Pharmaceutical analytical chemistry I

Lecture 5

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Chemical kinetics

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- **Chemical kinetics** is the study of REACTION RATES and their relation to the way the reaction proceeds, i.e., its MECHANISM.
- The study of the rate, or speed, of a reaction has important applications:

- to *know what conditions will help the reaction to proceed faster* : In the manufacture of ammonia from N_2 and H_2 .

- Reaction rates are also used *to understand how chemical reactions occur* (mechanism of reaction).

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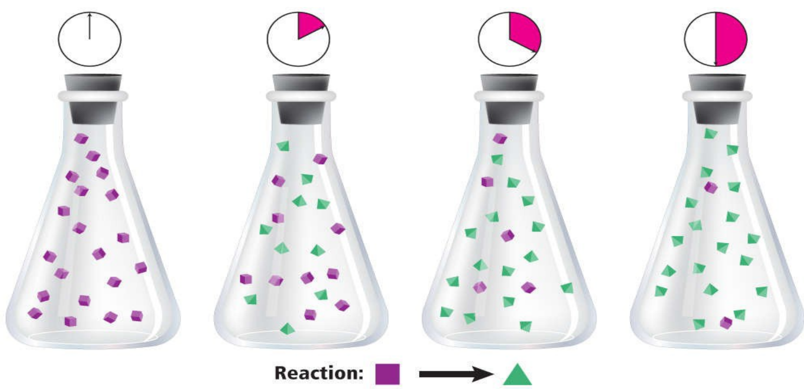
Reaction rates and their measurement

- The **reaction rate** of a chemical reaction is stated as the change in concentration of a reactant or product per unit of time.

$$\text{Rate of chemical reaction} = \frac{\textit{Change in concentration}}{\textit{time}} = \frac{mol/L}{s}$$



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- <u>Example:</u>

- Consider a hypothetical reaction, A $\longrightarrow$ B

Time (seconds)	Conc. Of A (mol/L)	Conc. Of B (mol/L)
0	1	0
2	0.98	0.02

- Calculate rate of appearance of B, and rate of disappearance of A.

- <u>Answer:</u>

rate of appearance of B = $\frac{\Delta B}{\Delta t} = \frac{final\ conc. - initial\ conc.}{\Delta t} = \frac{0.02 - 0}{2-0}$ = 0.01

rate of disappearance of A = $\frac{\Delta A}{\Delta t} = \frac{final\ conc. - initial\ conc.}{\Delta t} = \frac{0.98-1}{2-0}$ = - 0.01

<u>Note:</u> since that we are losing A, *so rate of disappearance must have a negative sign*

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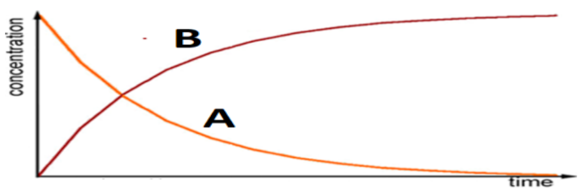

Curves showing changes in concentrations of substances with time for the reaction A → B

For the following reaction: $NO + O_3 \rightarrow NO_2 + O_2$

- Rate of disappearance of (reactants) NO or O_3 = $-\frac{\Delta[NO]}{\Delta t} = -\frac{\Delta[O_3]}{\Delta t}$

- Rate of appearance of (Products) NO_2 or O_2 = $\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$

Rate of product formation does not require the minus sign because $\frac{\Delta B}{\Delta t}$ or $\frac{\Delta[O_2]}{\Delta t}$ **is a positive quantity**

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Reaction rates and stoichiometry

For the following reaction: $2A \rightarrow B$

- Two moles of A disappear for each mole of B that is formed.

