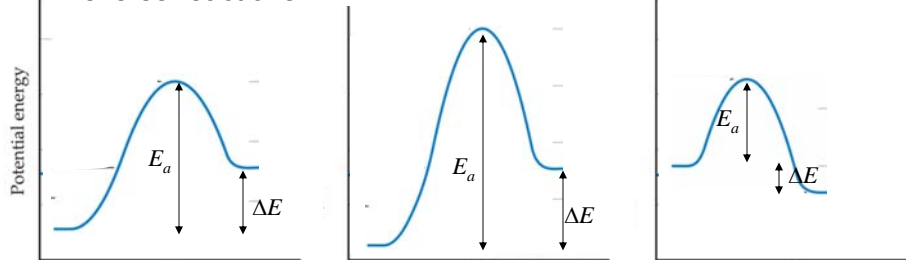
What would the energy profiles look like if you were talking about the reverse reactions?

## Reversing an energy profile

Forward reactions



Reverse reactions

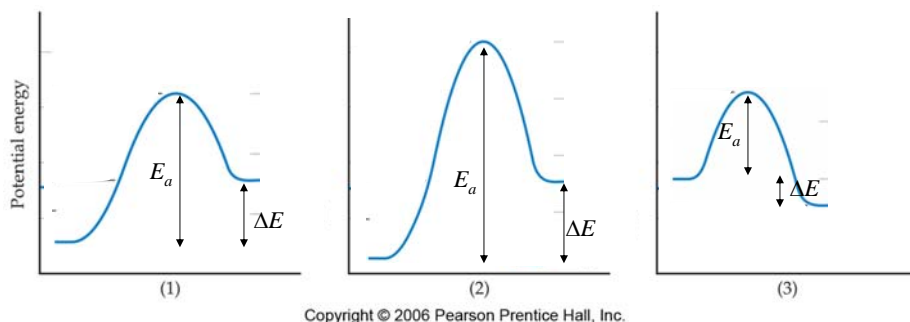


## Clicker question:



## Relating energy profiles, activation energies, and speeds of reaction

Rank the **reverse reactions** from slowest to fastest, assuming they have the same value for  $A$  (in Arrhenius equation,  $k = Ae^{-E_a/RT}$ ).



Clicker choices:

(A) Rxn (1) is the fastest

(B) Rxn (2) is the fastest

(C) Rxn (3) is the fastest

## What is a reaction mechanism?

- A proposed sequence of ELEMENTARY STEPS by which the reaction *could* proceed, in such a way that the EXPERIMENTALLY DETERMINED RATE LAW can be derived from the combination of the elementary steps.
  1. The steps must sum to the overall reaction
  2. The mathematical combination of the rates of the elementary steps must result in the experimentally determined rate law
- There is often more than one possible reaction mechanism that would result in the same experimentally determined rate law.
- Very important to remember: the only way to find out the form of the actual rate law is to determine it experimentally. The actual rate law cannot be predicted from the overall reaction.

## Elementary reactions

- An elementary reaction is one of the steps in a reaction mechanism
- Elementary reactions are (we propose) the actual steps that chemicals go through as they progress from initial reactants to final products
- Because elementary reactions are the actual steps, they contain information about the molecularity of the collisions that must happen in order for an elementary step to occur
- Since the molecularity information is in the elementary reaction, you can write down a rate law based on that molecularity
- Examples of rate laws for some elementary reactions
  - $A \rightarrow B$       rate =  $k [A]$
  - $2A \rightarrow C$       rate =  $k [A]^2$
  - $A + B \rightarrow D$       rate =  $k [A] [B]$
- Be careful: you cannot write down the rate law for an overall reaction by inspection of the reaction, because most overall reactions are not elementary (i.e., most reactions have complicated mechanisms)

## Example of a reaction mechanism

Molecularity is...

Overall reaction



Has experimentally observed rate law:



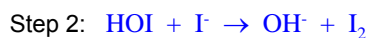
✓ Condition 2 is satisfied

Rate-determining step

Proposed reaction mechanism (is this plausible?)



