University of Baghdad

College of Science

Physical Chemistry (3) / Kinetics

Chemistry Department / Third Stage

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Physical Chemistry (3)

The Kinetics

Chemical kinetics:

Is the study of reaction rates, the changes in concentrations of reactants (or products) as a function of time. Reactant concentrations decrease quickly in a reaction with a high rate and slowly in a reaction with a low rate.

***Until now we've taken a rather simple approach to chemical change*:**
Reactants mix and products form. A balanced equation is an essential quantitative tool for calculating product yields from reactant amounts, but it tells us nothing about three dynamic aspects of the reaction, which are essential to understanding chemical change and which we will examine in this course:

- ***How fast is the reaction proceeding at a given moment?***
- ***What will reactant and product concentrations be when the reaction is complete?***
- ***Will the reaction proceed by itself and release energy, or will it require energy to proceed?***

This course addresses the first of these questions and focuses on the field of kinetics, which deals with the speed of a reaction and its mechanism, the stepwise changes that reactants undergo in their conversion to products.

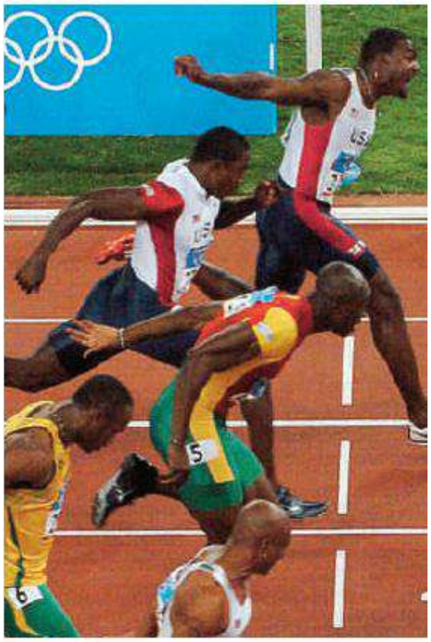
Knowing how fast a chemical change occurs can be essential.
How quickly a medicine acts or blood clots can make the difference between life and death.
How long it takes for cement to harden or polyethylene to form can make the difference between profit and loss.
In general, the rates of these diverse processes depend on the same variables, most of which chemists can manipulate to maximize yields within a given time or to slow down an unwanted reaction.

Expressing the Reaction Rate

In general terms, **a rate (speed) is a change in some variable per unit of time**. The most familiar examples relate to speed (see the photo), the change in position of an object **(x)** divided by the change in time **(t).**

For instance, if we measure a runner's **initial position, (x_1), at time (t_1)**, and **final position, (x_2) , at time (t_2)** , **the average speed is**:

$$\text{Rate of motion (speed)} = \frac{\text{change in position}}{\text{change in time}} = \frac{x_2 - x_1}{t_2 - t_1} = \frac{\Delta x}{\Delta t}$$



Runners change positions with time.

❖For The Rate of a Reaction,

We measure the changes in concentrations of reactants or products per unit time,

[Reactant concentrations decrease while *product concentrations increase].*

For the general reaction: **$A \longrightarrow B$**

We measure:

The initial reactant concentration (A_1) at (t_1) , allow the reaction to proceed, and then quickly measure **the final reactant concentration (A_2) at (t_2).**

The change in concentration divided by the change in time, gives the rate:

$$\text{Rate} = -\frac{\text{change in concentration of A}}{\text{change in time}} = -\frac{\text{conc } A_2 - \text{conc } A_1}{t_2 - t_1} = -\frac{\Delta(\text{conc A})}{\Delta t}$$

- The negative sign (-) is important because, by convention, reaction rate is a positive number.

- But since concentration (A_2) must be lower than concentration (A_1), The change in concentration (final - initial) of reactant A is negative value.
  Therefore, we use the negative sign to convert the negative change in reactant concentration to a positive value for the rate (speed).

