Chapter 13
Chemical Kinetics

* Thermodynamics: ~ Does a reaction take Place ?
← هو العلم الذي يخبرنا بإمكانية حدوث التفاعل من عدمه .

* Kinetics : ~ How fast does a reaction Proceed ?
← العلم الذي يبحث سرعة حدوث التفاعل .

* Reaction rate : is the change in the concentration of a reactant or a product with time . (M/S)
Molarity / second

$$A \longrightarrow B$$

$\Delta[A]$ = change in concentration of A over time Period Δt

$$\text{Rate} = \ominus \frac{\Delta [A]}{\Delta t} = \frac{\Delta [B]}{\Delta t}$$

* السالب بسبب حدوث نقصانه في التركيز للمتفاعلات *

* For reactions in solutions concentrations are measured by spectroscopic means.
↳ If ions involved, we can use electrical conduclan measurments too.

Spectrometer: Registers the amount of visible light absorbed by a species.
← بنقيس تركيز المادة عن طريقة معرفة كمية الضوء المرئي التي تمتص باستطاعة المادة .

* Beer's Law: A (absorbance) $\propto$ Concentration.
$\Delta [Br_2] \propto \Delta$ absorption

$Br_{2(aq)} + HCOOH_{(aq)} \longrightarrow 2Br^-_{(aq)} + 2H^+_{(aq)} + CO_{2(g)}$

Red-brown
بني محمر

Instantaneous rate : Rate for specific instant in time.
هو معدل سرعة التفاعل اللحظي "عند زمن محدد"

$$\text{Average rate} = -\frac{\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

* Rate Constant "K" : A constant of Proportionality between the reaction rate & the concentration of reactants

$$K = \frac{Rate}{[Br_2]} \rightarrow Rate = K[Br_2]$$

$$Rate \propto [Br_2]$$

كلما زاد تركيز المتفاعلات ، زادت سرعة التفاعل.

* K is not affected by the Concentration of Br_2.

If gases are involved in a reaction, we use Pressure measurments. For example : if one of the Products or reactants is a gas, a manometer is used to find the rate.

$$2H_2O_{2(aq)} \longrightarrow 2H_2O_{(l)} + \underline{O_{2(g)}} \rightarrow \text{Gas}$$

$$Rate = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta P}{RT\,\Delta t}$$

T : temperature , Δt : Time.

step by step
x x x x
day by day

※ For the reaction :

$$aA + bB \longrightarrow cC + dD$$

* $\text{Rate} = -\frac{1}{a} * \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} * \frac{\Delta[B]}{\Delta t}$

* $\text{Rate} = \frac{1}{c} * \frac{\Delta[C]}{\Delta t} = \frac{1}{d} * \frac{\Delta[D]}{\Delta t}$

Question : Write the rate expressions for the following reaction in terms of the disappearance of the reactants and the appearance of the Products,

$$I^-_{(aq)} + OCl^-_{(aq)} \longrightarrow Cl^-_{(aq)} + OI^-_{(aq)}$$

→ $\text{Rate} = -\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[OCl^-]}{\Delta t} = \frac{\Delta[Cl^-]}{\Delta t} = \frac{\Delta[OI^-]}{\Delta t}$

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

→ $\text{Rate} = -\frac{1}{4} * \frac{\Delta P_{NH_3}}{RT\Delta t} = -\frac{1}{5} * \frac{\Delta P_{O_2}}{RT\Delta t} = \frac{1}{4} * \frac{\Delta P_{NO}}{RT\Delta t} = \frac{1}{6} * \frac{\Delta P_{H_2O}}{RT\Delta t}$

Question : Consider the following reaction : $A \longrightarrow 2C$ the average rate of appearance of C is given by $\frac{\Delta[C]}{\Delta t}$, how is the average rate of appearance of C related to the average rate of disappearance of A ?

→ Solution :

* $\text{Rate} = -\frac{\Delta[A]}{\Delta t} = \frac{1}{2}\frac{\Delta[C]}{\Delta t}$

$$\therefore \frac{\Delta[C]}{\Delta t} = -2\frac{\Delta[A]}{\Delta t}$$

you can...

