• How to talk about Rate
  rate = $\Delta$[chemical]/$\Delta$time
  rate of disappearance of reactant or
  rate of appearance of product
  use coefficients to change one rate to
  another
  watch your signs ($\Delta$[React.] = -$\Delta$[Prod.])
  instantaneous rate is slope of [R] vs. time
  graph. Initial rate is often used.

• How to Speed Up a Reaction
  [Use Collision Theory, Kinetic Molecular Theory]
  increase the concentration of reactants
  - increase molarity of solutions
  - increase partial pressure of gases
    [collision model: more collisions]
  more surface area between unlike phases
  [collision model: more collisions]
  increase the temperature
  [collision model: more & harder collisions]
  add a catalyst
  - homogeneous catalyst (used & reformed)
  - heterogeneous catalyst (surface catalyst)
    [collision model: alternate mechanism that
    requires lower energy collision or
    ensures that correct particles collide]

• Two Important Diagrams
  PE energy profile of a reaction

ΔH of the reaction relates reactant and product
PE’s / exo- or endothermic/ downhill, -ΔH, or
uphill, +ΔH

Activation energy ($E_a$) = energy barrier
  • activated complex (at the peak)
  • whether a reaction is fast or slow depends
    on the activation energy in the PE profile
  • PE profile does not change with change in
    temperature of the reactants?
  • adding a catalyst lowers the $E_a$

The KE distribution of a substance

- temperature is a measure of the average KE
  - increasing temperature spreads out curve to the
    right, increases average KE

- adding a catalyst moves the threshold energy
  ($E_a$) to the left.

How do these two picture relate to each other
  (turn the KE on its side... the particles use their
  KE to provide the needed PE to react)

• Reaction mechanisms
  - step-by-step...two particles at a time
  - example

  overall:
  $4 \text{HBr} + \text{O}_2 \rightarrow 2 \text{Br}_2 + 2 \text{H}_2\text{O}$

  mechanism:
  $\text{HBr} + \text{O}_2 \rightarrow \text{HOOBr}$
  $\text{HOOBr} + \text{HBr} \rightarrow 2 \text{HOBr}$
  $\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$
  $\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$

  [note: HOOBr and HOBr are not in the
  overall reaction because they are neither
  reactants nor products, they are “reactive
  intermediates”]
  - overall reaction is sum of steps
  - slowest step is rate-determining step
Rate Laws
- what they mean
- how to determine them
- how they relate to the rate determining step
- how they help you choose a mechanism

General Form:
Equation: \( A + B \rightarrow C \)
Rate = \( k \ [A]^x [B]^y \)
k is the “specific rate constant”
Use experimental data to determine \( x \), \( y \), and \( k \).

The Rate Law CANNOT be determined from the overall reaction. It MUST be determined experimentally because the rate law reflects only the “rate determining step.”

Rate law can be determined from the initial rates.
See Sample Problems 16.2 and 16.3 in Silberberg

Rate Law matches the Reaction Mechanism

**PROBLEM:** The following two reactions are proposed as elementary steps in the mechanism of an overall reaction:

1. \( \text{NO}_2\text{Cl} + \text{Cl} \rightarrow \text{NO}_2\text{Cl} + \text{Cl}_2 \) (slow)
2. \( \text{NO}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{NO}_2\text{Cl} + \text{Cl}_2 \) (fast)

(a) Write the overall balanced equation.
(b) Determine the molecularity of each step.
(c) Write the rate law for the overall reaction.

**PLAN:** (a) The overall equation is the sum of the steps.
(b) The molecularity is the sum of the reactant particles in the step.
(c) The rate law of the reaction is the rate law of the slow (rate determining) step. Intermediates must be eliminated from the rate law. See problem 5 of ALE 5 as an example of how to do this.

**SOLUTION:**
(a) \( \text{NO}_2\text{Cl} \rightarrow \text{NO}_2\text{Cl} + \text{Cl}_2 \)
(b) Step(1) is unimolecular.
Step(2) is bimolecular.
(c) The rate law for the overall reaction is the rate law of the slow (rate determining) step.
rate = \( k \ [\text{NO}_2\text{Cl}] \)

Half-life
- relationship to radioactivity
  (a first order reaction)
- the equation
  \( \ln \frac{[A]_o}{[A]} = kt \)
- the special case of half-life
  \( \ln(2) = 0.693 = kt_{1/2} \)

Order of rxn
- first and second order reactions
- what these look like graphically
- how you can graphically tell the order of a reaction

<table>
<thead>
<tr>
<th>order</th>
<th>straight-line plot</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>[Reactant] vs. t</td>
<td>-k</td>
</tr>
<tr>
<td>1</td>
<td>( \ln [\text{Reactant}] ) vs. t</td>
<td>-k</td>
</tr>
<tr>
<td>2</td>
<td>( 1/[\text{Reactant}] ) vs. t</td>
<td>k</td>
</tr>
</tbody>
</table>

Rate law can be determined from the initial rates.
See Sample Problems 16.2 and 16.3 in Silberberg

Order of rxn matches the Reaction Mechanism

**Determining \( E_a \) from calculations using the Arrhenius Equation**

\( k = A e^{-\frac{E_a}{RT}} \)

where \( k \) is the kinetic rate constant at \( E_a \) is the activation energy
\( R \) is the energy gas constant
\( T \) is the Kelvin temperature
\( A \) is the collision frequency factor

\[ \ln \left( \frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

**Acknowledgement:** This document is adapted from a similar document from South Pasadena • AP Chemistry