- Suppose the concentration of [A] changes from *1.2 mol/L (conc. A_1)* to *0.75 mol/L (conc.A_2)* over a 125 second period. The rate is:

$$= -\frac{\text{conc } A_2 - \text{conc } A_1}{t_2 - t_1} = -\frac{\Delta(\text{conc A})}{\Delta t}$$

$$\text{Rate} = -\frac{0.75 \text{ mol/L} - 1.2 \text{ mol/L}}{125 \text{ s} - 0 \text{ s}} = 3.6\times10^{-3} \text{ mol/L·s}$$

Square brackets, [ ], indicate a concentration in *moles per liter*.
For example: *[A] is the concentration of A in mol/L,* and the rate expressed in terms of A is:

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

- The units for the rate of reaction are *moles per liter per second (mol L^{-1} s^{-1}, or mol/L.s),* or any time unit convenient for the reaction such as (minutes, years, and so on).
- If instead we measure *the product* concentrations to determine the rate of reaction, *we find that [conc. B_2] is always higher than [conc. B_1]*
- Thus, *the change* in product concentration, Δ[B], *is positive*, and the reaction rate for $A \longrightarrow B$, expressed in terms of B is:

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

→

THUS,

The mathematical expression for the rate of a particular reaction and the numerical value of the rate depend on which substance serves as the reference.

We can summarize these results for any reaction, as:

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

Where a, b, c, and d are coefficients of the balanced equation, as follows:

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

Expressing Rate in Terms of Changes in Concentration with Time:

PROBLEM

Because it has a nonpolluting combustion product (water vapor), hydrogen gas is used for fuel aboard the space shuttles and in earthbound cars with prototype engines:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

(a) Express the rate in terms of changes in $[H_2]$, $[O_2]$, and $[H_2O]$ with time.

(b) When $[O_2]$ is decreasing at 0.23 mol/L.s, at what rate is $[H_2O]$ increasing?

SOLUTION:

(a) Expressing the rate in terms of each component

Of the three substances in the equation, let's choose O_2 as *the reference* because its coefficient is 1.

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

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

(b) Calculating the rate of change of $[H_2O]$

$$\frac{1}{2}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = -(-0.23\ \text{mol/L}\cdot\text{s})$$

$$\frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = 2(0.23\ \text{mol/L}\cdot\text{s}) = \boxed{0.46\ \text{mol/L}\cdot\text{s}}$$

The $[H_2]$ and $[O_2]$ ***decrease***, so they take ***minus signs***; $[H_2O]$ ***increases***, so it takes ***a plus sign***. Another check is to use the general Equation:

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

With : A = H_2, a = 2;
B = O_2, b = 1;
C = H_2O, c = 2.

Therefore:

Given the rate expression, it makes sense that the numerical value of the rate of $[H_2O]$ increase is twice that of $[O_2]$ decrease.

HOMEWORK(1)

PROBLEM (1)

Express the rate of reaction in terms of the change in concentration of each of the reactants and products:

$$2A(g) \longrightarrow B(g) + C(g)$$

When [C] is increasing at 2 mol/L.s, how fast is [A] decreasing?

PROBLEM (2)

Reaction rate is expressed in terms of changes in concentration of reactants and products. Write a balanced equation for:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

PROBLEM (3)

Express the rate of reaction in terms of the change in concentration of each of the reactants and products:

$$2D(g) + 3E(g) + F(g) \longrightarrow 2G(g) + H(g)$$

When [D] is decreasing at 0.1 mol/L.s, how fast is [H] increasing**?**

PROBLEM (4)

Express the rate of reaction in terms of the change in concentration of each of the reactants and products:

$$D(g) \longrightarrow \tfrac{3}{2}E(g) + \tfrac{5}{2}F(g)$$

When [E] is increasing at 0.25 mol/L.s, how fast is [F] increasing?

PROBLEM (5)

Reaction rate is expressed in terms of changes in concentration of reactants and products. Write a balanced equation for

$$\text{Rate} = -\frac{\Delta[CH_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t}$$

THE RATE LAW AND ITS COMPONENTS

The centerpiece of any kinetic study is the rate law (or rate equation) for the reaction in question.