Question:\ Consider the reaction

$$4\,NO_{2(g)} + O_{2(g)} \longrightarrow 2\,N_2O_{5(g)}$$

Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 M/s. At what rate is N_2O_5 being formed

* Solution:\

$$Rate = \frac{-\Delta P_{O_2}}{RT\Delta t} = \frac{1}{2} * \frac{\Delta P_{N_2O_5}}{RT\Delta t}$$

$$\therefore -R_{O_2} = \frac{1}{2} R_{N_2O_7}$$

$$-(-0.024) = \frac{1}{2} R_{N_2O_7}$$

$$\therefore R_{N_2O_7} = 2 * 0.024 = \boxed{0.048\ M/s}$$

The Relation Between Reactants Concentration & Time

→ First order Reaction:\

Reaction whose rate depends on the reactant concentration raised to the first power.

$$A \longrightarrow Product$$

$$Rate = K[A]$$

* Unit of K :\

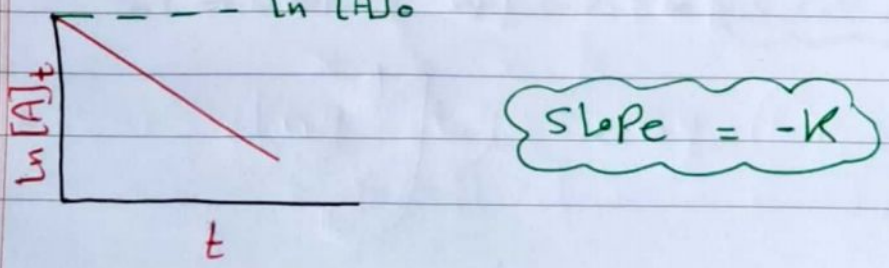
$$K = \frac{rate}{[A]} = \frac{M/S}{M} = \frac{1}{S} = \boxed{S^{-1}}$$

* تختلف وحدة قياس (K) باختلاف رتبة التفاعل الكلية.

خط الـ First order ← $\ln[A] = -Kt + \ln[A]_0$

$[A]$ → Concentration of A at any time (t)

$[A]_0$ → Concentration of A at (t = 0)



Question: The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4}\ s^{-1}$ at 500°C.

* If the initial concentration of cyclopropane was 0.25 M what is the concentration after 8.8 minute ?

* Solution:

$K = 6.7 \times 10^{-4}\ s^{-1}$, $t = 8.8 \times 60 =$ (528 Second)

$[A]_o = 0.25\ M$

$$\ln [A] = -Kt + \ln [A]_o$$
$$= (-6.7 \times 10^{-4} \times 528) + \ln (0.25)$$
$$= -1.74$$
$$e^{\ln [A]} = e^{-1.74}$$
$$\therefore [A] = 0.18\ M \quad \#$$

↳ How ~~long~~ (in minutes) will it take to convert 74% of the starting material.

* Solution:

$[A]$ = 26 % of starting material

$$\therefore [A] = \frac{26}{100} \times 0.25 = 0.065\ M$$

$$\ln [A] = -Kt + \ln [A]_o$$
$$Kt = \ln [A]_o - \ln [A]$$
$$t = \frac{\ln [A]_o - \ln [A]}{K}$$
$$= \frac{\ln (0.25) - \ln (0.065)}{6.7 \times 10^{-4}} = 2010.5\ s$$

$$\therefore t = 2010.5 \div 60 = (33.5 \text{ minutes}) \quad \#$$

* First order reaction "In gases"

$$\ln P = -Kt + \ln P_o$$

* بنغير التراكيز بالضغط للغازات .

Reaction Half-life

* Half life " $t_{1/2}$ ": The time required for the concentration of a reactant to decrease to half of its initial one.

