Chemical kinetics

Elementary Reaction

The single molecular event, in which product molecules are formed from reactant molecules, is called an elementary reaction.

$$
\begin{array}{rcll}
NO_2 + NO_2 & \longrightarrow & NO_3 + NO & \text{(elementary reaction)} \\
NO_3 + CO & \longrightarrow & NO_2 + CO_2 & \text{(elementary reaction)} \\
\hline
NO_2 + \cancel{NO_2} + \cancel{NO_3} + CO & \longrightarrow & \cancel{NO_3} + NO + \cancel{NO_2} + CO_2 & \text{(overall equation)}
\end{array}
$$

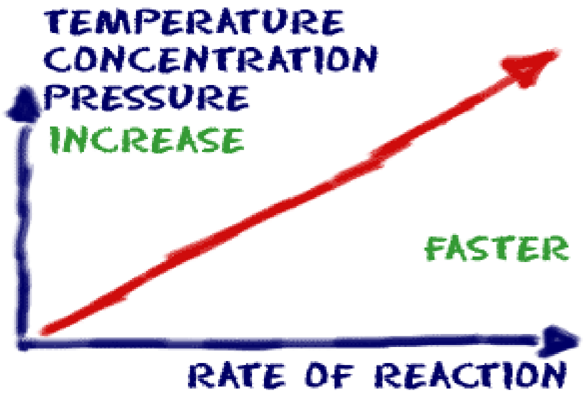
Q. Write down the rate of consumption/formation of A, B & P.

Rate of consumption = - $\dfrac{d[A]}{dt}$ (for A)

Rate of consumption = - $\dfrac{d[B]}{dt}$ (for B)

Rate of formation = $\dfrac{d[P]}{dt}$ (for P)

Factors influence the reaction rate



1. **Concentration**

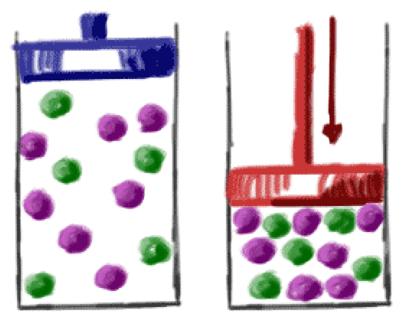
- Often the rate of reaction increases when the concentration of a reactant is increased.
- As the concentration increases the number of molecules increases. As a result, collisions are more likely to occur and give the higher rate.
- A piece of steel wool burns with some difficulty in air (20% O_2) but bursts into a dazzling white flame in pure oxygen. The rate of burning increases with the concentration of O_2.
- In some reactions, however, the rate is unaffected by the concentration of a particular reactant, as long as it is present at some concentration.

2. Temperature

- Generally, if temperature increases whether it is exothermic or endothermic reaction the rate increases. (except: complex and enzyme catalytic reaction)
- In case of enzyme catalytic reaction, at first reaction rate increases and then decreases with increasing temperature.
- For exothermic reaction, equilibrium constant decreases with increasing temperature
- For endothermic reaction, equilibrium constant increases with increasing temperature
- It has been experimentally found that, the reaction rate becomes double for every 10^0 C rise of temperature.
- At higher temperature, molecules in the reaction system have higher kinetic energy. So they move with a higher velocity and fraction of effective number of collisions increases with higher force and energy. As a result, most of the molecule achieve minimum amount of energy and overcome the energy hill of potential energy diagram. Therefore, the rate of reaction increases.

3. Pressure

When pressure applies the volume of a gas is reduced. So in unit volume higher numbers of molecules are present at higher pressure. Therefore, the concentration is increased with the increase of pressure. As a result, the collisions between the molecules are increased which enhance the reaction rate. Example: production of ammonia from N_2 and H_2.



AS PRESSURE INCREASES, THE GAS MOLECULES CAN HAVE MORE COLLISIONS.