The rate law expresses the rate as **a function of reactant concentrations, product concentrations, and temperature.**

Any hypothesis we make about how the reaction occurs on the molecular level must conform to the rate law because it is based on experimental fact.

In this lecture , ***we generally consider reactions for which the products do not appear in the rate law***.

In these cases, **the reaction rate depends only on reactant concentrations and temperature**.

First, we look at the effect of concentration on rate for reactions occurring at a fixed temperature. **For a general reaction,**

$$aA + bB + \cdots \longrightarrow cC + dD + \cdots$$

The rate law has the form:

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

Aside from the concentration terms, [A] and [B], the other parameters in the previous equation require some definition.

1- ***The proportionality constant k,*** **called the** ***rate constant,*** **is specific for a given reaction at a given temperature; it does not change as the reaction proceeds.** (As you'll see in later, **k** ***does change with temperature and therefore determines how temperature affects the rate.*)**

2 - The exponents ***m and n***, called ***the reaction orders***, **define how the rate is affected by reactant concentration.**

Thus, if the **rate doubles when [A] doubles**, the **rate depends on [A] raised to the first power, $[A]^1$, so m =1**.

3 - Similarly, if the ***rate quadruples (becomes fourth times) when [B] doubles***, the ***rate depends on [B] raised to the second power***, **$[B]^2$, so n = 2.**

4 - ***While in another reaction***, ***the rate may not change at all when [A] doubles; in that case***, ***the rate does not depend on [A]*** or, to put it another way, ***the rate depends on [A] raised to the zero power, $[A]^0$, so m = 0.***

Two key points to remember are

- **The balancing coefficients (a) & (b) in the chemical reaction equation are *not necessarily related in any way to the reaction orders* m & n.**
- **The components of the rate law—rate, reaction orders, and rate constant (k) ; must be *found by experiment*.**

- **If rate does not change when concentration doubles, must be zeroth order.**
- **If rate doubles when concentration doubles, must be first order.**
- **If rate quadruples when concentration doubles, must be second order.**

Reaction Order Terminology

Before we see how reaction orders are determined from initial rate data, let’s discuss the meaning of reaction order and some important terminology.

Each reaction has an individual order with respect to each reactant as well as an overall order, which is simply *the sum of the individual orders*.

The rate (R) is directly proportional to [A]

سرعة التفاعل تتناسب طرديا مع تركيز المواد المتفاعلة

$$\text{Rate} \;\; \alpha \;\; [A]$$

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

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

Determining Reaction Orders

Consider first the simplest case, a reaction with only one reactant, A:

$$\mathrm{A} \longrightarrow \text{products}$$

- **First order:**

If the rate doubles when [A] doubles, the rate depends on [A] raised to the first power, $[A]^1$ (the 1 is generally omitted). Thus, the reaction is ***first order*** **with respect to A, and** ***first order overall*****:**

$$\text{Rate} = k[\mathrm{A}]^1 = k[\mathrm{A}]$$

- **Second order:**

If the rate quadruples when [A] doubles, the rate depends on [A] squared, $[A]^2$. In this case, the reaction is ***second order with respect to A and second order overall*****:**

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

- **Zero order:**

If the rate does not change when [A] doubles**, the rate does not depend on [A], but we express this fact mathematically by raised to the zero power, $[A]^0$.** ***The reaction is zero order in A and zero order overall:***

$$\text{Rate} = k[\mathrm{A}]^0 = k(1) = k$$

An important point noted earlier

- ***Reaction orders can-not be deduced from the balanced equation but must be determined from experimental data.***

لا يمكن استنتاج مراتب التفاعل من المعادلة الكيميائية المتوازنة ولكن يجب تحديدها من النتائج التجريبية

- ***Although usually positive integers or zero, reaction orders can also be fractional or negative.***

