Collosion theory

- This theory requires that the atoms or molecules entering the reaction must collide each other in order for a reaction to occur.

- However, collusion of particles is not enough for the reaction to occur.

- In order for a reaction to occur, particles collide to each other «efficiently.»
- Efficient collusion means, after the collusion, the product (s) must form.
- Collusion theory shows that reaction rate of a reaction is proportional to the number of «efficient» collusions among particles
- Any factor that increases the efficient collusions will increase the reaction rate constant.

- At room temp., collusion frequency of a gas is “10^{30} collusion/mL s” under 1 atm of pressure.

- Out of 10^{18} collusion (billion times billion collusion), only 1 collusion is the «efficient» collusion that forms the products.

For the «<u>efficient</u>» collusion, there are two conditions

- The <u>**suitable configuration**</u> of particles is needed during collusion.

- The total energy level of the collided particles must have equal or higher activation energy value (E_a) of the reaction.

Total collusion frequency (z)

The number of collusions among particles in 1 mL of reaction mixture in 1 s.

Reaction rate

Reaction rate is proportional to the fraction of total collusion frequency and the fraction of the particles in suitable configuration (P) and the fraction of the particles with total energy level equal or higher than E_a vale of the reaction (f).

Factors affecting the collusion frequency (z)

- Concentration
- Temperature

Relationship between collusion frequency and reactant concentration

$z \alpha [A] [B]$

$z = C x [A] x [B]$

C is the constant and depends on the reaction rate of particles entering the reac.

$$rate = C x P x f x [A] x [B]$$

$$rate = k x [A] x [B]$$

Effects of temperature increase

- Increase in temp. do not directly cause the change in activation energy. However, increase in temp will cause the increase in th energy level of particles..
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Effect of temperature on energy factor

- $f = e^{-Ea/2.3\,RT}$ (fraction of collisions with energy greater than E_a)

E_a: Activation energy (kcal/mole or kJ/mole)

R: Gas constant (1.987 cal/mole.K or 8.314 J/mole.K)

T: Temperature (Kelvine)

Not: The remarkable increase in the reaction rate as a result of small increase in temperature is due to the exponential nature of the energy factor.

Example

Assume that a particular reaction has an E_a of 10 kcal/mole. Determine how many folds increase will occur in the number of collisions when temperature of reaction mixture increases from 27°C (300 K) to 100°C (373 K).

Effect of activation energy on energy factor

Example

E_a values for three different reactions in all occurring at 300°C (573 K) were given below. Show mathematically the effects of E_a on reaction rates.

$Ea_1 = 1.2$ kcal/mole

$Ea_2 = 3.8$ kcal/mole

$Ea_3 = 18.6$ kcal/mole

Solution

E_a (kcal/mole)	Fraction of collisions with energy greater than E_a (f)	Number of collisions with energy greater than E_a (out of 10^8 col.)
1.2	0.35	35 000 000
3.8	0.035	3 500 000
18.6	0.00000008	8

Example

Determine the increase in reaction rate of a reaction if the temperature is increased from 27°C to 37°C with E_a of 20 kcal/mole and k_o of $1 \times 10^{14}\ s^{-1}$.

$$\ln k_{27°C} = \left(\frac{-20 \text{ kcal mole}^{-1}}{1.987 \times 10^{-3} \text{ kcal mole}^{-1} \text{ K}^{-1}} \; \frac{1}{300 \text{ K}}\right) + \ln 1\text{x}10^{14} \text{ s}^{-1}$$

$$k_{27°C} = 0.27 \text{ s}^{-1}$$

$$\ln k_{37°C} = \left(\frac{-20 \text{ kcal mole}^{-1}}{1.987 \times 10^{-3} \text{ kcal mole}^{-1} \text{ K}^{-1}} \; \frac{1}{310 \text{ K}}\right) + \ln 1 \times 10^{14} \text{ s}^{-1}$$

$$k_{37°C} = 0.79 \text{ s}^{-1}$$

$$\frac{k_{27°C}}{k_{37°C}} = \frac{0.79}{0.27} = \sim \mathbf{3 \text{ times}}$$

Example

In previous reaction, determine the increase in reaction rate if E_a value is increased from 20 kcal/mole to 40 kcal/mole.

- $\ln k_{27°C} = \left(\dfrac{-40 \text{ kcal mole}^{-1}}{1.987 \times 10^{-3} \text{ kcal mole}^{-1} \text{ K}^{-1}} \dfrac{1}{300 \text{ K}}\right) + \ln 1 \times 10^{14} \text{ s}^{-1}$

$k_{27°C} = 7.2 \times 10^{-16} \text{ s}^{-1}$

- $\ln k_{37°C} = \left(\dfrac{-40 \text{ kcal mole}^{-1}}{1.987 \times 10^{-3} \text{ kcal mole}^{-1} \text{ K}^{-1}} \dfrac{1}{310 \text{ K}}\right) + \ln 1 \times 10^{14} \text{ s}^{-1}$

$k_{37°C} = 6.3 \times 10^{-15} \text{ s}^{-1}$

$$\frac{k_{27°C}}{k_{37°C}} = \frac{6.3 \times 10^{-15} \text{ s}^{-1}}{7.2 \times 10^{-16} \text{ s}^{-1}} = \sim 9 \text{ times}$$