Chemical Kinetics: Rates of Reaction

S T U D Y   I N F O   F r o m   P a u l   G r o v e s

Three Ways to Speed Up a Reaction
 Temperature (more and harder collisions)
 Concentration (more collisions)
  increase *concentration* (of solutions)
  increase *partial pressure* (of gases)
  increase *surface area* (different phases)
 Catalyst (more effective collisions)
  homogeneous (used & reformed)
  heterogeneous (surface catalyst)
  [catalyst provides an alternate mechanism
  that requires lower energy collision or
  ensures that correct particles collide]

Converting Rates
 Reaction: $2A + 3B \rightarrow 4C$

 $$-\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{3}\frac{\Delta[B]}{\Delta t} = \frac{1}{4}\frac{\Delta[C]}{\Delta t}$$

NOTE: 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 matches the Rate Determining Step
Examples for: $2A + 3B \rightarrow C$

Rate Law matches	Rate Determining Step in the mechanism
Rate = k [A][B]	$A + B \rightarrow X$ (slow)
Rate = k [A]^2	$A + A \rightarrow X$ (slow)
Rate = k [A]^2[B]	$A + A \leftrightarrows X$ (fast) $B + X \rightarrow Y$ (slow)
Rate = k	This could be a mechanism that depends on an enzyme. Concentrations do not matter.

Graphical Method of Order of Reaction

order	straight-line plot	Slope
0	[R]$_t$ vs. t	-k
1	ln[R]$_t$ vs. t	-k
2	1/[R]$_t$ vs. t	k

Two Important Diagrams
 **PE energy profile** of a reaction

reaction coordinate
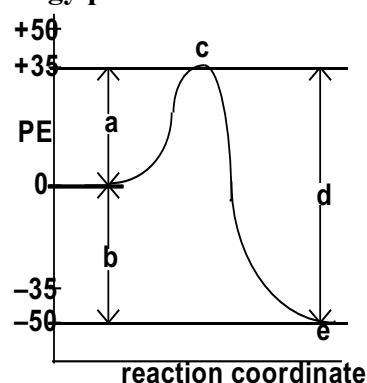
Exothermic, downhill, negative ΔH
Endothermic, uphill, positive ΔH

 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
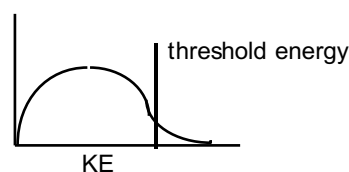
The **KE distribution** of a substance
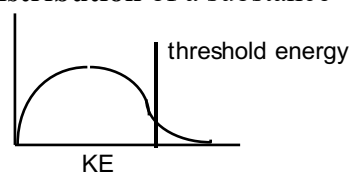
- **temperature** is the **average** KE
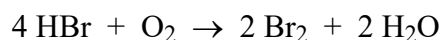-increasing temperature spreads out curve to the
 right, increases average KE
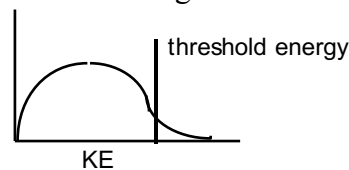
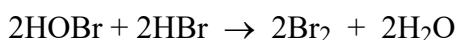- adding a **catalyst** moves the threshold energy to
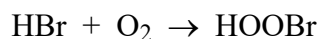 the left.

Reaction mechanisms

Overall:

$$4 \, HBr + O_2 \rightarrow 2 \, Br_2 + 2 \, H_2O$$

Mechanism:

$$HBr + O_2 \rightarrow HOOBr$$
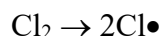$$HOOBr + HBr \rightarrow 2 \, HOBr$$
$$2HOBr + 2HBr \rightarrow 2Br_2 + 2H_2O$$

[NOTE: HOOBr and HOBr are "intermediates"]

Chain Reactions
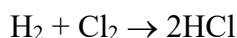
$$H_2 + Cl_2 \rightarrow 2HCl$$

- initiation steps

$$Cl_2 \rightarrow 2Cl\bullet$$

- propagation steps

$$Cl\bullet + H_2 \rightarrow HCl + H\bullet$$
$$H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$$

- termination step

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$

$$2O_3 \rightarrow 3O_2$$

- initiation step

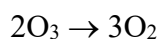$$F_2CCl_2 + UV \, light \rightarrow F_2CCl\bullet + Cl\bullet$$

- propagation steps

$$Cl\bullet + O_3 \rightarrow O_2 + ClO\bullet$$
$$ClO\bullet + O_3 \rightarrow 2O_2 + Cl\bullet$$

- termination step

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$
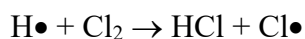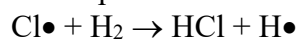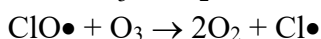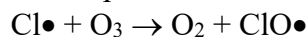
One $Cl\bullet$ can destroy 100,000 O_3 molecules.

Arrhenius Equation

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$R = 8.31$ J mol^{-1} K^{-1} (Units: E_a is in kJ mol^{-1})

Use the rate law to calculate the rate constant, k, at two different temperatures.

Determine activation energy, E_a, using the Arrhenius Equation. Since the above equation fits the "y = mx + b" expression, you can plot a graph of ln k (y-axis) vs. 1/T (x-axis). The slope of the line is $-E_a/R$.

Here is how the **equations** are given on the AP Exam and how they will appear on your chapter test:

These are the first order integrated rate law, the second order integrated rate law, and the Arrhenius Equation.

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

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

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

1. UV causes a chlorine atom to break way from the CFC molecule.

Stratosphere

2. The free chlorine atom hits an ozone molecule.

3. The chlorine atom pulls one oxygen atom away.

4. A free oxygen atom hits the chlorine monoxide molecule.

5. The result is another free chlorine atom.

6. Free chlorine will continue to deplete ozone in the stratosphere.