(slow step)      Rate =  $k_1 [\text{I}^-] [\text{H}_2\text{O}_2]$



(fast step)      Rate =  $k_2 [\text{HOI}] [\text{I}^-]$



(fast step)      Rate =  $k_3 [\text{H}^+] [\text{OH}^-]$



Intermediates       $2 \text{I}^- + 2 \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{I}_2 + 2 \text{H}_2\text{O}$       ✓ Condition 1 is satisfied

## Another example of a reaction mechanism

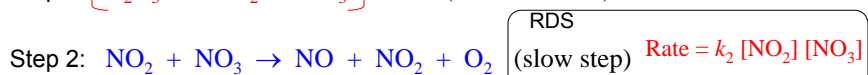
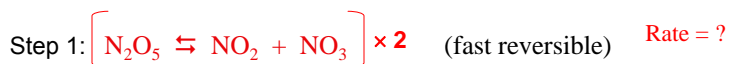
Overall reaction



Has experimentally observed rate law:

$$\text{Rate} = k [\text{N}_2\text{O}_5]$$

Proposed reaction mechanism (is this plausible?)



✓ Condition 1 is satisfied

## What is a “fast reversible” reaction?

- Reversible means reaction proceeds in both directions
- Equilibrium means forward rate = reverse rate (a state of dynamic equilibrium)
- Sometimes “fast reversible” is written “fast equilibrium”  
these are equivalent terms



is shorthand for saying



happens simultaneously with



$$\text{Rate}_{\text{forward}} = k_{\text{forward}} [\text{N}_2\text{O}_5]$$

and

$$\text{Rate}_{\text{reverse}} = k_{\text{reverse}} [\text{NO}_2] [\text{NO}_3]$$

but since forward rate and reverse rate are equal,

$$k_{\text{forward}} [\text{N}_2\text{O}_5] = k_{\text{reverse}} [\text{NO}_2] [\text{NO}_3]$$

## How do we combine a fast reversible rate with a rate-determining step?

Goal: to find out if the rate law predicted by the mechanism has the same mathematical form as the experimentally determined rate law

So far we have:

Experimentally determined rate law:  $\text{Rate} = k [\text{N}_2\text{O}_5]$

Proposed mechanism's RDS:  $\text{Rate} = k_2 [\text{NO}_2] [\text{NO}_3]$

Proposed mechanism's fast reversible:  $k_{\text{forward}} [\text{N}_2\text{O}_5] = k_{\text{reverse}} [\text{NO}_2] [\text{NO}_3]$

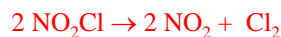
Solve the second equation for  $([\text{NO}_2][\text{NO}_3])$  and substitute into RDS

$$\begin{aligned} \text{Rate} &= k_2 \left( \frac{k_{\text{forward}}}{k_{\text{reverse}}} \right) [\text{N}_2\text{O}_5] \\ &= k_{\text{combination}} [\text{N}_2\text{O}_5] \quad \checkmark \text{ Condition 2 is satisfied} \end{aligned}$$

## Another example

(similar to Sample Exercise 14.15, p. 606)

Overall reaction



Has experimentally observed rate law:

$$\text{Rate} = k \frac{[\text{NO}_2\text{Cl}]^2}{[\text{NO}_2]}$$

Is the following proposed reaction mechanism plausible?

Step 1:  $\text{NO}_2\text{Cl} \rightleftharpoons \text{NO}_2 + \text{Cl}$  (fast reversible)

Step 2:  $\text{NO}_2\text{Cl} + \text{Cl} \rightarrow \text{NO}_2 + \text{Cl}_2$  (slow step)

- Identify intermediates
- What effect does increasing the concentration of the product  $\text{NO}_2$  have on the reaction rate?

## Key points about rxn mechanisms

- A rxn mechanism is plausible if it satisfies two conditions
  1. The elementary steps must sum to the overall rxn
  2. The rate of the slowest elementary step has the same form as the experimentally determined rate law (may involve mathematical manipulation)
- You cannot write down a rate law by inspection of an overall reaction
- You CAN write down a rate law by inspection of an elementary step, because it contains information about the molecularity of the step
- Fast equilibrium/fast reversible reaction means forward rate equals reverse rate
- The chemicals that cancel out when you sum elementary steps are the intermediates in a rxn mechanism