So rate of chemical reaction = $-\frac{1}{2} . \frac{\Delta A}{\Delta t} = \frac{\Delta B}{\Delta t}$

In general, for the reaction: $aA + bB \rightarrow cC + dD$

Reaction rate $= -\frac{1}{a} . \frac{\Delta A}{\Delta t} = -\frac{1}{b} . \frac{\Delta B}{\Delta t} = \frac{1}{c} . \frac{\Delta C}{\Delta t} = \frac{1}{d} . \frac{\Delta D}{\Delta t}$

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Factors affecting the rate of chemical reaction

- **1- The physical state of reactants and products and suface area:**

Some reactions are just **naturally fast and others are naturally slow,**

depending on the physical states of reacting substances

If reactant molecules exist in different phases, as in a heterogeneous mixture, the rate of reaction will be limited by the surface area of the phases that are in contact.
For example, if a solid metal reactant and liquid are mixed, only the molecules present on the surface of the metal are able to collide with the liquid molecules.

The rate for smaller particles will be greater because the **surface area in contact with the other reactant phase is greater**.

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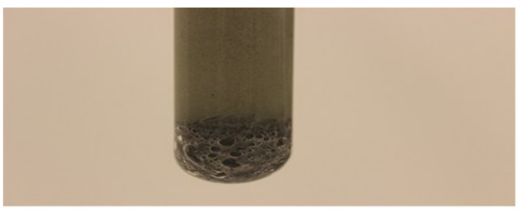
Factors affecting the rate of chemical reaction

1- The physical state of reactants and products and suface area:

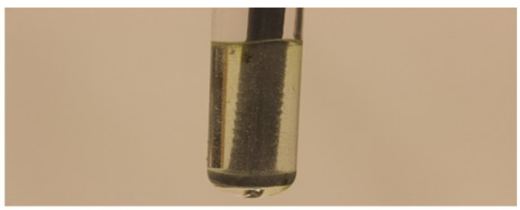
Example 1: Calcium carbonate($CaCO_3$) powder reacts rapidly with dilute hydrochloric acid because it has a large total surface area.

But A stick of **chalk has a much smaller surface area**, so it **reacts much more slowly**

Example 2, large pieces of iron react more slowly with acids than they do with finely divided iron powder



(a)

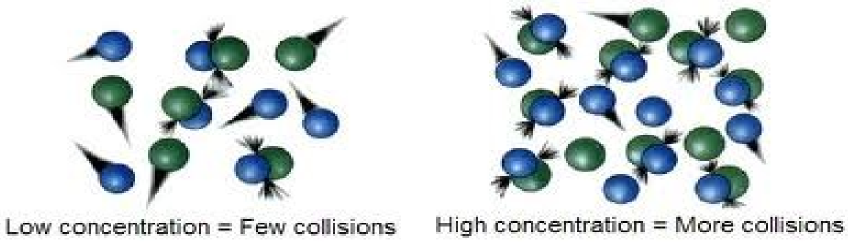


(b)

(a)Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq) \longrightarrow 2FeCl_3(aq) + 3H_2(g)$

b**) An iron nail reacts more slowly because the surface area exposed to the acid is much less.**

- **2- The concentration of reacting species:**
- Most chemical reactions proceeds faster if the concentration of one or more of the reactants is increased.
- **Increase in reaction rate** is due to **increase in collisions of particles**.
- For heterogeneous reactions, the rate also depends on the area of contact, **small particles** have **larger area** than larger particles → **increase in reaction rate**



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3. Temperature: Changes in temperature produce corresponding changes in the speed of the moving molecules or ions. This causes changes in the number of collisions per unit of time, and consequently changes in reaction rate. In general an increase in temperature of 10° C approximately doubles the reaction rate.

4. Catalyst: The reaction rate may be altered by use of a catalyst ‘ substance alters rate of reaction without include in reaction’.

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Rate laws

- The rate law shows how the rate of a reaction depends on the concentration of the reactants.

$A \rightarrow B$

Rate $\propto [A]^x$

Rate = $k\,[A]^x$

Where: - [A] is the concentration

- k is the **specific rate constant**, a numerical value that relates the reaction rate and the concentrations of reactants at a given temperature.

- x is called the order of the reaction

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Reaction order: shows how the rate of reaction is affected by concentration of the reactants.