4. Surface area of a solid reactant or catalyst

- If a reaction involves a solid with a gas or liquid, the surface area of the solid affects the reaction rate.
- Because the reaction occurs at the surface of the solid, the rate increases with increasing the surface area.
- A wood fire burns faster if the logs are chopped into smaller pieces.
- Similarly, the surface area of a solid catalyst is important to the rate of reaction. The greater the surface area per unit volume, the faster the reaction.

5. Catalyst

- A catalyst is a substance that increases the rate of reaction without being consumed in the overall reaction.
- Catalysts are of enormous importance to the chemical industry, because they allow a reaction to occur with a reasonable rate at a much lower temperature than otherwise; lower temperatures translate into lower energy costs.

- ➢ The catalyst must participate in at least one step of a reaction and be regenerated in a later step.

Q. How do you explain the increase in speed of the catalyzed reaction over the uncatalyzed reaction?

Hints

The Arrhenius equation provides an answer. The catalyzed reaction mechanism makes available a reaction path having an increased overall rate of reaction. It increases this rate either by increasing the frequency factor “A” or, more commonly, by decreasing the activation energy Ea. The most dramatic effect comes from decreasing the activation energy by the formation of intermediate product, because it occurs as an exponent in the Arrhenius eq^n ($k = Ae^{-Ea/RT}$).

Example: The depletion of ozone in the stratosphere by Cl atoms provides an example of the lowering of activation energy by a catalyst.

$$\begin{array}{rcl} Cl(g) + O_3(g) & \longrightarrow & ClO(g) + O_2(g) \\ ClO(g) + O(g) & \longrightarrow & Cl(g) + O_2(g) \\ \hline O_3(g) + O(g) & \longrightarrow & 2O_2(g) \end{array}$$

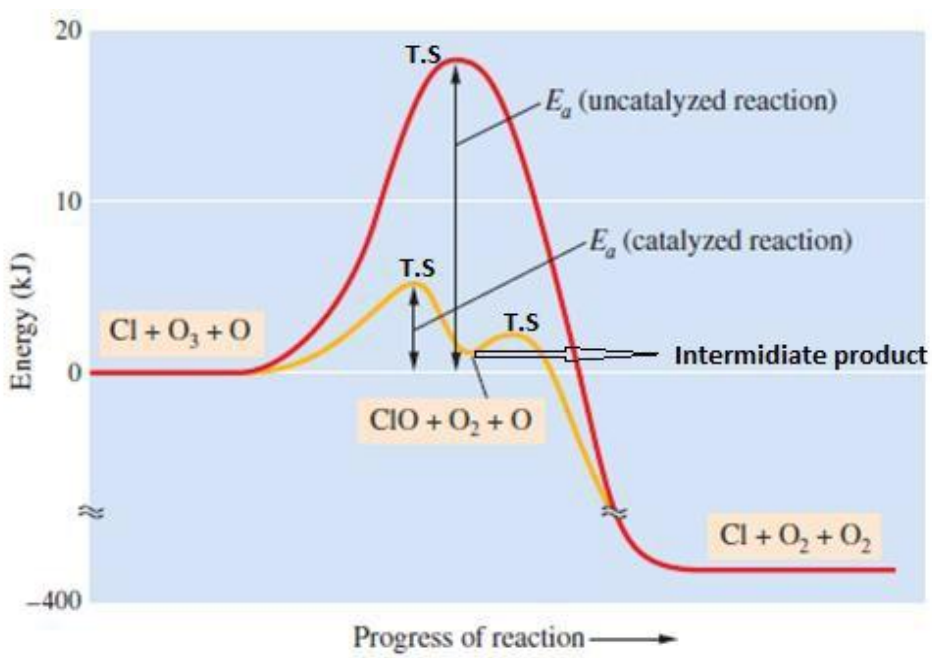


Fig. Comparison of activation energies in the uncatalyzed and catalyzed decompositions of ozone.