

## Notes for Chemistry Chapter 13 – Chemical Kinetics

I'm leaving out everything that's in the Bluffer's Guide and that I know well (meaning, common stuff that you should know from reading the book, listening in class, etc). A copy of the bluffer's guide as been included for your convenience.

1. **Chemical Kinetics** – Chemical Dynamics, concerned with the speeds, or rates, of chemical reactions
2. Rates dependent on nature of reactions, concentrations, temperature, catalysts
3. **Rate in is units of moles/Liter \* second**
4. Coefficients of OVERALL reactions show RELATIVE rates of formation/consumption
5. At any one given point on the graph of concentration/time, the slope is the rate
6. Positive rate = something is forming. Negative rate – something is disappearing. REMEMBER THIS
7. **Order of Reaction** – the exponent                      **Overall Order** – sum of all the exponents
8. **Rate of 0** – independent of the concentration
9. **K** – this constant is the constant for THAT REACTION at THAT TEMPERATURE
10. **Read Bluffer's Guide or Section 3 for Half Life and Concentrations at a specific point in time**
11. **Collision Theory** – Rate is proportional to the number of collisions/second
12. In  $A + B \rightarrow$  Products, doubling A or B doubles the rate (1<sup>st</sup> order only)
13. In  $A + A \rightarrow$  Products, doubling A QUADRUPLES the rate (Twice the rate of colliding for each one, so 4 total)
14. **Bimolecular collision** – two molecules collide
15. **Termolecular collision** – three molecules collide (extremely rare)
16. **Elementary Processes** – larger reactions can be split up into these simple equations that add up to the final equation
17. **Reaction Mechanism** – a sequence of simple reactions that add up to the overall reaction
18. **Rate Determining Step** – the slowest step in the mechanism. Rate law for slowest step is rate law for the overall reaction
19. In order to “substitute one reaction into another” in determining mechanisms, the elementary process must be equilibrium
20. **Read Section 5 on exactly how to derive mechanisms**
21. **Effective collisions** – bad collision geometry makes many collisions useless. Must be moving fast enough
22. **Temperature on effective collisions** – higher temp, more molecules with high KE, more effective collisions
23. **Rate = pfZ**      **Z** = Total collisions/second      **F** = fraction of effective collisions      **p** = orientation
24. **Transition State Theory** – molecules must overcome activation NRG and become an unstable molecule when a high PE in a transition state, which then reacts to form the final product/products
25. **Activated Complex** – the name of the highly unstable transition molecule
26. **Activation Energy** – the minimum KE that molecules must possess to overcome the electron repulsions when they collide
27. **Reaction Coordinate** – the X axis on the PE/Activation Energy/“hump” graph
28. **See Charts of Page 506 to see what each part of the graph represents, especially activation energy**
29. Activation energy is inversely proportional to the reaction rate
30. **As temperature rises, reaction rate rises**– Higher KE, more molecules with enough KE to overcome activation energy. Many rates are doubled when raised by 10 degrees Celsius
31. Activation Energy –  $k = Ae^{-E_a/RT}$       **R** = gas constant      **T** = temperature in K      **A** = Arrhenius Constant
32. **Know the equations he gave to us in class, for both first/second order reactions, and how to tell them apart**
33. **Catalyst** – substance that increases rate of reaction w/o being consumed. Lowers activation energy  
Increases number of EFFECTIVE collisions, not the number of TOTAL collisions
34. **Homogeneous catalyst** – present in the same phase as the reactants, speeds up by forming reactive intermediate
35. **Heterogeneous catalyst** – Not in the same phase as reactants, ex, metal surface. Read Pages 512 – 513.

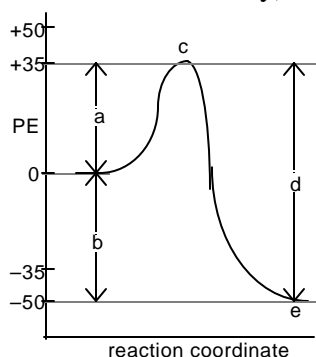
## 13 • Kinetics: Rates of Reaction

## A BLUFFER'S GUIDE

**The BIG ideas:**

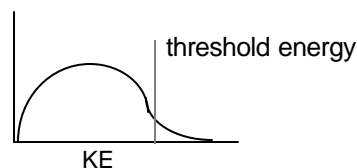
- How to **Speed Up** a Reaction
  - increase the **concentration** of reactants
    - increase **molarity** of solutions
    - increase partial **pressure** of gases
    - more **surface area** between unlike phases
  - increase the **temperature**
    - more collisions
    - harder collisions
  - add a **catalyst**
    - homogeneous catalyst (used & reformed)
    - heterogeneous catalyst (surface catalyst)

- How to **Explain** Reaction Rates
  - **collision** theory (reaction **kinetics**)  
(kinetic molecular theory)

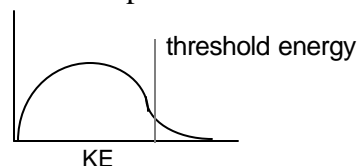


- the PE energy profile of a reaction
  - $\Delta H$  of the reaction
  - exothermic or endothermic (downhill or uphill)
  - activation energy or energy barrier
  - activated complex (at the peak)
  - fast or slow... depends on the activation energy
  - how does this picture change when you heat up the reactants?
  - how does this picture change when you add a catalyst

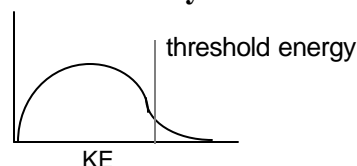
- the **KE** distribution of a substance



- **temperature** is the **average** KE
- how does this picture change when you **heat up** the reactants?

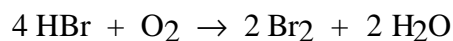


- how does this picture change when you add a **catalyst**?

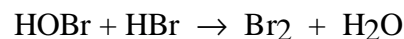
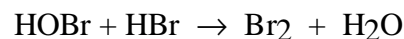
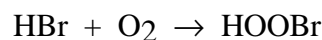


- how do these two picture **relate** to each other (turn the KE on its side... the particles use their KE to provide the needed PE to react)
- reaction **mechanisms**
  - step-by-step...two particles at a time
- example

overall:



mechanism:



[note: HOBr and HOBr are not in the overall reaction because they are not reactants or products, they are "reactive intermediates"]

- overall reaction is sum of steps
- slowest step is the 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:



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."

Examples for:  $2A + 3B \rightarrow C$

Rate Law	Rate Determining Step in the mechanism
Rate = $k [A][B]$	
Rate = $k [A]^2$	
Rate = $k [A]^2 [B]$	
Rate = $k$	

## order of rxn

- first and second order reactions
- what these look like graphically
- how you can graphically tell the order of a reaction
- how this relates to the rate law

## half-life

- relationship to radioactivity (a first order reaction)
- the equation
- the special case of half-life

## chain reactions

- 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