

CHEMISTRY 203

Factors Affecting Reaction Rates

Purpose

1. To introduce the basic principles of *Chemical Kinetics*.
2. To *study* the various factors affecting the rates of chemical reactions.
3. To *determine* the *order* of two different reactions with respect to each reactant, and then deduce the overall order.
4. To *determine* the *rate*, and the *rate constant* for one reaction at a given temperature.

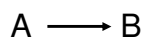
Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

Chemical Kinetics: is the area of chemistry concerned with the speeds, or rates, at which a chemical reaction occurs.

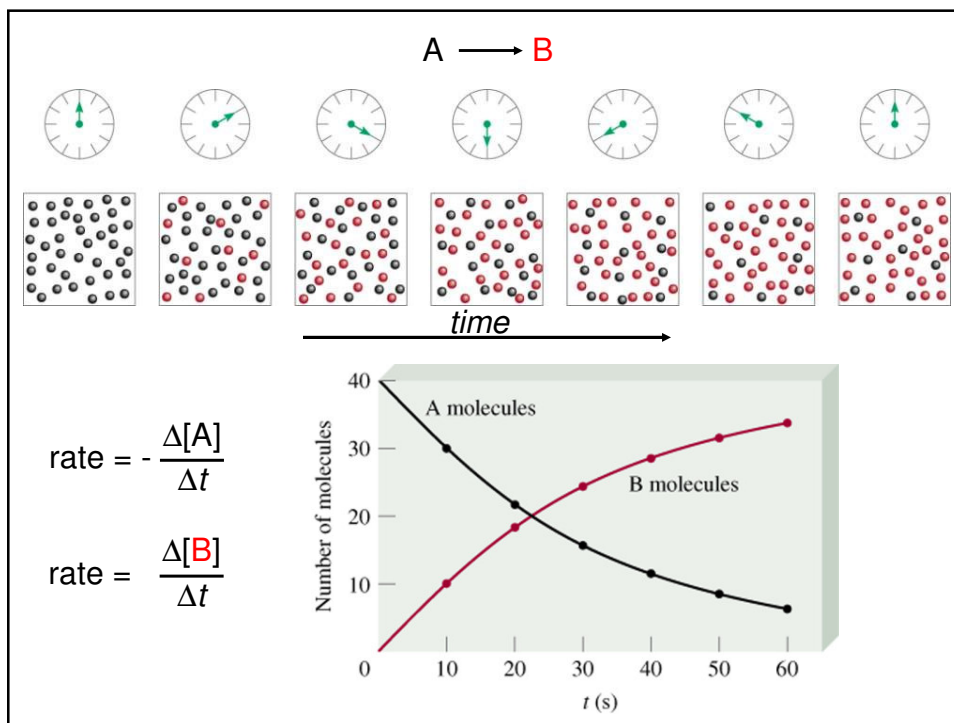
Reaction rate is the **change** in the concentration of a reactant or a product with time (M/s).



$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \Delta[A] = \text{change in concentration of A over time period } \Delta t$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t} \quad \Delta[B] = \text{change in concentration of B over time period } \Delta t$$

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



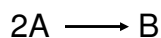
In general, the **rate** of a chemical reaction depends on several factors:

- The **nature** of the reaction
- The **concentrations** of reactants
- The **surface area**
- The **temperature**
- The presence of a **catalyst**.

In this experiment, the first three listed factors will be investigated.

The effect of temperature on a reaction will be investigated in a later experiment.

Reaction Rates and Stoichiometry



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

$$\text{rate} = - \frac{1}{2} \frac{\Delta[A]}{\Delta t} \quad \text{rate} = \frac{\Delta[B]}{\Delta t}$$



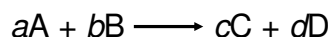
$$\text{rate} = - \frac{1}{a} \frac{\Delta[A]}{\Delta t} = - \frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

The rate of product formation does not require the minus sign because $\Delta[C]$ and $\Delta[D]$ are positive quantities.

In addition, “a” moles of A and “b” moles of B must be destroyed for the formation of “c” moles of C and “d” moles of D.

The Rate Law

The **rate law** expresses the relationship of the **rate** of a reaction to the **rate constant** and the **concentrations** of the reactants **raised** to some powers.



