

# KINETICS

## Lecture 15



Dr Ewa Kazimierska

[e.kazimierska@uwtsd.ac.uk](mailto:e.kazimierska@uwtsd.ac.uk)

# WHAT IS A CHEMICAL KINETICS?

study of the rate of change of chemical reactions:

very fast – instantaneous detonation of explosive material

moderate – dissolving sugar in water

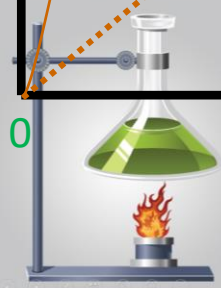
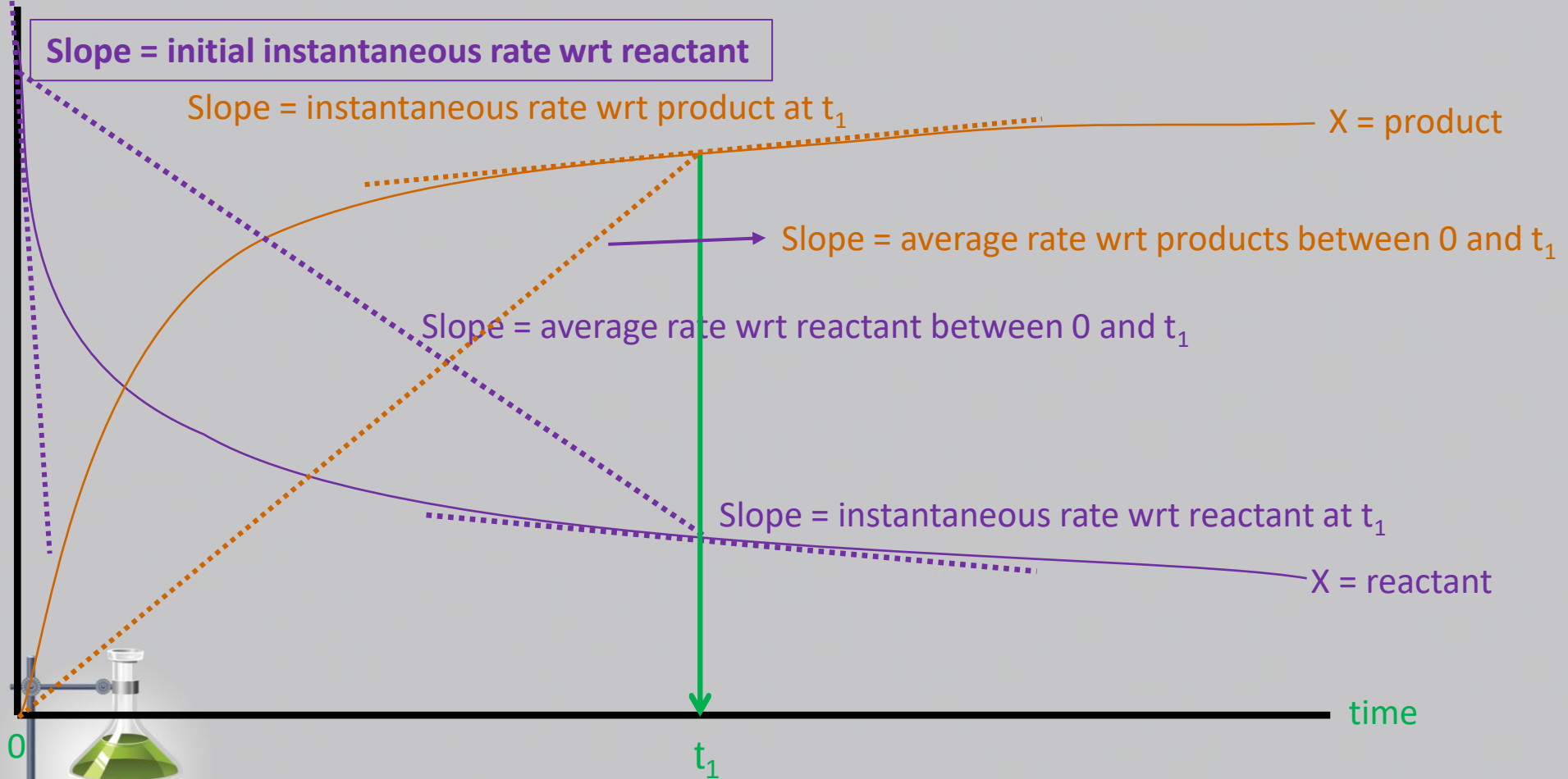
slow – rusting the metal



# RATE OF REACTIONS

Rate of reaction =  $\frac{\text{Change of concentration}}{\text{Change of time}} = \frac{\Delta[X]}{\Delta t}$  measure and plot  $[X]$  on vertical,  $t$  on horizontal, **SLOPE**

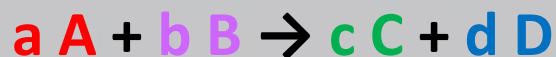
kinetic profile



# RATE OF REACTION

**initial rate of reaction** – instantaneous rate at the very beginning of the reaction

(tangent at the start) where no products are present



$$-\frac{1}{a} \times \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \times \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \times \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \times \frac{\Delta[D]}{\Delta t}$$

## factors affecting rate of reaction:

- concentration of reactants
- temperature of reaction
- intensity of light
- particle size of a solid (large surface area)
- polarity of the solvent (for reactions of ions in solution)
- presence of catalyst



## units of rate of reaction

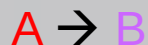
concentration – mol/L

time – s

rate of reaction - mol/L-s

# RATE LAW

rate of reaction measured experimentally at any stage of the reaction:



$$\text{rate} = k_1 \times [A]^a$$



$$\text{rate} = k_2 \times [A]^a \times [B]^b$$



$$\text{rate} = k_3 \times [A]^a \times [B]^b \times [C]^c$$

**k** - rate constant independent of concentration but depends on temperature and has to be determined experimentally

a, b, c – order of reaction in A, B, C (0, 1, 2); the power to which the concentration of a species is raised in the rate law

a + b + c - overall order of reaction with respect to a reactant is an indication of how the reaction takes place, not its stoichiometry !!!

**every reaction has its own characteristic rate law and rate constant k**



# SAMPLE PROBLEM

A group of students carried out a series of experiments on the reaction:  
 **$\text{BrO}_3^- (\text{aq}) + 5 \text{Br}^- (\text{aq}) + 6 \text{H}^+ (\text{aq}) \rightarrow 3 \text{Br}_2 (\text{aq}) + 3 \text{H}_2\text{O} (\text{l})$**  to discover how the initial rate of disappearance of  $\text{BrO}_3^-$  ion varies as the concentrations of the reactants are changed . Use the experimental data in the table below to determine the order of the reaction with respect to each reactant and the overall order. Write the rate law for the reaction and determine the value of k.

| experiment | initial concentration mol/L |               |              | initial rate,<br>mol $\text{BrO}_3^-$ /L-s |
|------------|-----------------------------|---------------|--------------|--------------------------------------------|
|            | $\text{BrO}_3^-$            | $\text{Br}^-$ | $\text{H}^+$ |                                            |
| 1          | 0.10                        | 0.10          | 0.10         | $1.2 \times 10^{-3}$                       |
| 2          | 0.20                        | 0.10          | 0.10         | $2.4 \times 10^{-3}$                       |
| 3          | 0.10                        | 0.30          | 0.10         | $3.6 \times 10^{-3}$                       |
| 4          | 0.20                        | 0.10          | 0.20         | $5.8 \times 10^{-3}$                       |



# PRACTICE PROBLEM

Write the rate law for the disappearance of persulfate ions in the reaction

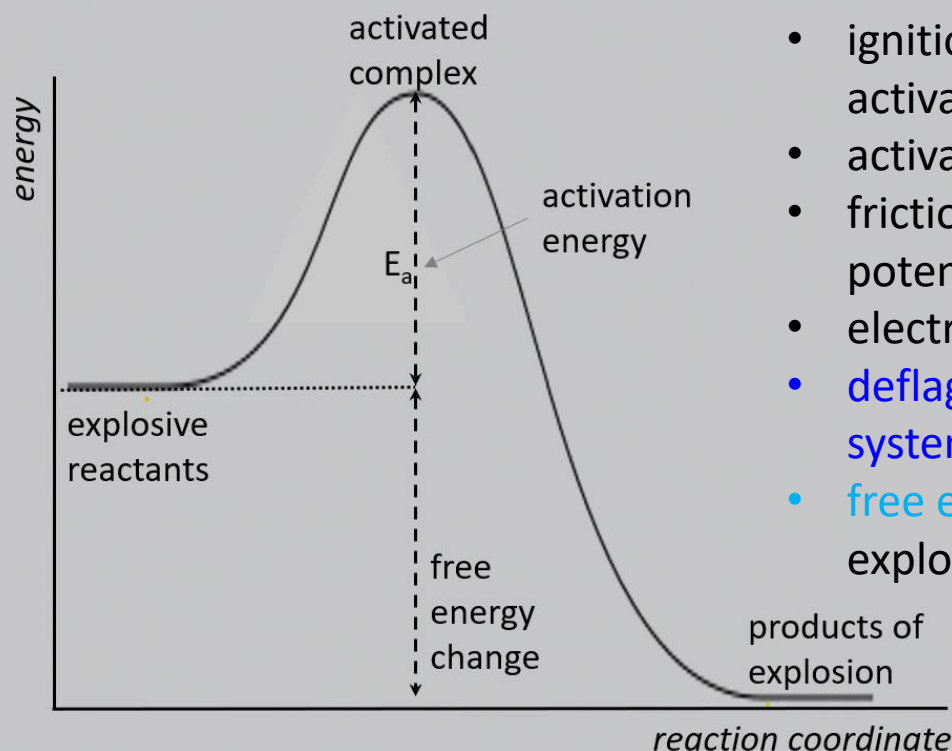
$\text{S}_2\text{O}_8^{2-} + 3 \text{I}^- \rightarrow 2 \text{SO}_4^{2-} + \text{I}_3^-$  with respect to each reactant and determine the value of  $k$  if the following data was collected.

| experiment | initial concentration mol/L |              | initial rate,<br>mol $\text{S}_2\text{O}_8^{2-}$ /L-s |
|------------|-----------------------------|--------------|-------------------------------------------------------|
|            | $\text{S}_2\text{O}_8^{2-}$ | $\text{I}^-$ |                                                       |
| 1          | 0.15                        | 0.24         | 0.87                                                  |
| 2          | 0.30                        | 0.24         | 1.70                                                  |
| 3          | 0.30                        | 0.48         | 1.68                                                  |



# THE KINETICS OF EXPLOSIONS

- **exothermic reaction** – energy of reactants > energy of products
- energy is needed to start the reaction
- **activation energy ( $E_a$ )** - energy needed to break bonds in the reactants and to allow the less stable intermediates, or activated complex, before the products are formed



- ignition involves giving the explosive material the activation energy to start deflagration (**hot spot**)
- activation by various stimuli
- friction, impact and heat initiation (provide thermal, potential or kinetic energy to the system)
- electrical impulses - supply electrical energy
- **deflagration can then provide heat energy to the system to allow the rest of the explosive to react.**
- **free energy of change** – energy liberated in the explosion

e.g.  $\text{TNT} \rightarrow \text{C} + \text{CO} + \text{H}_2\text{O} \text{ and } \text{N}_2$

e.g. glycerine and nitric acid  $\rightarrow$  nitroglycerine and water



The values for  $E_a$  can be used to measure the ease with which an explosive composition will initiate (the larger  $E_a$ , the more difficult it will be to initiate the explosive composition)

# EFFECT OF TEMPERATURE

Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

$k$  – rate constant

$A$  – constant for a given material

$E_a$  – activation energy, kJ/mol

$R$  – gas constant, 8.314 J/mol-K

$T$  – temperature, K

$A$  – frequency factor or collision factor; determined from the number of collisions per unit volume per second between the molecules

$e^{-E_a/RT}$  – quantifies the fraction of colliding molecules that result in a reaction

if  $E_a = 0$ ,  $e^{-E_a/RT} = 1$  and all colliding molecules react

if  $E_a/RT \gg 1$ ,  $E_a \gg RT$  (high activation energy), majority of molecules do not react

$E_a, A$  (primary explosives, PE) <  $E_a, A$  (secondary explosives, SE)

Less energy needed to initiate PE → more sensitive to external stimuli (friction, light, etc)



# KINETICS OF THERMAL DECOMPOSITION

- all explosives undergo thermal decomposition at temperatures lower than the temperature needed for detonation
- used to determine the **stability** and **shelf life** of the explosive
- shelf-life and stability susceptibility to heat
- measured at constant temperature by measuring the rate of gas released from a sample of explosive at a series of controlled temperatures

$$V = k^T + C$$

**V** – volume of gas evolved

**k** – reaction rate constant

**T** – temperature, degC

**C** – constant for particular explosive

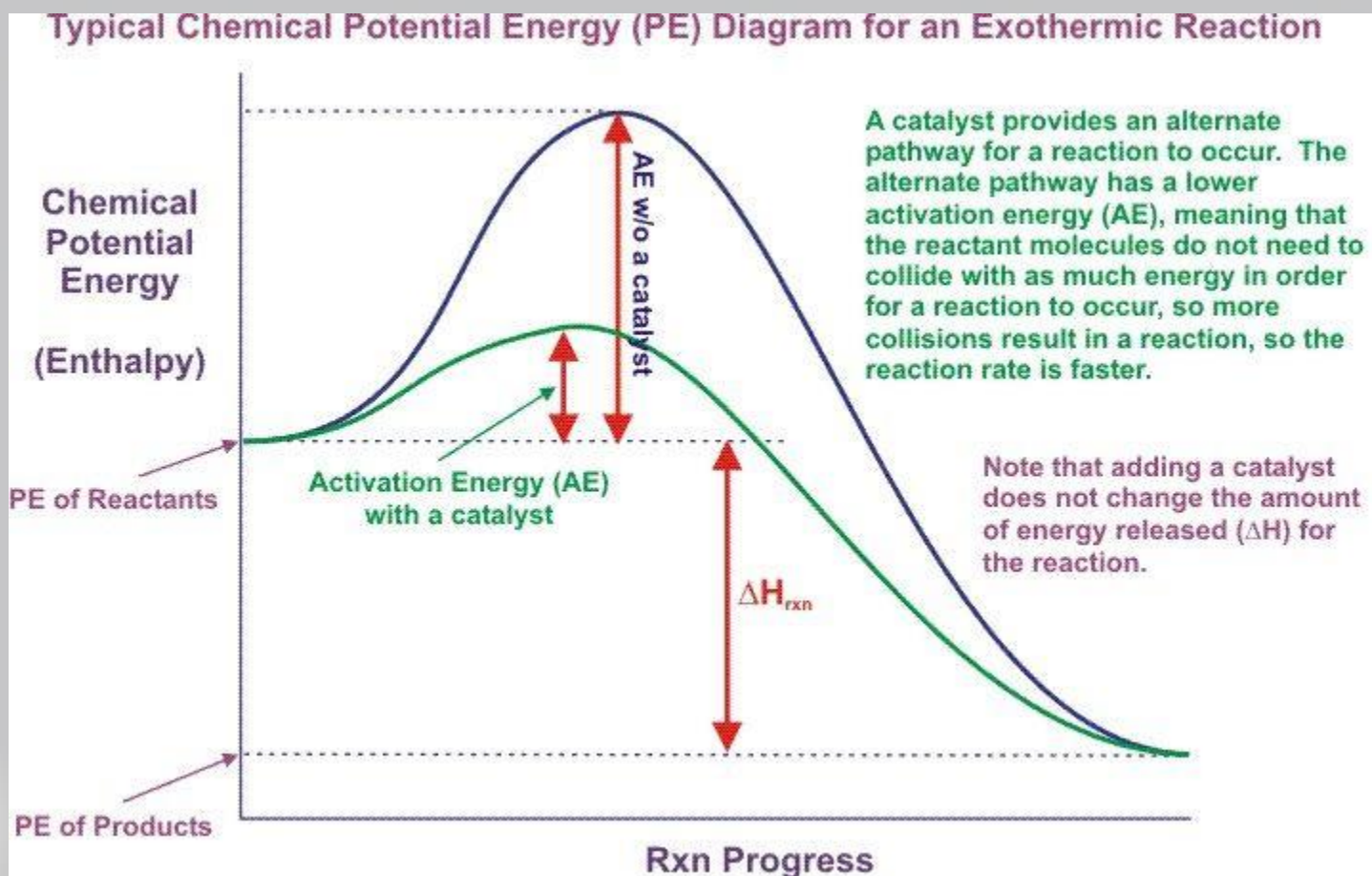
- for every **10 degC** increase in temperature, the **rate of decomposition** is approximately **doubled** (may increase 50 times if the explosion is in the molten state)
- **rates of decomposition** depend on the **condition of storage**
- presence of **moisture** increases the rate of decomposition
- presence of **impurities** which may act as **catalysts**



# EFFECT OF CATALYST

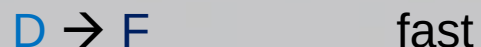
The rate of a reaction can be increased by adding a suitable catalyst.

A catalyst is a substance which increases the rate of a chemical reaction but it is not used up (remains chemically unchanged at the end). It provides an alternative reaction pathway of lower activation energy.



# MULTISTEP REACTIONS

mechanism – series of elementary steps

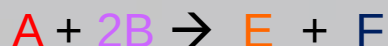
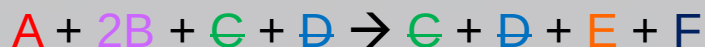


$$\text{rate} = k[\text{A}][\text{B}]^2$$

rate determining

$$\text{rate} = k[\text{C}]$$

$$\text{rate} = k[\text{D}]$$



$$\text{rate} = k[\text{A}][\text{B}]^2$$

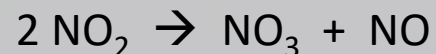
C, D – intermediates

In the case of elementary steps, the order = coefficient



# SAMPLE PROBLEM

The mechanism of decomposition of  $\text{NO}_2$  proceeds through two-step mechanism:



Find the net balance equation for the decomposition of  $\text{NO}_2$ . If the first reaction was slower than reaction 2, what is the rate law for the overall reaction?