* For first order reaction → $t_{1/2} = \frac{0.693}{K}$

#Question: The decomposition of ethane to methyl radical is a first-order reaction with a rate constant of $5.36 * 10^{-4}$

* Calculate the half time reaction in minutes

$$C_2H_{6(g)} \longrightarrow 2CH_{3(g)}$$

* solution :

∵ first-order reaction ⇒ $t_{1/2} = \frac{0.693}{K}$

∴ $t_{1/2} = \frac{0.693}{5.36 * 10^{-4}} = 1.29 * 10^3 \ s$

$t_{1/2} = (1.29 * 10^3) * \frac{1}{60} =$ (21.5 minutes) #

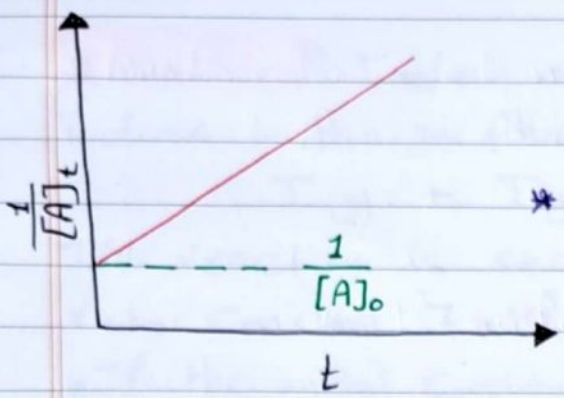
→ Second-order reaction: Reaction whose rate depends on the concentration of one reactant raised to the second power, or two reactants each raised to the first power.

$2A \longrightarrow$ Products rate = $K[A]^2$

$A + B \longrightarrow$ Products rate = $K[A][B]$ "more common"

Unit of K: $K = \frac{rate}{[A]^2} = \frac{M/s}{M^2} = 1/M.s$

$= M^{-1}.s^{-1}$



* for second-order reaction

* $\frac{1}{[A]} = Kt + \frac{1}{[A]_0}$

* slope $= K$

$A + B \longrightarrow$ Products

Rate $= K[A][B]$

* for this kind of reaction we use "Pseudo-first-order Kinetics) condition:

→ Reactant B in large excess, the rate $= K_{obs}[A]$

where K_{obs} is the Pseudo-first-order rate constant

$K_{obs} = K[B]$.

* Question: Write the rate law of the reaction

$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

* H_2O موجودة بكمية كبيرة

* Solution:

$K_{obs} = K[H_2O]$

$R = K_{obs}[CH_3COOC_2H_5]$

∞ Second order reaction Half-Life:

$t_{1/2} = \frac{1}{K[A]_0}$ ⇝ second-order

Imagine

Believe

Achieve

Question: Iodine atoms combine to form molecular iodine in the gas phase.

$$I_{(g)} + I_{(g)} \longrightarrow I_{2(g)}$$

This reaction is second-order kinetics & has the high rate constant $7 * 10^9$ /M.s at 23°C.

* If the initial concentration of I was 0.086 M, Calculate the concentration after 2 minutes.

* Solution:\

→ $t = 2 * 60 = 120$ second

$$\frac{1}{[A]} = Kt + \frac{1}{[A]_o}$$

$$= (7 * 10^9 * 120) + \frac{1}{0.086} = 8.33 * 10^{11}$$

$$\therefore \frac{1}{[A]} = 8.33 * 10^{11} \rightarrow [A] = 1.2 * 10^{-12}\ M \ \#$$

* Calculate the half life of the reaction if the initial concentration of I is 0.6 M

* Solution:\

* second-order → $t_{1/2} = \frac{1}{K[A]_o}$

$$t_{1/2} = \frac{1}{7 * 10^9 * 0.6} = 2.4 * 10^{-10}\ s \ \#$$

Question: For the reaction $A + B \longrightarrow C + D$, the following experiments were carried out:\

[A]	[B]	Rate
0.15	0.3	4.6
0.15	0.6	4.6
0.45	0.3	41.4

Find the rate law for this reaction.

$$Rate = K [B]^x [A]^y$$

* From firs & second experiments

$$0.6 = K(0.3)^x * (0.15)^y$$
$$\underline{0.6 = K(0.6)^x * (0.15)^y}$$
$$1 = (\tfrac{1}{2})^x \Rightarrow \boxed{x = 0}$$

