Ministry of Higher Education and Scientific Research
AL-Mustaqbal University College of Science
Department of Biochemistry

Physical Chemistry

Lecture 1

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First semester

Chemical Kinetics

By

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What is chemical kinetics

Chemical kinetics is the part of chemical science dealing with the study of the

- **rates of chemical reactions**

  and

- **the factors which affect the reaction rates.**

Reaction Rates

Rate of a chemical reaction = change in concentration (mol/L) of a reactant or product with time (s, min, hr);

$$\text{Rate of Reaction} = \frac{\text{Change in Concentration}}{\text{Change in Time}}$$

Chemical Kinetics

$$A \longrightarrow B$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

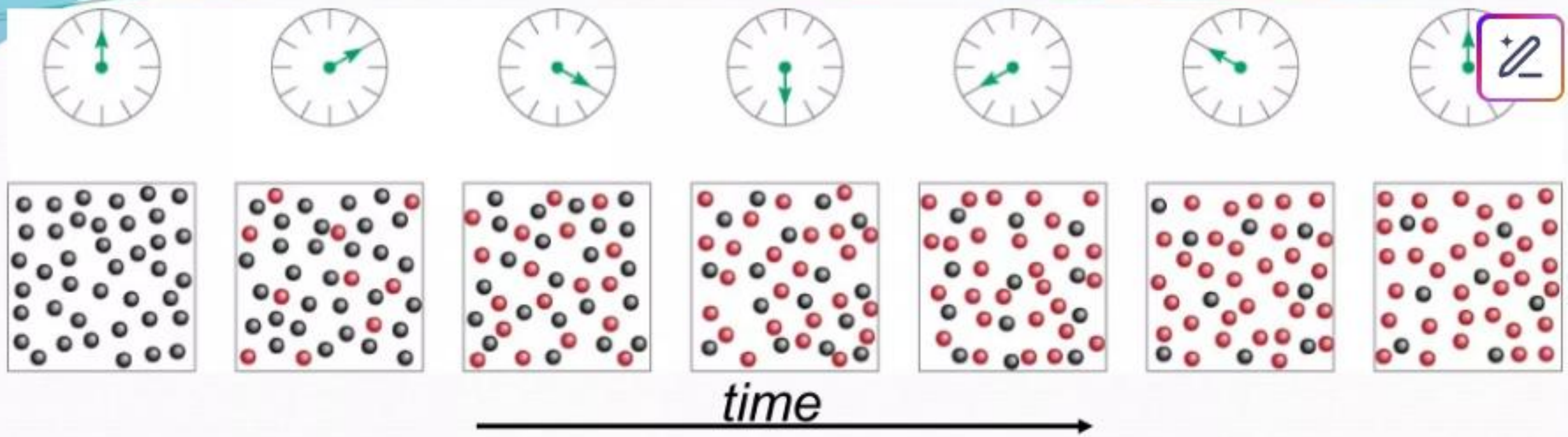
$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