First order reaction: is a reaction whose rate depends on the reactant concentration raised to the first power

Second order reaction: is a reaction whose rate depends on the reactant concentration raised to the second power or on the concentration of two different reactants , each raised to the first power

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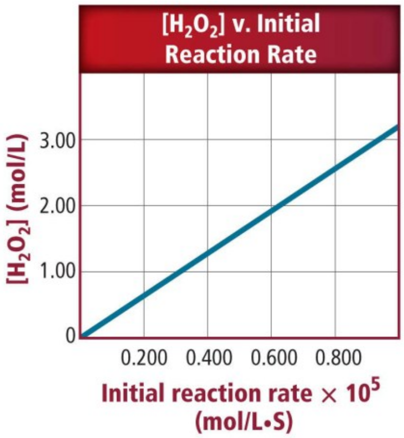
- Example 1:
- Rate = k [H_2O_2]
- X=1
- The reaction is first order,

so the rate changes in the
same proportion the concentration of H_2O_2 changes.



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Example 2:

Rate = k $[NO]^2[H_2]$

– If [H_2] is doubled, the rate doubles.
– If [NO] is doubled, the rate quadruples because $2^2 = 4$.

Conclusion: the reaction is first-order for H_2, second-order for NO and the overall reaction is third-order.

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- **<u>In general:</u>** Rate = $k\,[A]^x$

x = 1
- We have first order reaction: if the reaction rate is doubled by doubling the concentration of a reactant.

X=2
- We have second order reaction: if the rate is increased by a factor of four when the concentration of a reactant is doubled ($2^2 = 4$).

X=3
- We have third order reaction: if the rate undergoes an eightfold increase, when the concentration is doubled ($2^3 = 8$).

X= zero
- We have zero order reaction: if the rate is constant and does not depend on the concentration of reactant.

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- <u>Generally :</u> A + B $\rightarrow$ products
- Rate $\propto$ $[A]^x\,[B]^y$ $\Rightarrow$ rate = K $[A]^x\,[B]^y$

- order of the reaction with respect to A is x.
- order with respect to B is y
- the **overall order** (i.e., the sum of the individual orders) is x + y

where K is the proportionality constant, which we call the **rate constant** which varies with temperature.

The resulting equation, termed the **rate law** for the reaction is:

$$\textbf{rate} = K\,[A]^x\,[B]^y$$

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N.B:

There is no direct relationship between the coefficient in the chemical equation for a reaction and the order of the reaction. **The value of x and k can only be determined from experiment**.

Concentration and time: Half - lives

Half lives($t_{1/2}$): the length of time required for the concentration of the reactant to be decreased to half of its initial value. At this point $t = t_{1/2}$, and $[A]t_{1/2} = {}^{1}/_{2}[A]_o$.

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Chemical reactions

When a chemical reaction proceeds in one direction, i.e: from reactant to products, reaction is known as <u>irreversible reaction</u> or complete reaction.

$$A + B \longrightarrow AB$$

On the contrary, reactions that proceed either in forward or in backward (reverse) directions are known as **<u>reversible reaction</u>** and equation for reaction can be written.

$$\mathbf{N_{2(g)} + 3H_{2(g)} \leftrightarrow 2\,NH_3(g)}$$

Double arrow ($\leftrightarrow$) indicates that equation can be read in either direction.

All reversible processes tend to attain a state of equilibrium.

- **An equilibrium state is attained *when* the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.**

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Chemical equilibrium

Chemical equilibrium is a condition in the course of a reversible chemical reaction in which no net change in the amounts of reactants and products occurs

Example:

If pure hydrogen iodide is heated in a closed vessel to a temperature of about 450°C:

it decomposes to form hydrogen and iodine, but no matter how prolonged the heating, some hydrogen iodide remains unchanged. This is an example of a **reversible reaction in gaseous phase.**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

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Chemical equilibrium

Law of mass action states that rate of a chemical reaction is directly proportional to product of concentrations of reactants raised to their respective stoichiometric coefficients.