"بقسمة المعادلتين"

* From second & third experiments

$$0.6 = K(0.6)^0 * (0.15)^y$$
$$\underline{11.4 = K(0.3)^0 * (0.45)^y}$$
$$\tfrac{1}{9} = (\tfrac{1}{3})^y \Rightarrow \boxed{y = 2}$$

"بقسمة المعادلتين"

$$\therefore \text{Rate} = K[A]^2$$

Zero-order Reaction:

$$A \longrightarrow \text{Products}$$

* $\text{Rate} = K[A]^0 = \boxed{K}$
* Unit of K: $K = \frac{\text{rate}}{[A]^0} = M/s$
* For zero-order Reaction → $[A] = -Kt + [A]_0$
* The rate of a zero-order reaction is Constant.

* Half life of zero-order reaction

$$t_{1/2} = \frac{[A]_0}{2K}$$

#Question: A Compound decomposes according to the first order Kinetics with a half life of 112 days. the Compound to be at a Concentration of 0.106M after decaying 25 days. What was the Concentration at the start of the 25 days?

* First-order reaction. $[A] = 0.106\,M$

$$t = 25 * 24 * 60 * 60 = 2.16 * 10^6$$
$$t_{1/2} = 112 * 24 * 60 * 60 = 9.67 * 10^6\ s$$

∵ first-order reaction ⇒ $t_{1/2} = \frac{0.693}{K}$

$9.67 * 10^{6} = \frac{0.693}{K}$ → $K = 7.16 * 10^{-8}\ s^{-1}$

* $\ln [A] = -Kt + \ln [A]_o$

$\ln [A]_o = \ln [A] + Kt$

$= \ln(0.106) + (7.16 * 10^{-8} * 2.16 * 10^{6})$

∴ $\ln [A]_o = -2.09$

$[A]_o = e^{(-2.09)} = 0.124\ M$ #

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* Activation energy & Temperature defendence of rate constant

* In general: Reaction rate increases with temperature.

← معدل سرعة التفاعل يزداد عادة مع زيادة الحرارة. "مستمر دائماً"

* According to collision theory:

Rate ∝ $\frac{\text{number of collision}}{\text{second}}$

← بناء على نظرية التصادم، معدل سرعة التفاعل يتناسب تناسباً طردياً مع عدد التصادمات في الثانية.

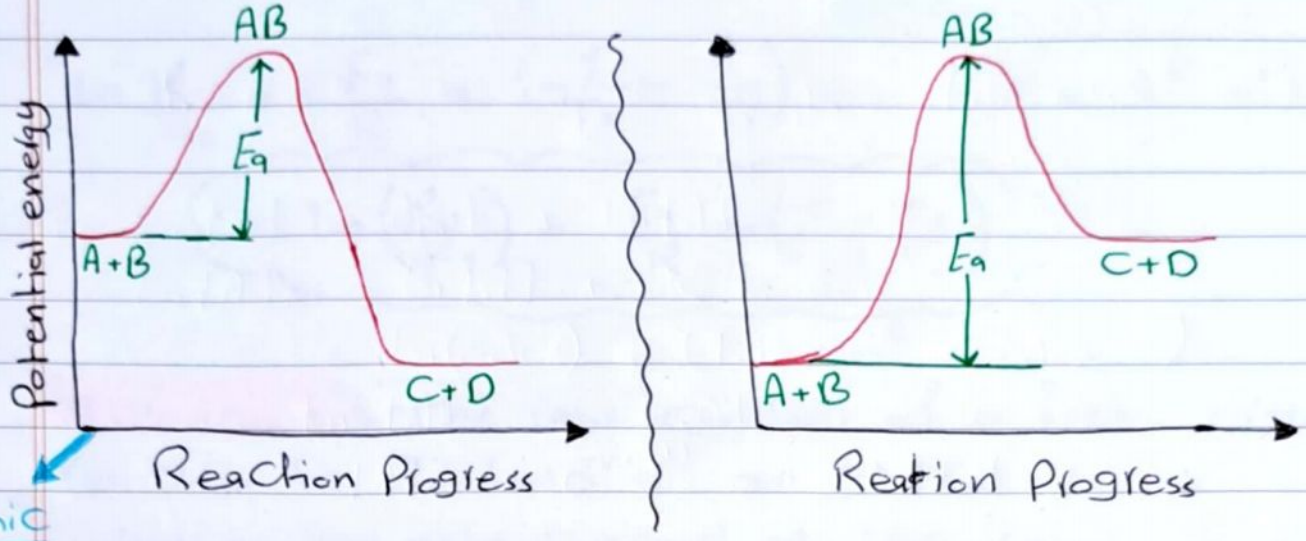
Activation energy (E_a): is the minimum amount of energy required to initiate a chemical reaction.

Activated Complex: "Transition state"

A temporary species formed by the reactant molecules as a result of the collision before they form products.

← المعقد المنشط: حالة انتقالية بين المتفاعلات والنواتج

"Exothermic & Endothermic Reaction"



exothermic

$A + B \rightarrow AB \rightarrow C + D$

Reactants — Activated Complex — Products

exothermic reaction:
Products more stable than reactants.

endothermic reaction:
Reactants more stable than Products.

Arrhenius equation

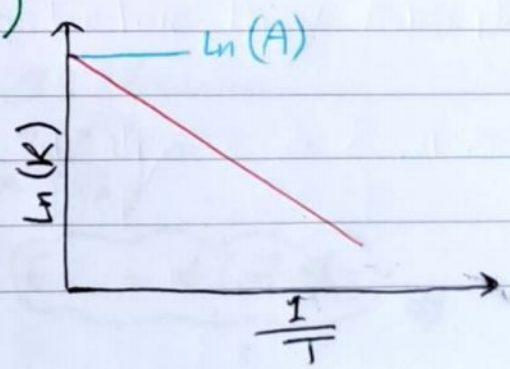
 # Arrhenius equation: shows the dependence of rate constant on temperature.

$$K = A * e^{(-E_a/RT)}$$

- A: frequency factor
- E_a: Activation energy
- R: Gas Constant = 8.314
- T: absolute temp.

$$Ln(K) = \frac{-E_a}{RT} + Ln(A)$$

$$\text{slope} = \frac{-E_a}{R}$$



At two temperatures & Activation energy is Known.

$$\ln \frac{K_1}{K_2} = \frac{E_a}{R} * \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\therefore \ln\left(\frac{K_1}{K_2}\right) = \frac{E_a}{R} * \left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

 # Question: The rate constant of a first-order reaction is $3.46 * 10^{-2}\ s^{-1}$ at 298 Kelvin. What is the rate constant at 350 Kelvin if the activation energy for the reaction is 50.2 KJ/mol ?

* Solution:

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{E_a}{R} * \left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

$$\ln\left(\frac{3.46 * 10^{-2}}{K_2}\right) = \frac{50.2}{8.314} * \left(\frac{298 - 350}{298 * 350}\right)$$

$$\ln\left(\frac{3.46 * 10^{-2}}{K_2}\right) = -3.01$$

$$\frac{3.46 * 10^{-2}}{K_2} = e^{(-3.01)} = 0.0493$$

$$\therefore K_2 = \frac{3.46 * 10^{-2}}{0.0493} = 0.702\ s^{-1} \#$$

 # Question: What is the activation energy of a reaction whose rate constant increases by a factor of 10 when the temperature is increased from 3.3K to 333K ?

* solution: $K_2 = 10\ K_1$

$T_1 = 3.3$ Kelvin , $T_2 = 333$ Kelvin

$$\ln \frac{K_1}{10 K_1} = \frac{E_a}{8.314} * \left(\frac{3.3 - 333}{3.3 * 333}\right)$$

$$-19.14 = E_a * (-0.3) \Rightarrow E_a = 63.7\ KJ \#$$

#Question: The activation energy of a reaction is 2.45 KJ/mol. The rate constant is $7.7 * 10^{-2}\ min^{-1}$ at 500 Kelvin. At what temperature in Kelvin will the rate constant be $1.5 * 10^{-2}\ min^{-1}$?

*solution:

$$\ln \frac{K_1}{K_2} = \frac{E_a}{R} * \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{7.7*10^{-2}}{1.5*10^{-2}}\right) = \left(\frac{2.45*10^{3}}{8.314}\right) * \left(\frac{1}{T_2} - \frac{1}{500}\right)$$

$$1.635 = 294.68 * \left(\frac{1}{T_2} - 2*10^{-3}\right)$$

$$1.635 = \frac{294.68}{T_2} - 0.59$$

$$2.22 = \frac{294.68}{T_2} \rightarrow T_2 = \frac{294.68}{2.22} = 132.5\,K \ \#$$

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*Importance of molecular orientation#

→ For simple reactions "Between atoms".
*Frequency factor (A) = frequency of Collisions.

→ For Complex reactions. "Between molecules".
* Orientation factor is considered.

*في التفاعلات المعقدة "التي تحدث بين الجزيئات" يجب أن تكتسب الجزيئات activation energy ولازم يكون الorientation تبع التصادم effective.

orientation factor: (P) : How molecules are oriented relative to each other. "Unitless"
* simple reactions ⇒ $P = 1$
* Complex reactions ⇒ $P < 1$

Types of collisions

effective
- Formation of Products.

ineffective
- No Product formed.

$K = PA \cdot e^{(-Ea/RT)}$ — P: orientation factor

↳ Arrhenius equation for complex reactions.

Reaction Mechanisms

* An overall balanced Chemical equation doesn't tell us much about how a reaction takes Place.

← المعادلة الكيميائية الموزونة لا توضح كيف يحدث التفاعل بالزبط.

* The overall Progress of a Chemical reaction can be represented at the molecular level by a series of simple elementary steps.

* **Reaction mechanism:** The sequence of elementary steps that leads to Product formation.

elementary step → $NO + NO \longrightarrow N_2O_2$

elementary step → $N_2O_2 + O_2 \longrightarrow 2NO_2$

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overall reaction → $2NO + O_2 \longrightarrow 2NO_2$

Note: The sum of elementary steps must give the overall blanced equation.

Intermediates: Are species that appear in a reaction mechanism but not in the overall balanced equation.

↳ are always formed in an early elementary step & Consumed in a later one.

← المادة الوسيطة: هي مادة تظهر في خطوات آلية التفاعل ولكنها لا تظهر في المعادلة الكلية.

Molecularity of a reaction

* The number of molecules reacting in an elementary step.

1) Unimolecular reaction:

$A \longrightarrow$ Products Rate $= K[A]$

2) Bimolecular reaction:

* $A + B \longrightarrow$ Products Rate $= K[A][B]$

* $A + A \longrightarrow$ Products Rate $= K[A]^2$

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* The rate-determining step: The slowest step in the sequence of steps leading to Product formation.

ex: Rate $= K[A]^2[B]$

↳ The rate-determining step:

$2A + B \longrightarrow$ ☐

* elementary steps must satisfy two requirments:

- Measuring the rate of a reaction.
- Formulating the Rate law.

↳ Postulating a reasonable reaction mechanism.

Catalysis

 # A Catalyst: is a substance that increases the rate of a chemical reaction without being consumed.
هي مادة تعمل على تسريع معدل سرعة التفاعل بدون أن تستهلك.

* What does the Catalyst do in a reaction?

1. Increases the rate by providing an alternative reaction Pathway
2. Increases the rate by Lowering the activation energy.
3. enhances the rates of the forward & reverse reactions equally

* Rate "Catalyzed" > Rate "unCatalyzed"
* Catalyzed Ea < UnCatalyzed Ea

* Types of Catalysts

Heterogeneous Catalysis

- Reactants & Catalyst are in different Phases
  - Usually the Catalyst is solid.

* Types:
  - Haber synthesis of NH_3
  - ostwald Process for production of HNO_3.
  - Catalytic Converts

Homogeneous Catalysis

- Reactants & the Catalyst are is a single Phase
  - Usually the Catalyst is Liquid.