6.4 Collision Theory and Rates of Reaction

Concepts of the Collision Theory

- A chemical system consists of *particles* (atoms, ions, or molecules) that are in constant random motion at various speeds. The average kinetic energy of the particles is proportional to the temperature of the sample.
- A chemical reaction must involve *collisions of particles* with each other or the walls of the container.
- An *effective collision* is a collision between particles that has sufficient energy and correct orientation (alignment or positioning) of the colliding particles so that bonds can be broken and new bonds formed.
- *Ineffective collisions* involve particles that rebound from the collision, essentially unchanged in nature.
- The rate of a given reaction depends on the *frequency* of collisions and the *fraction* of those collisions that are effective.
- See figure 1 from page 383

explain the graph!

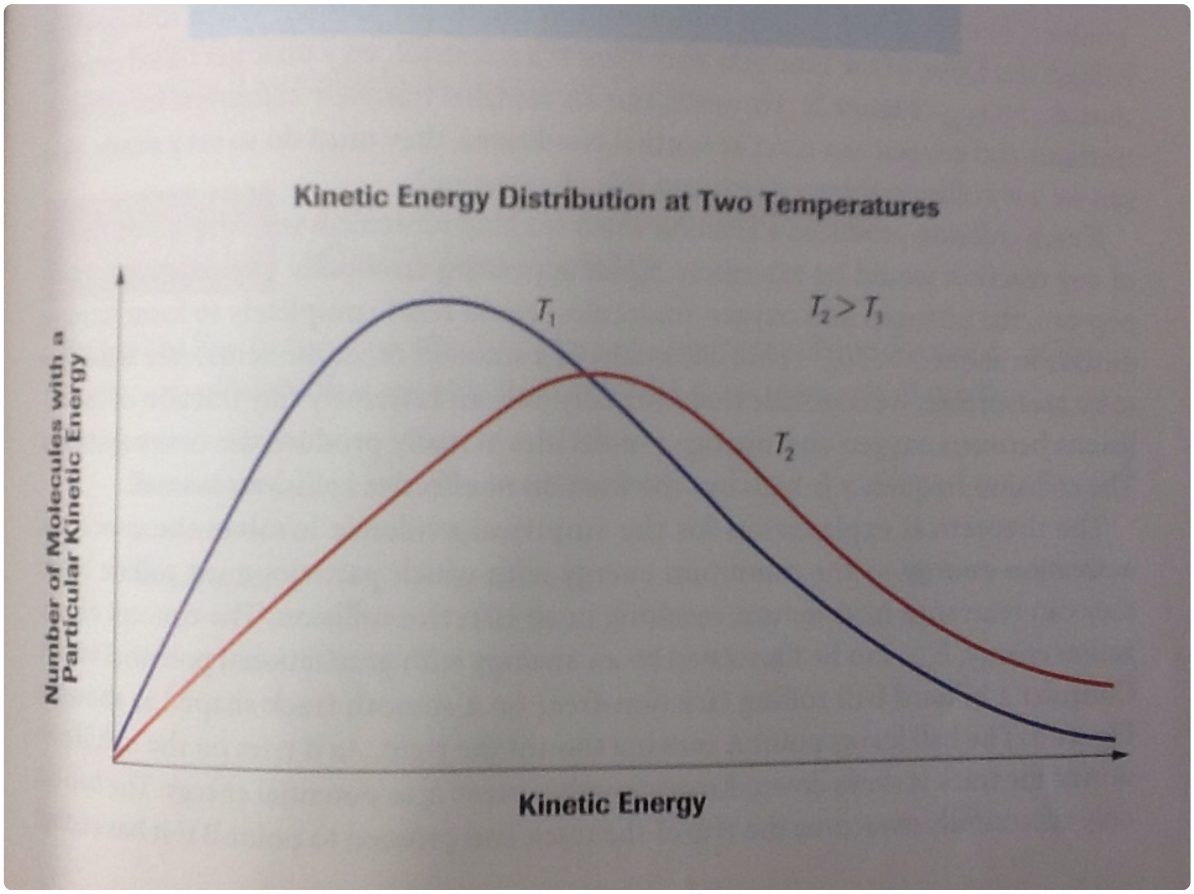
what factors? – pg 385

Calculating Reactions per Second

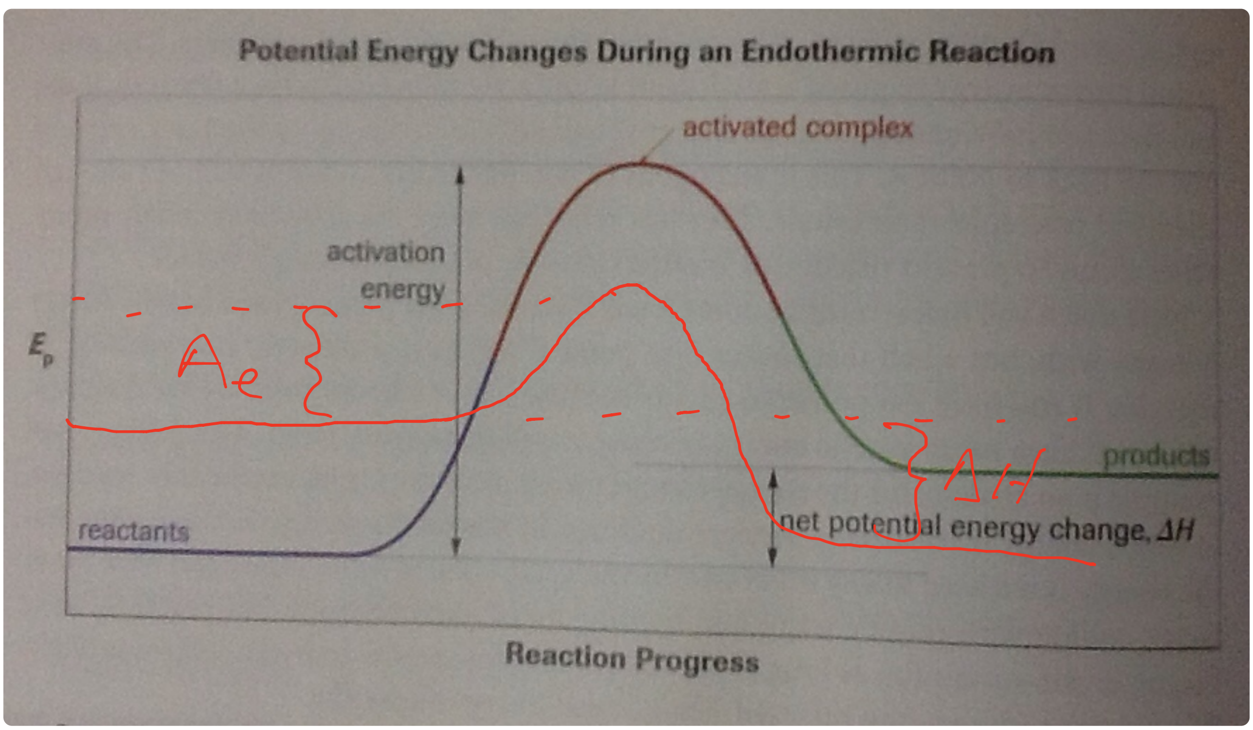
- rate = frequency of collisions × fraction of effective collisions
- If the reaction has 1000 collisions per second and only 1/100 are effective, what is the reaction rate?
- Rate = 1000 collisions/1 second × 1 reaction/100 collisions = 10 reactions/s

Activation Energy

- The activation energy is the minimum kinetic energy that reacting molecules must possess in order to react for an effective collision.
- At room temperature H_2 and O_2 do not readily react to form H_2O but if you add energy the reaction will vastly increase.
- Other things to take into consideration for an effective collision: collision rate, collision geometry, the activated complex, and the presence of a catalyst.
- The activated complex is a short lived, high energy, unstable intermediate that is formed during a reaction.
- Be able to understand, label potential energy diagrams figure 5 and 6 from page 386-7



Kinetic Energy Distribution at Two Temperatures
T_1
$T_2 > T_1$
T_2
Number of Molecules with a Particular Kinetic Energy
Kinetic Energy



Potential Energy Changes During an Endothermic Reaction
activated complex
activation energy
E_p
A_e
ΔH
products
reactants
net potential energy change, ΔH
Reaction Progress

Reaction Mechanisms

- Even the simplest looking reaction (decomposition) may be in fact a series of intermediate steps involving several collisions of different particles
- A reaction is determined to be a single step reaction if the experimental derived rate law has exponents that are the same as the coefficients

  - Single step reactions with 1 molecule decomposing are called **unimolecular** reactions.