Example:

$$aA(g) + bB(g) \Leftrightarrow cC(g) + dD(g)$$

- Forward reaction rate would be $k_f [A]^a[B]^b$
- Backward reaction rate would be $k_b [C]^c[D]^d$

- where, [A], [B], [C] and [D] being the active masses
- k_f and k_b are rate constants of forward and backward reactions,
- a, b, c, d are stoichiometric coefficients related to A, B, C and D respectively.

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Chemical equilibrium

- Since at equilibrium the forward and the backward rates are equal,

Rate of forward reaction = Rate of backward reaction

$$K_f[A]^a[B]^b = K_b[C]^c[D]^d$$

$$\frac{K_f}{K_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\boxed{K_c = \frac{K_f}{K_b}}$$

Where: Kc is equilibrium constant expressed in terms of molar concentrations

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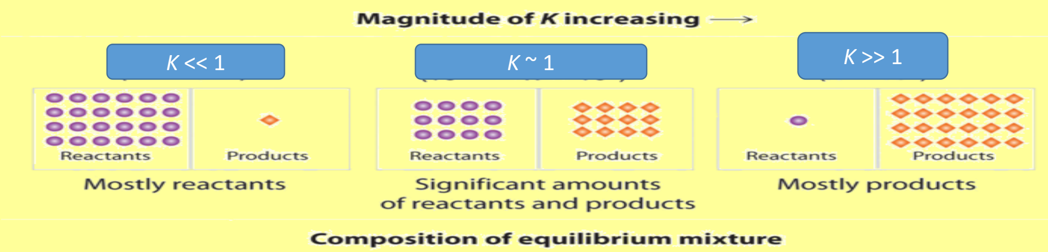
Chemical equilibrium

Example: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\mathbf{Keq = [NH_3]^2/[N_2][H_2]^3}$$

- **Notice**: superscript 2 outside the [ ] of NH_3 and superscript 3 outside [ ] of H_2 . This is the coefficient in front of product in the equilibrium equation above.

●Magnitude of K can tell us how far a reaction proceeds to the products at a given temperature:



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Note that:when a chemical reaction reaches dynamic equilibrium:
- The rate of the forward reaction equals the rate of the reverse reaction, and the concentrations of reactants and products become constant.
- But the concentrations of reactants and products will not necessarily be equal at equilibrium.

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Question The equilibrium constant for the reaction $A(g) \rightleftharpoons B(g)$ is 10. A reaction mixture initially contains [A] = 1.1 M and [B] = 0.0 M. Which statement is true at equilibrium?

(a) The reaction mixture contains [A] = 1.0 M and [B] = 0.1 M.
(b) The reaction mixture contains [A] = 0.1 M and [B] = 1.0 M.
(c) The reaction mixture contains equal concentrations of A and B.

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Chemical equilibrium

Direction of chemical equation and K :

The equilibrium constant of a reaction in the reverse direction is the reciprocal of equilibrium constant of the forward reaction.

Forward reaction: $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$

Bachward reaction: $2HI(g) \rightleftarrows H_2(g) + I_2(g)$

$K_f = [HI]^2 / [H_{2(g)}][I_2]$ $K_f = 54$

$K_b = [H_{2(g)}][I_2] / [HI]^2$ $K_b = 0.01851$

$K_f = 1/K_b$

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Chemical equilibrium for reaction that occur in more than one step

●Example : ionization of hydrogen sulphide H_2S,

1- $H_2S \leftrightarrow H^+ + HS$ $K_1 = [H^+][HS^-] / [H_2S]$

K_1 is first equilibrium constant

2- $HS^- \leftrightarrow H^+ + S^{--}$ $K_2 = [H^+][S^{--}] / [HS^-]$

K_2 is second equilibrium constant

●Equilibrium constant for the overall change is the product of the equilibrium constants of each the steps:

$$K_c = K_1 K_2$$

● **homework: Write the equilibrium constants representing ionization of phosphoric acid H_3PO_4 and the overall equilibrium constant**

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