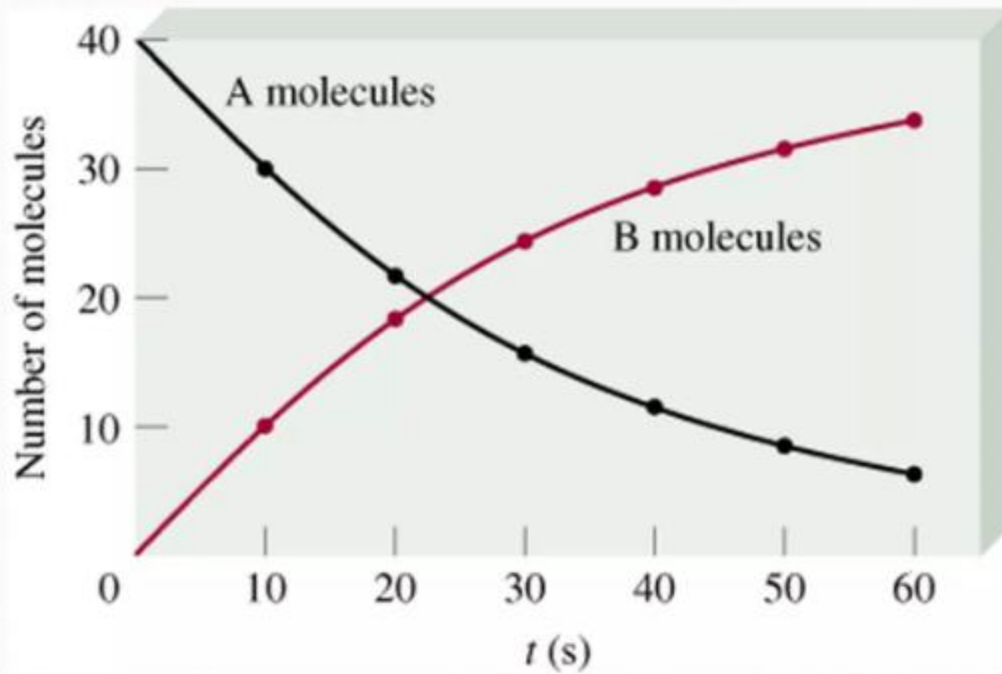
Because [A] decreases with time, $\Delta[A]$ is negative.

$$A \longrightarrow B$$



$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



The rate expression

We know how to work out the rate of reaction ...

... but that doesn't tell us if the all the reactants make the same contribution to the overall reaction

That's where the **rate expression** comes in

Look at this reaction ...

$$X + Y \rightarrow Z$$

X may make more contribution to the rate of the reaction than Y

Or X may make no contribution to the rate of the reaction – instead it depends on Y

The only way to find this out is through experimentation

The rate expression

When you see square brackets around a formula it means concentration of

[HCl]

… means concentration of HCl

So, we could say that the rate is proportional to the concentrations of the reactants …

$$\text{rate} \propto [X][Y]$$

The rate expression

rate $\propto$ [X][Y]

This suggests that X and Y both have an equal affect on the rate of this reaction

Question …

What would happen if we double the concentration of X or Y?

The rate of reaction would also double

Question …

What would happen if we had $[Y]^2$?

Doubling the concentration of Y would quadruple the reaction rate

The rate constant

Unfortunately, proportionality signs aren't very useful to us, so we need to replace it with a constant …

k is the symbol for the rate constant

$$rate = k[X][Y]$$

k is different for every reaction

k varies with temperature so temperature must be stated when quoting *k*

The order of a reaction

Let's look at the rate equation for X and Y again …

$$\text{rate} = k[X][Y]^2$$

… means that Y has double the effect of X on the rate of reaction

This is the order with respect to Y

X must have an order of 1
[X] and $[X]^1$ are the same

The overall reaction order of X + Y is …

1 + 2

3rd order

The rate expression

So, taking into account the rate constant and the reaction order, the overall rate expression is …