    (1) $SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$

  - Single step reactions with 2 molecules are called **bimolecular** reactions.

    (2) $NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$

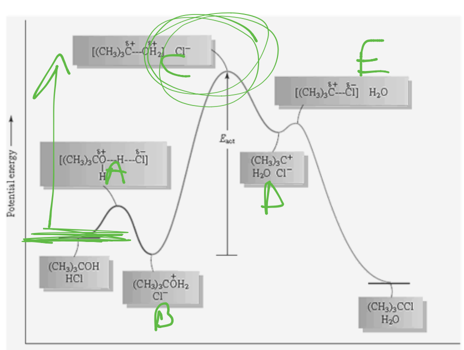
  - Single step reactions with 3 molecules are rare and are called **termolecular** reactions

- With single step reactions the rate law is connected to the coefficients of the balanced chemical equation

  (1) $r=k[SO_2Cl_2]^1$

  (2) $r=k[NO]^1[O_3]^1$

- Many reactions proceed by a more complicated process involving 2 or more steps. (Page 388: $4HBr + O_2 \rightarrow 2H_2O + 2Br_2$)
- Each step is called an elementary process and may create reaction intermediates that are not found in the final equation.
- Each steps has their own rate and their own activation energy
- Usually fast steps have low activation energies and slow steps have high activation energies



Elementary Processes

- Elementary processes are <u>one-step processes</u> that when added together make up a reaction mechanism (similar to Hess's Law).

- E.g. $2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$

  Possible Mechanism 1:

step 1	$2NO_{(g)} + H_{2(g)} \rightarrow N_{2(g)} + \cancel{H_2O_{2(g)}}$
step 2	$H_{2(g)} + \cancel{H_2O_{2(g)}} \rightarrow 2H_2O_{(g)}$

  This termolecular mechanism is highly unlikely since the probability of 3 gaseous molecules colliding at the same time is highly improbable.

  Possible Mechanism 2:

step 1	$NO_{(g)} + H_{2(g)} \rightarrow NO\text{—}H_2$ (an activated complex)
step 2	$NO_{(g)} + NO\text{—}H_2 \rightarrow N_{2(g)} + H_2O_{2(g)}$
step 3	$H_2O_{2(g)} + H_{2(g)} \rightarrow 2H_2O_{(g)}$

  ex. page 388

  This bimolecular mechanism is highly probable but we cannot prove that it is the only mechanism.

- To determine possible reaction mechanism:
  - Each step must be elementary (one or two molecules colliding)
  - The slowest step must be consistent with the rate equation (coefficients are the orders of the reactants)
  - Any reaction intermediates created in the products must be used in the reactant side
  - All steps must add up to the overall balanced chemical equation

Page 389-390 sample problems:

Homework: Practice 1,2 Questions 1,2,3

because all substances are simple molecu

$$4\,HBr_{(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(g)} + 2\,Br_{2(g)}$$

It is highly unlikely that this reaction

the steps sum to give the overall equation for the react

$$\begin{array}{llr}
HBr_{(g)} + O_{2(g)} & \rightarrow HOOBr_{(g)} & \text{(slow)} \\
HOOBr_{(g)} + HBr_{(g)} & \rightarrow 2\,HOBr_{(g)} & \text{(fast)} \\
2\,\{HOBr_{(g)} + HBr_{(g)} & \rightarrow H_2O_{(g)} + Br_{2(g)}\} & \text{(fast)} \\
\hline
4\,HBr_{(g)} + O_{2(g)} & \rightarrow 2\,H_2O_{(g)} + 2\,Br_{2(g)} &
\end{array}$$

the rate, but measuremen
determined rate equation

$$r = k[HBr][O_2]$$

We explain by theorizin