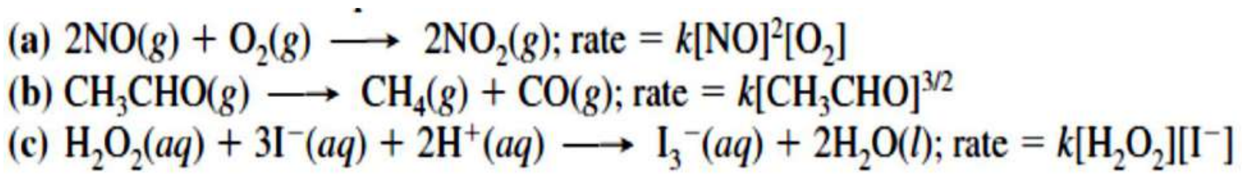
على الرغم من أن مراتب التفاعل عادة ما تكون أعداد صحيحة موجبة أو صفر ، إلا أن مراتب التفاعل يمكن أن تكون كسرية أو سالبة في بعض التفاعلات.

المرتبة الكلية للتفاعل = مجموع مراتب المواد المتفاعلة

المرتبة الكلية للتفاعل = $m + n + \dots$

Determining Reaction Orders from Rate Laws

Q1 -For each of the following reactions, use the given rate law to determine the reaction order with respect to each reactant and the overall order:



(a) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$; rate $= k[NO]^2[O_2]$

(b) $CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$; rate $= k[CH_3CHO]^{3/2}$

(c) $H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \longrightarrow I_3^-(aq) + 2H_2O(l)$; rate $= k[H_2O_2][I^-]$

Solution:

(a) The exponent of [NO] is 2, so the reaction is second order with respect to NO, first order with respect to O_2, and third order overall.

(b) The reaction is 3/2 order in CH_3CHO and 3/2 order overall

(C) The reaction is first order in H_2O_2, first order in I^-, and second order overall. The reactant H^+ does not appear in the rate law, so the reaction is zero order in H^+.

Rate = k $[H_2O_2]^1$ $[I^-]^1$ $[H^+]^0$

Homework 2 :

Experiment shows that the reaction:

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(l) + 3H_2O(l)$$

obeys this rate law: rate $= k[Br^-][BrO_3^-][H^+]^2$. What is the reaction order in each reactant and the overall reaction order?

Determining Reaction Orders by Changing Reactant Concentrations:

Let's see how reaction orders are found before the rate law is known.

Before looking at a real reaction, we'll go through the process for substances A and B in this reaction:

$$A + 2B \longrightarrow C + D$$

The rate law, expressed in general terms, is:

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

- **To find the values of m and n, *we run a series of experiments in which one reactant concentration changes while the other is kept constant , and we measure the effect on the initial rate in each case*.**

Q 2:

Experiment	Initial Rate (mol/L·s)	Initial [A] (mol/L)	Initial [B] (mol/L)
1	1.75×10^{-3}	2.50×10^{-2}	3.00×10^{-2}
2	3.50×10^{-3}	5.00×10^{-2}	3.00×10^{-2}
3	3.50×10^{-3}	2.50×10^{-2}	6.00×10^{-2}
4	7.00×10^{-3}	5.00×10^{-2}	6.00×10^{-2}

1. **Finding m, the order with respect to A:**

   By comparing experiments 1 and 2, in which [A] doubles and [B] is constant, we can obtain m:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[\mathrm{A}]_2^m[\mathrm{B}]_2^n}{k[\mathrm{A}]_1^m[\mathrm{B}]_1^n}$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[\mathrm{A}]_2^m\cancel{[\mathrm{B}]_2^n}}{\cancel{k}[\mathrm{A}]_1^m\cancel{[\mathrm{B}]_1^n}} = \frac{[\mathrm{A}]_2^m}{[\mathrm{A}]_1^m} = \left(\frac{[\mathrm{A}]_2}{[\mathrm{A}]_1}\right)^m$$

$$\frac{3.50\times10^{-3}\ \text{mol/L·s}}{1.75\times10^{-3}\ \text{mol/L·s}} = \left(\frac{5.00\times10^{-2}\ \text{mol/L}}{2.50\times10^{-2}\ \text{mol/L}}\right)^m$$

$$2.00 = (2.00)^m, \qquad \text{so } m = 1$$

2. **Finding n, the order with respect to B:**

   To find n, we compare experiments 3 and 1 in which [A] is held constant and [B] doubles:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[\mathrm{A}]_2^m\,[B]_3^n}{k[\mathrm{A}]_1^m\,[B]_1^n}$$

As before, k is a constant, and in this pair of experiments, [A] does not change,

So those quantities cancel, and we have:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{\cancel{k}\cancel{[A]_3^m}[B]_3^n}{\cancel{k}\cancel{[A]_1^m}[B]_1^n} = \frac{[\mathrm{B}]_3^n}{[\mathrm{B}]_1^n} = \left(\frac{[\mathrm{B}]_3}{[\mathrm{B}]_1}\right)^n$$

The actual values give

$$\frac{3.50\times10^{-3}\ \text{mol/L·s}}{1.75\times10^{-3}\ \text{mol/L·s}} = \left(\frac{6.00\times10^{-2}\ \text{mol/L}}{3.00\times10^{-2}\ \text{mol/L}}\right)^n$$

Dividing, we obtain

$$2.00 = (2.00)^n, \qquad \text{so } n = 1$$

The overall order = m + n =1+1=2 the order of the reaction

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

Q3:

For a real reaction, the one between oxygen and nitrogen monoxide, a key step in the formation of acid rain and in the industrial production of nitric acid:

$$O_2(g) + 2NO(g) \longrightarrow 2NO_2(g)$$

The general rate law is

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

Find the values of m and n, *from a series of experiments?*

Experiment	Initial Rate (mol/L·s)	Initial Reactant Concentrations (mol/L)	
		$[O_2]$	[NO]
1	3.21×10^{-3}	1.10×10^{-2}	1.30×10^{-2}
2	6.40×10^{-3}	2.20×10^{-2}	1.30×10^{-2}
3	12.8×10^{-3}	1.10×10^{-2}	2.60×10^{-2}
4	9.60×10^{-3}	3.30×10^{-2}	1.30×10^{-2}
5	28.8×10^{-3}	1.10×10^{-2}	3.90×10^{-2}

Solution

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[O_2]_2^m[NO]_2^n}{k[O_2]_1^m[NO]_1^n}$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[O_2]_2^m\cancel{[NO]_2^n}}{\cancel{k}[O_2]_1^m\cancel{[NO]_1^n}} = \frac{[O_2]_2^m}{[O_2]_1^m} = \left(\frac{[O_2]_2}{[O_2]_1}\right)^m$$

$$\frac{6.40\times10^{-3}\ \text{mol/L·s}}{3.21\times10^{-3}\ \text{mol/L·s}} = \left(\frac{2.20\times10^{-2}\ \text{mol/L}}{1.10\times10^{-2}\ \text{mol/L}}\right)^m$$

$$1.99 = (2.00)^m$$

$$2 = 2^m, \qquad \text{so } m = 1$$

Sometimes, the exponent is not as easy to find by inspection as it is here. In those cases, we solve for m with an equation of the form $a = b^m$:

$$m = \frac{\log a}{\log b} = \frac{\log 1.99}{\log 2.00} = 0.993$$

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[O_2]_3^m[NO]_3^n}{k[O_2]_1^m[NO]_1^n}$$

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \left(\frac{[NO]_3}{[NO]_1}\right)^n$$

$$\frac{12.8\times10^{-3}\ \text{mol/L·s}}{3.21\times10^{-3}\ \text{mol/L·s}} = \left(\frac{2.60\times10^{-2}\ \text{mol/L}}{1.30\times10^{-2}\ \text{mol/L}}\right)^n$$

$$3.99 = (2.00)^n$$

$$n = \frac{\log 3.99}{\log 2.00} = 2.00 \quad (\text{or } 2)$$

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

In this case, the reaction orders happen to be the same as the equation coefficients; nevertheless, they must always be determined by experiment.

Determining the Rate Constant (k): أيجاد ثابت السرعة

The rate constant (k) for the reaction of O_2 and NO.

With the rate, reactant concentrations, and reaction orders known, the sole remaining unknown in the rate law is the rate constant, k.

We can use data from any of the experiments in Table to solve for k.

From experiment 1:

$$\text{Rate} = k[O_2]_1[NO]_1^2$$

$$k = \frac{\text{rate 1}}{[O_2]_1[NO]_1^2} = \frac{3.21\times10^{-3}\ \text{mol/L·s}}{(1.10\times10^{-2}\ \text{mol/L})(1.30\times10^{-2}\ \text{mol/L})^2}$$

$$= \frac{3.21\times10^{-3}\ \text{mol/L·s}}{1.86\times10^{-6}\ \text{mol}^3/\text{L}^3} = 1.73\times10^{3}\ \text{L}^2/\text{mol}^2\text{·s}$$

$$\boldsymbol{k = \frac{Rate\ (mol.L^{-1}s^{-1})}{[A]^m[B]^n} = \frac{mol.L^{-1}s^{-1}}{[mol.L^{-1}]^m[mol.L^{-1}]^n}}$$

Overall Reaction Order	**Units of *k* (*t* in seconds)**
0	mol/L·s (or mol $L^{-1}s^{-1}$)
1	1/s (or s^{-1})
2	L/mol·s (or L $mol^{-1}s^{-1}$)
3	L^2/mol^2·s (or $L^2\ mol^{-2}s^{-1}$)

General formula:

$$\text{Units of } k = \frac{\left(\frac{\text{L}}{\text{mol}}\right)^{\text{order}-1}}{\text{unit of } t}$$

Integrated Rate Law for First- order reaction:

For a general first-order reaction, the rate is the negative of the change in [A] divided by the change in time: **$A \longrightarrow$ Product**

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

It can also be expressed in terms of the rate law:

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

Setting these two expressions equal to each other gives

$$-\frac{\Delta[\mathrm{A}]}{\Delta t} = k[\mathrm{A}] \qquad \text{or} \qquad -\frac{\Delta[\mathrm{A}]}{[\mathrm{A}]} = k\Delta t$$

Through the methods of calculus, we integrate over time to obtain the integrated rate law for a first-order reaction:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k\int_0^t dt \quad ; \quad \ln\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = kt \qquad (\text{first-order reaction; rate} = k[\mathrm{A}])$$

where ln is the natural logarithm, $[\mathrm{A}]_0$ is the concentration of A at $t = 0$, and $[\mathrm{A}]_t$ is the concentration of A at any time t.

$$\mathbf{t = \frac{1}{k} \ln \frac{[A]_\circ}{[A]_t}}$$

First - order reaction

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$$\ln[A]_t - \ln[A]_0 = -kt \quad ; \quad \ln[A]_t = -kt + \ln[A]_0$$

	A	$\longrightarrow$	Products
Initial conc.	a		0
Final conc.	$a - x$		x

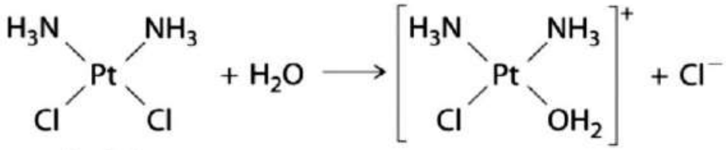
$[A]_o = a$, $[A]_o - X = [A]_t$, or $[A]_o - [A]_t = X$

$[A]_o$ = Initial conce. ; $[A]_t$ = Remaining conce. ; X = Product conce.

Example : First-order kinetics is the hydrolysis of the anticancer drug cis-platin.

The hydrolysis of the anticancer drug cisplatin. Cis-platin, the first “inorganic” anticancer drug to be discovered is unique in its ability to cause complete remission of the relatively rare but deadly cancers of the reproductive organs in young adults.