$$\text{rate} = k[X]^m[Y]^n$$

… where m and n are the orders of the reaction with respect to X and Y

The overall reaction order is m + n

Difference between Order and Molecularity of reactions

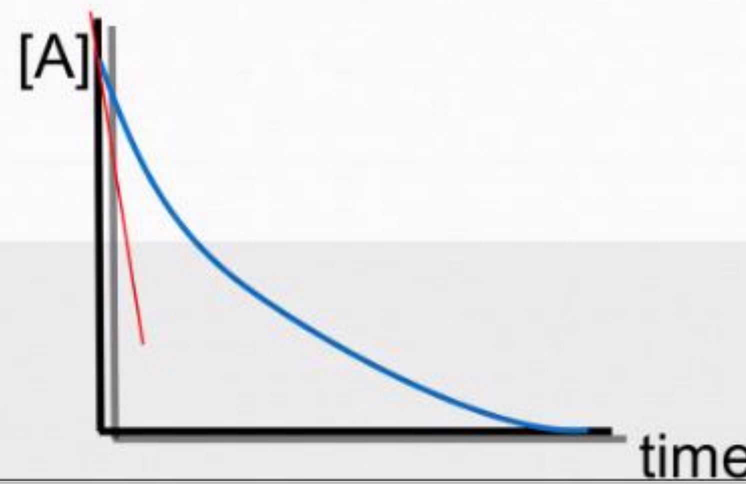
Order of a reaction	Molecularity of a reaction
1. It is the sum of powers raised on concentration terms in the rate expression.	1. It is the number of molecules of reactants taking part in elementary step of a reaction.
2. Order of a reaction is an experimental value, derived from rate expression.	2. It is a theoretical concept.
3. Order of a reaction can be zero, fractional or integer.	3. Molecularity can neither be zero nor fractional.
4. Order of a reaction may have negative value.	4. Molecularity can never be negative.
5. It is assigned for overall reaction.	5. It is assigned for each elementary step of mechanism.
6. It depends upon pressure, temperature and concentration (for pseudo order)	6. It is independent of pressure and temperature.

Orders of Reaction

The order can be determined experimentally using the initial rate method, but …

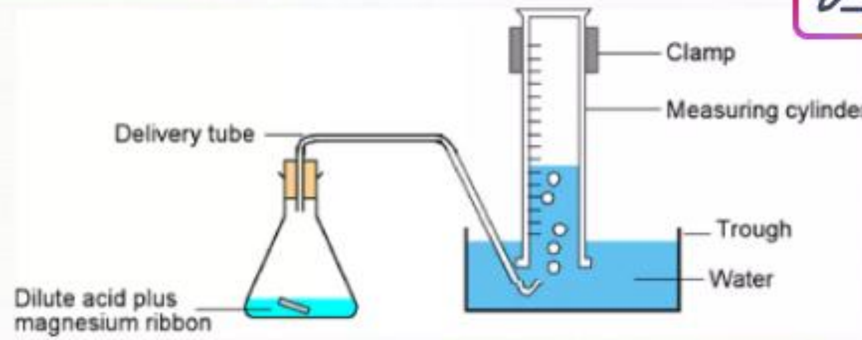
… to do so, the concentration of the reactant under investigation should be changed – the other reactant's concentration should remain the same

The initial rate method involves plotting the data obtained from an experiment and using the tangent from time 0 to calculate the rate



First order reactions

If rate doubles because the concentration is doubled, then it is a first order reaction



[X] mol dm^{-3}	[Y] mol dm^{-3}	Rate mol dm^{-3} s^{-1}
0.01	0.02	0.0004
0.01	0.04	0.0008

Concentration remains the same

Concentration doubled

Rate of reaction doubled

Since the rate is doubled when [Y] is doubled the order with respect to Y is 1

Note: we don't know the order of X and would have to do another experiment to find out

First order reactions

Let's add another result …

[X] mol dm⁻³	[Y] mol dm⁻³	Rate mol dm⁻³ s⁻¹
0.01	0.02	0.0004
0.01	0.04	0.0008
0.005	0.04	0.0004

Question …

What is the order of X?

1

So, the overall rate equation is … rate = k[X][Y]