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

reaction is **m^{th} order** in A

reaction is **n^{th} order** in B

reaction is **$(m + n)^{\text{th}}$ order overall**

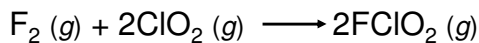


Table 13.2 Rate Data for the Reaction between F_2 and ClO_2

$$\text{Rate} = k [\text{F}_2]^m [\text{ClO}_2]^n$$

	$[\text{F}_2](M)$	$[\text{ClO}_2](M)$	Initial Rate (M/s)
1.	0.10	0.010	1.2×10^{-3}
2.	0.10	0.040	4.8×10^{-3}
3.	0.20	0.010	2.4×10^{-3}

Double $[\text{F}_2]$ with $[\text{ClO}_2]$ constant

Rate **doubles**

$$m = 1$$

Quadruple $[\text{ClO}_2]$ with $[\text{F}_2]$ constant

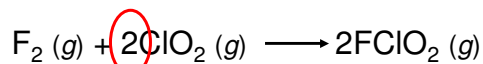
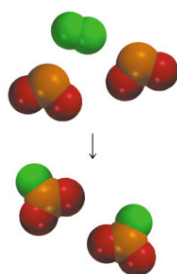
$$\text{Rate} = k [\text{F}_2][\text{ClO}_2]$$

Rate **quadruples**

$$n = 1$$

Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of **reactant** (not product) concentrations.
- The order of a reactant is **not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$\text{Rate} = k [\text{F}_2][\text{ClO}_2]^1$$

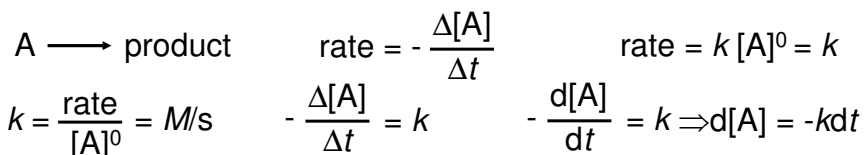
Types of rate laws:

1. Differential rate law shows how the rate of a reaction depends on concentration, called rate law.
2. Integrated rate law shows how the concentrations of species in the reaction depend on time,

Order	Rate Law	Integrated Rate Law
0	rate = k	$[A] = [A]_0 - kt$
1	rate = $k[A]$	$\ln[A] = \ln[A]_0 - kt$
2	rate = $k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

The rate of a reaction most of the time, **increases** with temperature.

Zero-Order Reactions



$$\int_{[A]_0}^{[A]} d[A] = -k \int_0^t dt \quad [A] \text{ is the concentration of A at any time } t$$

$$[A]_0 \text{ is the concentration of A at time } t=0$$

$$[A] = [A]_0 - kt$$

$$[A] = -kt + [A]_0$$

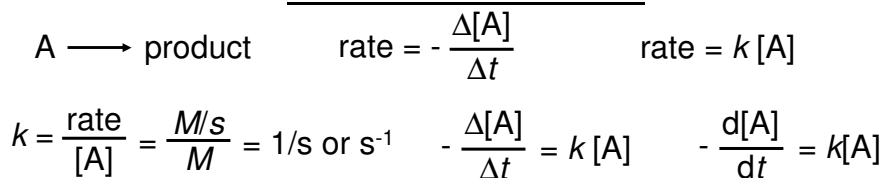
Integrated Rate Law

The **half-life**, $t_{1/2}$, is the time required for the concentration of a reactant to **decrease to half of its initial** concentration.

$$t_{1/2} = t \quad \text{when} \quad [A] = [A]_0/2$$

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

First-Order Reactions



$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

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

Integrated Rate Law

[A] is the concentration of A at any time t

[A]₀ is the concentration of A at time $t=0$

$$t_{1/2} = t \quad \text{when} \quad [A] = [A]_0/2$$

$$t_{1/2} = \frac{\ln \frac{[A]_0}{[A]_0/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$



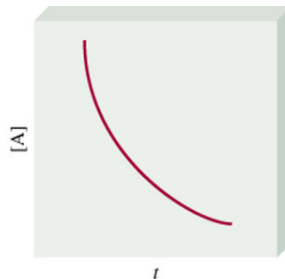
What is the half-life of N_2O_5 if it decomposes with a rate constant of $5.7 \times 10^{-4} s^{-1}$?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4} s^{-1}}$$

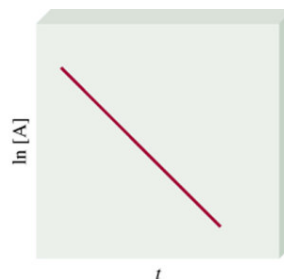
$$= 1200 \text{ s} = 20 \text{ minutes}$$

