

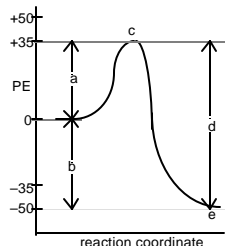
# 15 • Chemical Kinetics: Rates of Reaction

## A BLUFFER'S GUIDE

- How to talk about Rate  
 $\text{rate} = \Delta[\text{chemical}]/\Delta\text{time}$   
 rate of **disappearance** of reactant or  
 rate of **appearance** of product  
 use **coefficients** to change one rate to another  
 watch your **signs** ( $\Delta[\text{React.}] = -\Delta[\text{Prod.}]$ )  
**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

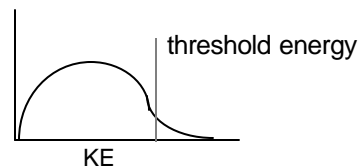


**?H** of the reaction relates reactant and product PE's / exo- or endothermic/ downhill,  $-\Delta H$ , or uphill,  $+\Delta H$

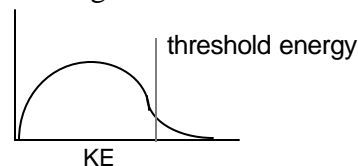
activation energy ( $E_a$ ) = energy barrier

- 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  $E_a$

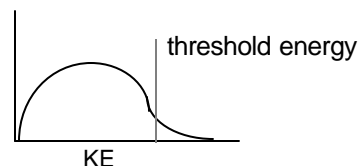
The **KE distribution** of a substance



- **temperature** is the **average KE**  
 - increasing temperature spreads out curve to the right,  
 increases average KE



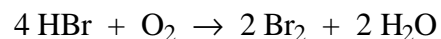
- adding a **catalyst** moves the threshold energy to the left.



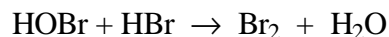
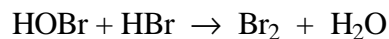
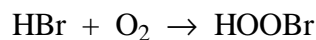
How do these two picture **relate** to each other (turn the KE on its side... the particles use their KE to provide the needed PE to react)

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

overall:



mechanism:



[note: HOBr 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:



$$\text{Rate} = k [A]^x [B]^y$$

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 Example 15.3 and Exercise 15.3*

Rate Law matches the Mechanism

Examples for:  $2A + 3B \rightarrow C$  (fill in from lecture)

Rate Law	Rate Determining Step in the mechanism
Rate = k [A][B]	$A + B \rightarrow X$ (slow)
Rate = k [A] <sup>2</sup>	$A + A \rightarrow X$ (slow)
Rate = k [A] <sup>2</sup> [B]	$A + A \rightleftharpoons X$ (fast) $B + X \rightarrow Y$ (slow) Each step is usually bimolecular. A third order overall reaction often comes from a fast equilibrium before a slow step.
Rate = k	This could be a mechanism that depends on a catalyst only. The concentrations would not matter.

order of rxn

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

order	straight-line plot	Slope
0	[R] <sub>t</sub> vs. t	-k
1	ln[R] <sub>t</sub> vs. t	-k
2	1/[R] <sub>t</sub> vs. t	k

- how this relates to the rate law

half-life

- relationship to radioactivity (a first order reaction)

- the equation

$$\ln \frac{[A]_o}{[A]_t} = kt$$

- the special case of half-life

$$\ln(2) = 0.693 = kt_{1/2}$$

chain reactions (fill in from lecture & video)

- initiation steps

- propagation steps

- termination steps

examples:

- $H_2 + Cl_2 \rightarrow 2 HCl$
- polymerization reactions (addition)
- ozone depletion

ozone layer

- specifics on why CFC's are dangerous to the ozone layer and are economically desirable here on the surface

Determining E<sub>a</sub> from calculations using the Arrhenius Equation