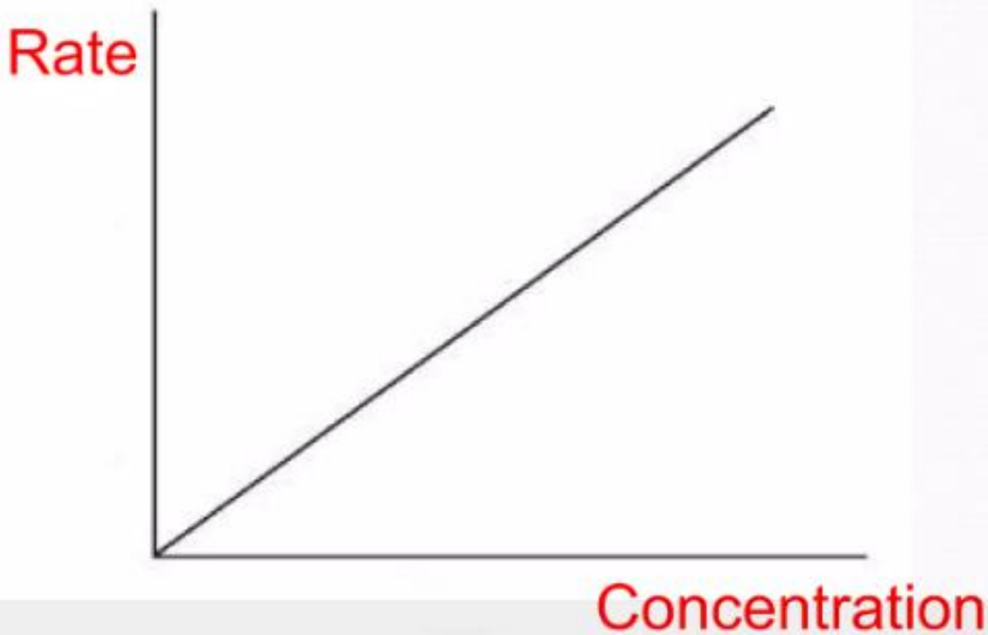
Question …

What is the value of the rate constant?

$$k = \frac{rate}{[X][Y]} = \frac{0.0004}{0.01 \times 0.04} = 1.0\ mol^{-1}\ dm^{-3}\ s^{-1}$$

First order reactions

If the concentrations are not simple whole numbers, then it may be easier to draw a graph of rate against concentration



A first order reaction will be a straight line through 0

The gradient in this case is the rate constant (*k*)

Second order reactions

[X] mol dm^{-3}	[Y] mol dm^{-3}	Rate mol dm^{-3} s^{-1}
0.01	0.02	0.0004
0.01	0.04	0.0016
0.02	0.02	0.0032

Question …

What is the order of Y?

Order of reaction with respect to Y is 2

Concentration remains the same

Concentration doubled

Rate of reaction quadrupled

Question …

What is the order of X?

