

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

Calculating Reactions per Second

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

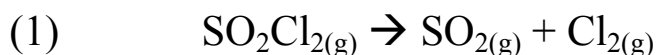
Activation Energy

- 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

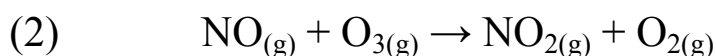
Reaction Mechanisms

- 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.

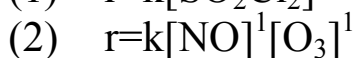
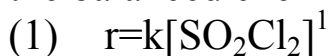


- Single step reactions with 2 molecules are called **bimolecular** reactions.

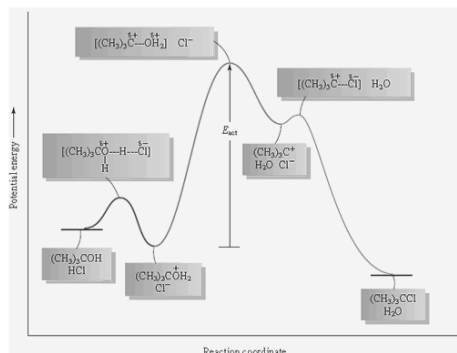


- Single step reactions with 3 molecules are rare and are called **termolecular** reactions

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



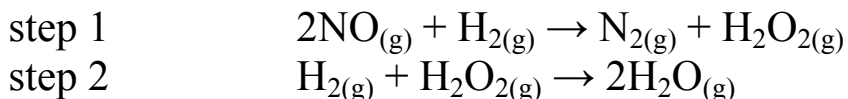
- Many reactions proceed by a more complicated process involving 2 or more steps. (Page 388: $4\text{HBr} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2$)
- Each step is called an elementary process and may create reaction intermediates that are not found in the final equation.
- Each steps 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

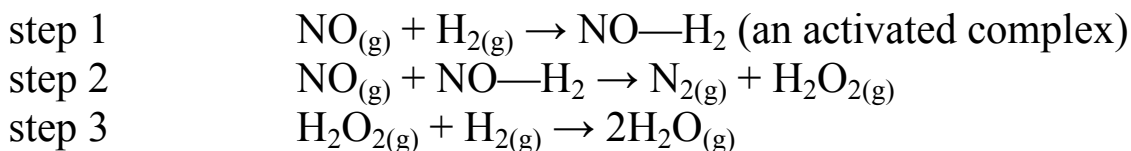
- Elementary processes are one-step processes that when added together make up a reaction mechanism (similar to Hess's Law).
- E.g. $2\text{NO}_{(g)} + 2\text{H}_{2(g)} \rightarrow \text{N}_{2(g)} + 2\text{H}_2\text{O}_{(g)}$

Possible Mechanism 1:



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

Possible Mechanism 2:



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: