

# Chemical Kinetics Notes

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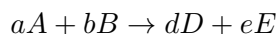
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# 1 Definitions

## 1.1 Reaction rate

Either the **increase** in the concentration of a product per unit time or the **decrease** in the concentration of a reactant per unit time.

General reaction:



$$\text{Rate of reaction} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = -\frac{1}{d} \frac{d[D]}{dt} = -\frac{1}{e} \frac{d[E]}{dt}$$

### 1.1.1 Example



$$\text{Rate of reaction} = \frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\text{Rate of reaction} = k[N_2O_5]^2$$

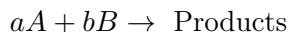
$$\text{Rate of consumption of reactant} = -\frac{d[N_2O_5]}{dt} = 2 \cdot k[N_2O_5]^2$$

$$\text{Rate of formation of product} = -\frac{d[NO_2]}{dt} = 4 \cdot k[N_2O_5]^2$$

$$\text{Rate of formation of product} = -\frac{d[O_2]}{dt} = k[N_2O_5]^2$$

## 1.2 Rate law

The rate law is an equation that shows the dependence of the reaction rate on the concentration of each reactant.



$$\text{Rate} \propto [A]^m[B]^n$$

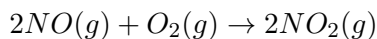
$$\text{Rate} = k[A]^m[B]^n$$

$k$  is the **rate constant**.

The values of the exponents in the rate law must be **determined experimentally**. They cannot be deduced from the stoichiometry of the reaction.

### 1.2.1 Units of the rate constant $k$

The units of  $k$  must be determined based on the order of the reaction. For example, given a third order reaction:



$$\text{Rate} = k[NO]^2[O_2]$$

Units of  $k$  for this third-order reaction:

$$k = \frac{\text{Rate}}{[NO]^2[O_2]} = \frac{\frac{M}{s}}{M^2 \cdot M} = \frac{1}{M^2 s}$$

### 1.2.2 The rate constant $k$ is dependent on temperature

The **rate constant**  $k$  is dependent on temperature and the **rate of reaction** usually **increases** when the **temperature increases**.

## 1.3 Half-life

The half-life is the **time** required for the reactant concentration to drop to **one-half** of its initial value.

## 1.4 Transition state

The transition state is the configuration of atoms at the maximum in the potential energy profile. This is also called the activated complex.

## 1.5 Collision theory

Collision theory states that as the average **kinetic energy** increases, the average **molecular speed** increases and thus the **collision rate** increases.

## 1.6 Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

Where:

- $k$  is the rate constant
- $A$  is the collision frequency factor
- $E_a$  is the activation energy
- $R$  is the gas constant
- $T$  is the temperature in Kelvin (K)

### 1.6.1 Using the Arrhenius equation

$$\ln(k) = \ln(A) + \ln \left[ e^{\frac{-E_a}{RT}} \right]$$

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

$$\ln(k) = \frac{-E_a}{R} \frac{1}{T} + \ln(A) \text{ which is in the form: } y = mx + c$$

So, we get:

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Plotting the graph of  $\ln(k)$  versus  $\frac{1}{T}$  gives a straight line graph with a **slope (gradient)** of  $\frac{-E_a}{R}$ .

### 1.6.2 Which gas constant ( $R$ ) value to use?

The gas constant can be either:

- $R$  value: 8.314  
Units:  $\text{J K}^{-1} \text{mol}^{-1}$ ,  $\text{m}^3 \text{Pa K}^{-1} \text{mol}^{-1}$
- $R$  value: 0.0821  
Units:  $\text{L atm K}^{-1} \text{mol}^{-1}$

$$\ln \left( \frac{k_2}{k_1} \right) = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

For the term  $\frac{-E_a}{R}$ , the final units should be K.

If  $R = 8.314 \text{ J K}^{-1} \text{mol}^{-1}$ , the units for  $E_a$  should be  $\text{J mol}^{-1}$ .

If  $R = 0.0821 \text{ L atm K}^{-1} \text{mol}^{-1}$ , the units for  $E_a$  should be  $\text{L atm mol}^{-1}$ .

## 1.7 Elementary reaction (elementary step)

A single step in a reaction mechanism. An elementary reaction describes an individual molecular event.

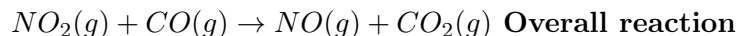
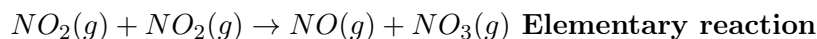
## 1.8 Overall reaction

The overall reaction described the reaction stoichiometry and is a summation of elementary reactions.

## 1.9 Reaction mechanism

The reaction mechanism is a sequence of reaction steps that describes the pathway from reactants to products.

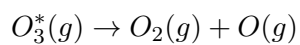
### 1.9.1 Example



## 1.10 Molecularity

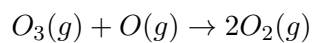
Molecularity is a classification of an elementary reaction based on the number of molecules or atoms on the reactant side of the chemical equation.

#### 1.10.1 Unimolecular reaction



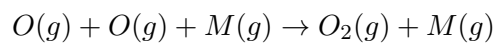
$$\text{Rate} = k[O_3]$$

#### 1.10.2 Bimolecular reaction



$$\text{Rate} = k[O_3][O]$$

#### 1.10.3 Termolecular reaction



$$\text{Rate} = k[O]^2[M]$$

### 1.11 Rate-determining step

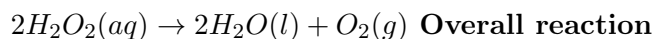
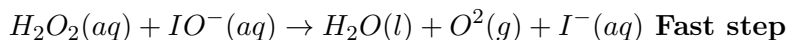
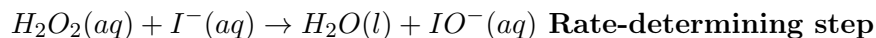
The rate-determining step is the **slow step** in a reaction mechanism since it acts as a bottleneck and limits the rate at which reactants can be converted to products.

## 1.12 Catalyst

A catalyst is a substance that increases the rate of a reaction without itself being consumed in the reaction. A catalyst is used in one step and regenerated in a later step.

### 1.12.1 Example

$I^-(aq)$  is acting as a catalyst in the reaction below as it is regenerated and not used up:



Since the catalyst is involved in the **rate-determining step**, it often appears in the rate law. The rate law for the reaction above is:

$$\text{Rate} = k[H_2O_2][I^-]$$

### 1.12.2 Effect of a catalyst

A catalyst will **decrease** the **activation energy** ( $E_a$ ) of a reaction and there will usually be **two transition states** in the reaction, which means 2 humps in the energy level diagram for the reaction. The first hump will be **larger** than the second one as the first hump represents the activation energy for the reaction.

## 1.13 Homogeneous catalyst

A homogeneous catalyst is a catalyst that exists in the **same phase** as the reactants.

## 1.14 Heterogeneous catalyst

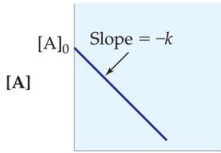
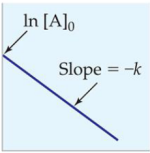
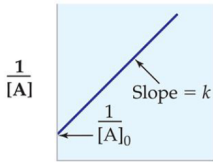
A catalyst that exists in a **different phase** from that of the reactants.

### 1.14.1 Example mechanism

Using a metal catalyst for the reaction between  $H_2$  and  $C_2H_4$ :

1.  $H_2$  and  $C_2H_4$  are adsorbed on the metal surface.
2. The  $H-H$  bond breaks as  $H$ -metal bonds form, and the  $H$  atoms move about on the surface.
3. One  $H$  atom forms a bond to a  $C$  atom of the adsorbed  $C_2H_4$  to give a metal-bonded  $C_2H_5$  group. A second  $H$  atom bonds to the  $C_2H_5$  group.
4. The resulting  $C_2H_6$  molecule is desorbed from the surface.