3

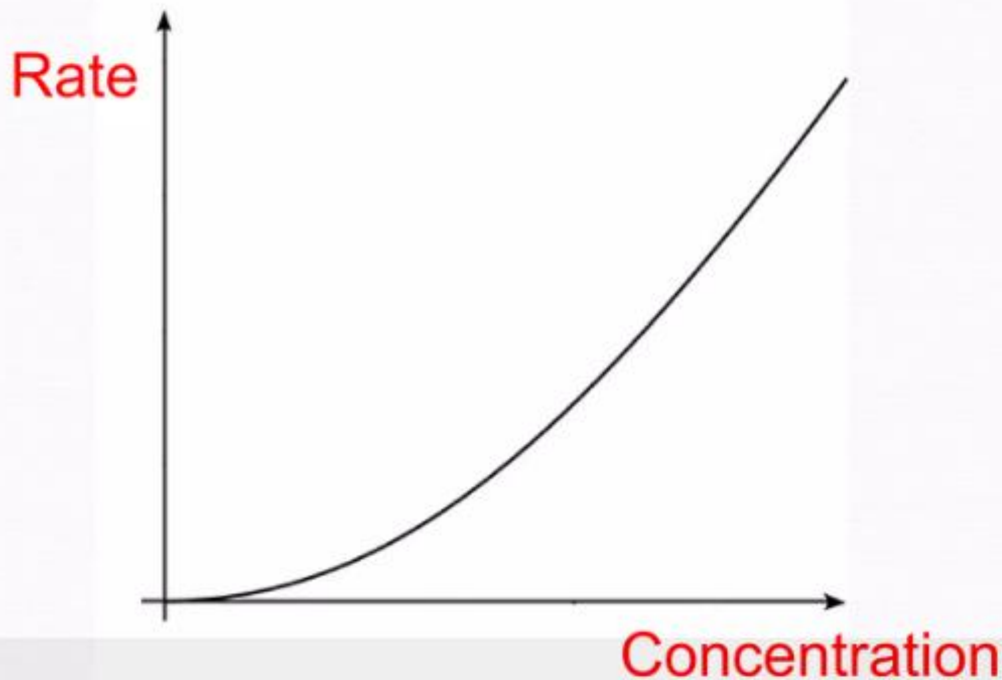
Question …

What is rate equation?

$$\text{rate} = k[X]^3[Y]^2$$

Second order reactions

In this case the rate is $[X]^2$, giving a curve through the origin



Reaction orders

Question …

What is the order of X?

1

[X] mol dm^{-3}	[Y] mol dm^{-3}	Rate mol dm^{-3} s^{-1}
0.2	0.1	0.0004
0.4	0.1	0.0008
0.8	0.2	0.0064

We cannot work out Y straight away – instead let's look at the whole reaction …

Both reactant concentrations have doubled …

… the reaction rate has increased by x8

Question …

What is the overall reaction rate? 3

So, the order of reaction with respect to Y is …

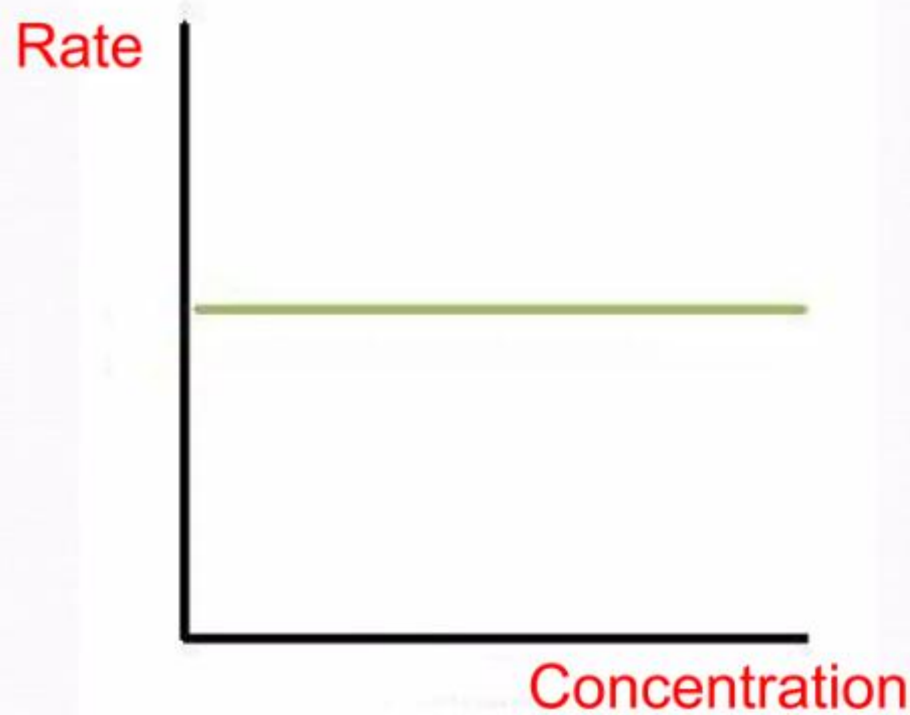
overall order = X order + Y order = 2

Zero order reactions

In a zero order reaction you get a straight line as concentration does not change with rate

In this case the rate = rate constant

This means the reactant has no influence over the rate of reaction



FACTORS AFFECTING RATE OF A CHEMICAL REACTION

- Temperature
- Concentration
- Pressure
- Surface area
- Presence of a catalyst


Thank you