First-Order Reactions

$$[A] = [A]_0 \exp(-kt)$$

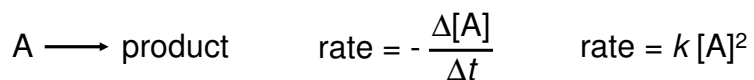


$$\ln[A] = \ln[A]_0 - kt$$



Ref. Chang, Fig.13.3

Second-Order Reactions



$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = 1/M \cdot s$$

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

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

Integrated Rate Law

[A] is the concentration of A at any time t

[A]₀ is the concentration of A at time $t=0$

$$t_{1/2} = t \text{ when } [A] = [A]_0/2$$

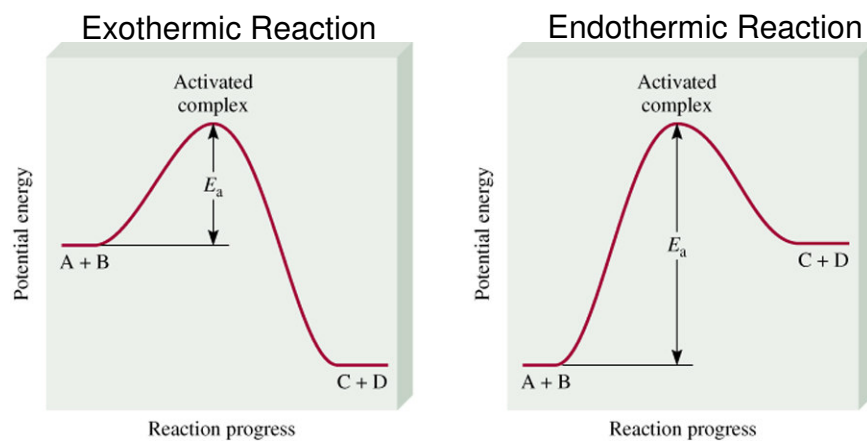
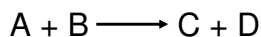
$$t_{1/2} = \frac{1}{k[A]_0}$$

Ref. Chang, Sect.13.3

Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

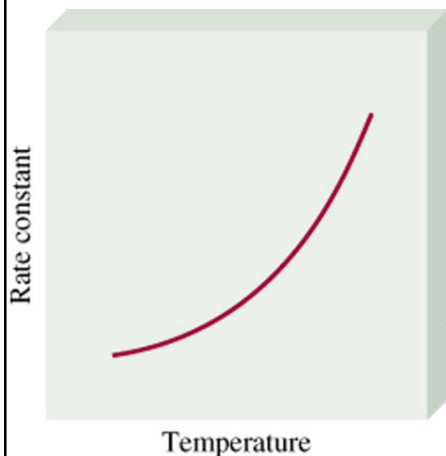
Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k[A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$

Ref. Chang, Sect.13.3



The **activation energy (E_a)** is the **minimum** amount of energy required to initiate a chemical reaction.

Temperature Dependence of the Rate Constant (*Arrhenius equation*)



$$k = A \cdot e^{(-E_a/RT)}$$

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A$$

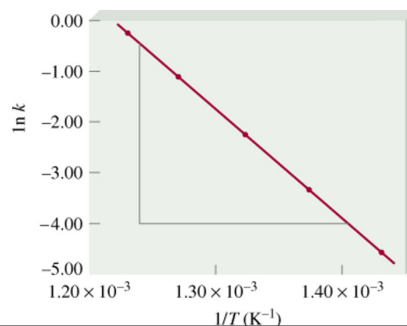
Activation Energy E_a : is the *minimum* amount of energy required to initiate a chemical reaction, in order to react, the reactant species must have a total kinetic energy equal to or greater than the activation energy.

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \text{constant}$$

Activation energy can be determined from:

- the **slope** of the line obtained by measuring k at different temperatures, then plotting $\ln k$ versus $1/T$
- the values of k at **two** different temperatures using the formula

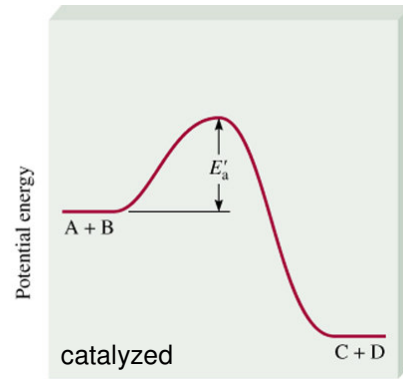
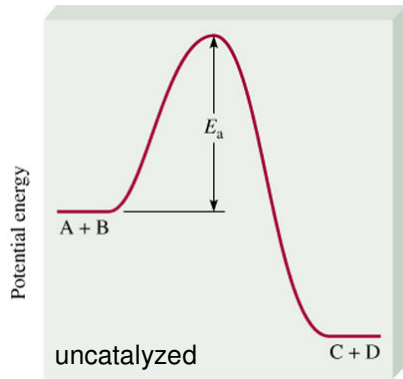
$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$



A **catalyst** is a substance that **increases** the rate of a chemical reaction without itself being consumed.

$$k = A \cdot e^{-E_a/RT}$$

$$E_a \downarrow \quad k \uparrow$$



$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

$$E'_a < E_a$$

Experimentally

Nature of Reactants:

Reactivity of **different acids** (hydrochloric acid, sulfuric acid, acetic acid and phosphoric acid), with **Magnesium** metal.

Reactivity of **different metals** (zinc, magnesium and copper) with the same acid (**HCl**).

Surface Area

The **larger the surface area** of a solid, the **more atoms** is available to react.

The reaction rate of **two different forms** of marble chips (CaCO_2) will be investigated.

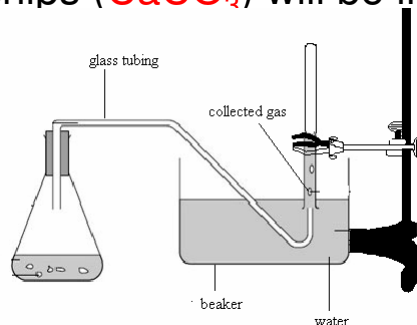


Figure 1 Set-up for the gas collection

Concentration of Reactants:

1. Reaction of Mg with HCl



The general rate law expression for this reaction is:

$$\text{rate} = k [\text{H}^+]^n \quad n \text{ is the order of the reaction}$$

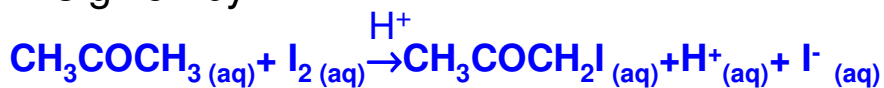
The rate can be expressed in terms of reciprocal time since the concentration of the magnesium is a constant. Thus, rate is directly proportional to $1/t$

$$1/t = k' [\text{H}^+]^n \quad \Rightarrow \quad \ln(1/t) = n \ln[\text{H}^+] + \ln k'$$

By measuring the time required for magnesium metal to react with HCl solutions of different concentrations and plotting $\ln(1/t)$ versus $\ln[\text{H}^+]$, the **linear curve** will give you the slope as the order of the reaction.

2. Iodination of Acetone:

The equation of the reaction in this experiment is given by



- The **rate law** is expressed as

$$\text{rate} = k [\text{acetone}]^m [\text{I}_2]^n [\text{H}^+]^p$$

$$\text{rate} = k [\text{A}]^m [\text{I}_2]^n [\text{H}^+]^p$$

Where the exponents **m, n, p** and the rate constant **k** are to be determined.

By measuring the rate for a series of reactions in which only **one** reactant concentration is varied at a time, the **order** of the reaction for each reactant can be determined.

- The reaction of acetone with iodine, in the vicinity of room temperature, can be very easily investigated experimentally because:

- It proceeds at a moderate, relatively easily measured rate.

- Iodine has a color so that one can readily follow changes in iodine concentration visually.

- This reaction is zero order in I_2 concentration i.e. the rate of the reaction does not depend on $[\text{I}_2]$ at all. $[\text{I}_2]^0 = 1$, no matter what the value of I_2 is, as long as it is not itself zero.

Determination of the **order** of the reaction:

The **order** of the reaction for each reactant can be found by comparing **two** experiments in which the **concentration** of **one** reactant **varies**. In the experiment for example,

- keeping $[H^+]$ and $[I_2]$ at the **same** values they had previously (at Rate1),
- and **doubling** $[A]$ will make the new rate of the reaction equal to Rate 2, as follows

$$\text{Rate 2} = k (2[A])^m [I_2]^n [H^+]^p$$

compared to

$$\text{Rate 1} = k [A]^m [I_2]^n [H^+]^p$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{(2[A])^m}{[A]^m} = 2^m$$

m can be determined by taking the log of both sides

$$\log\left(\frac{\text{Rate 2}}{\text{Rate 1}}\right) = m \log 2$$

Similarly, the **order** of the reaction with respect to H^+ can be determined.

The **order** of the reaction with respect to I_2 ($n=0$) can be confirmed also. (**Note:** Take half the amount of iodine and not the double of it).

Calculate and record the order of the reaction for each reactant to two significant figures, then round to the nearest integer value.

Determination of the **rate constant K**:

The **experimental** rate constant for each run is **calculated** by substituting the **values** for the **rate** and **concentrations** into the rate expression.