## 2 Characteristics of zeroth, first, and second-order reactions

	Zeroth-Order	First-Order	Second-Order
Rate law	$-\frac{\Delta[A]}{\Delta t} = k$	$-\frac{\Delta[A]}{\Delta t} = k[A]$	$-\frac{\Delta[A]}{\Delta t} = k[A]^2$
Integrated Rate Law	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
Linear graph	<p><math>[A]</math> versus <math>t</math></p> 	<p><math>\ln [A]</math> versus <math>t</math></p> 	<p><math>\frac{1}{[A]}</math> versus <math>t</math></p> 
Graphical determination of $k$	$k = -(\text{Slope})$	$k = -(\text{Slope})$	$k = \text{Slope}$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$ (not constant)	$t_{1/2} = \frac{0.693}{k}$ (constant)	$t_{1/2} = \frac{1}{k[A]_0}$ (not constant)



### 3 Zeroth-order reactions

For a zeroth-order reaction, the rate is **independent** of the concentration of the reactant.



$$\text{Rate} = k[A]^0 = k$$

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

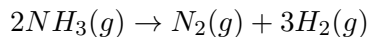
The **integrated rate law** for a zeroth-order reaction is:

$$[A]_t = -kt + [A]_0, \text{ which is in the form: } y = mx + c$$

Where  $[A]_t$  is the concentration of  $A$  at time  $t$  and  $[A]_0$  is the initial concentration of  $A$ .

A plot of  $[A]$  versus **time** gives a straight-line graph and the **slope (gradient)** will be  $-k$ .

#### 3.1 Example



$$\text{Rate} = k[NH_3]^0 = k$$

##### 3.1.1 Explanation (not very important)

Most of the  $NH_3$  molecules are in the gas phase above the surface and are unable to react. As the  $NH_3$  molecules on the surface decompose, they are replaced by molecules from the gas phase, so the number of  $NH_3$  molecules on the surface remains constant. Because only the  $NH_3$  molecules on the surface react under these conditions, the reaction rate is independent of the total concentration of  $NH_3$ .

## 4 First-order reaction



$$\text{Rate} = k[A]$$

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

Deriving the **integrated rate law**:

$$\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

Hence, the **integrated rate law** is:

$$\ln[A]_t = -kt + \ln[A]_0, \text{ which is in the form: } y = mx + c$$

$$[A]_t = e^{-kt} + [A]_0$$

Where  $[A]_t$  is the concentration of  $A$  at time  $t$  and  $[A]_0$  is the initial concentration of  $A$ .

A plot of  $\ln[A]$  versus **time** gives a straight-line graph and the **slope (gradient)** will be  $-k$ .

### 4.1 Half-life

Finding the half life of a first-order reaction:



$$\text{Rate} = k[A]$$

$$\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt$$

When  $t = t_{\frac{1}{2}}$  and  $[A]_{t_{\frac{1}{2}}} = \frac{[A]_0}{2}$ :

$$\ln \frac{1}{2} = -kt_{\frac{1}{2}}$$

Hence, the half-life of a first-order reaction is:

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

The half-life of a first-order reaction is **independent** of the initial concentration. Each successive half-life is an equal period of time.

## 5 Second-order reaction



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

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2$$

The **integrated rate law** of a second-order reaction is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \text{ which is in the form: } y = mx + c$$

Where  $[A]_t$  is the concentration of  $A$  at time  $t$  and  $[A]_0$  is the initial concentration of  $A$ .

A plot of  $\ln[A]$  versus **time** gives a curve. However, plotting  $\frac{1}{[A]}$  versus **time** gives a straight-line graph with the **slope (gradient)** will be  $k$ .

### 5.1 Half-life

Finding the half life of a second-order reaction:



$$\text{Rate} = k[A]$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

When  $t = t_{\frac{1}{2}}$  and  $[A]_{t_{\frac{1}{2}}} = \frac{[A]_0}{2}$ :

$$\frac{2}{[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

Hence, the half-life of a second-order reaction is:

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

For a second-order reaction, the half-life is **dependent** on the initial concentration. Each successive half-life is **twice** as long as the preceding one.