The structures of cis-platin and its hydrolysis product are as follows:



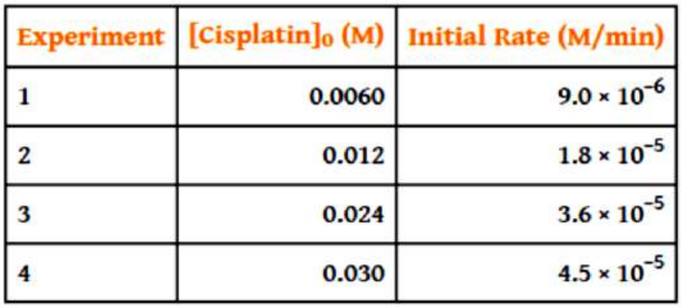
Cisplatin

Both platinum compounds have 4 groups arranged in a square plane around a Pt(II) ion. The reaction is important because cis-platin, the form in which the drug is administered, is not the form in which the drug is active.

Instead, at least one chloride ion (Cl^-) must be replaced by H_2O molecule to *produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth*. Consequently, the kinetics of the reaction has been studied extensively to find ways of maximizing the concentration of the active species.

Knowing *the rate constant (k) for the hydrolysis of cis-platin and the rate constants (k) for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with* solutions *that contain only the desired form of the drug.*

Q: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C



Experiment	[Cisplatin]$_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

- **$R2/R1 = k\,[\text{Cisplatin}]_2^m / k\,[\text{Cisplatin}]_1^m$**

  $1.8\times10^{-5} / 9\times10^{-6} = k\,[0.012]_2^m / k\,[0.006]_1^m$

  $2 = 2^m$ ……… m=1

- **$R4/R1 = k\,[\text{Cisplatin}]_4^m / k\,[\text{Cisplatin}]_1^m$**

  $4.5\times10^{-5} / 9\times10^{-6} = k\,[0.03]_4^m / k\,[0.006]_1^m$

  $5 = 5^m$ …….m= 1

Q1: **A reaction which follows first-order kinetics has a rate constant (k) of 0.0463 sec^{-1}. Given a starting concentration of 0.500 M, What is the molarity of the remaining reactant after 15.0 sec?**

Solution:

$[A]_0$ = 0.5M (Starting concentration of reactant)
$[A]_t$ = ? (Remaining concentration of reactant)
K= 0.0463 sec^{-1}
t = 15 sec

$$t = \frac{1}{k} \ln \frac{[A]_\circ}{[A]_t} \;;\; 15 = \frac{1}{0.0463} \ln \frac{[0.5M]}{[A]_t}$$

$15 = 21.598\,[\ln(0.5) - \ln[A]_t]$
$15 = -14.970 - 21.598 \ln[A]_t$
$29.970 = -21.598 \ln[A]$
{ $\ln[A] = -29.970 / 21.598 = -1.3876$ } / ln

$[A]_t$ = 0.249M

Q2: **A reaction which follows first-order kinetics is 17.9% complete after 11.4 seconds. What is the rate constant?**

Solution:

$[A]_0$ = The initial concentration of the reactant
X = The concentration of the product
$[A]_t$ = The remaining concentration of the reactant
$[A]_0 - [A]_t = X$

$100 - [A]_t = 17.9 \longrightarrow [A]_t = 100 - 17.9 = 82.1M$

$$k = \frac{1}{t} \ln \frac{[A]_\circ}{[A]_t} = (1/ 11.4)\,(\ln(100/82.1)) = 0.0877 \text{ x } 0.1972 = 0.0173 \text{ M.s}^{-1} = k$$

Homework 1

A reaction which follows first-order kinetics has a rate constant k of 0.0197 sec^{-1}. Given a starting concentration of 2.35 M, How many minutes are required for the concentration of reactant to reach 0.122 M?

Integrated Rate Law for Second-order reaction

For a general **second-order reaction** involving **two reactants, A and B, the expression including time is complex**. In the simpler case, **the rate law contains only reactant A**. Setting the two rate expressions equal to each other gives as below:

$$A+B \longrightarrow \text{Products}$$

If [A]=[B], the rate equation and the rate law will express by [A] only.

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{and} \quad \text{rate} = k[A]^2$$

So:

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2 \quad \text{or} \quad -\frac{\Delta[\text{A}]}{[\text{A}]^2} = k\Delta t$$

Integrating over time gives the integrated rate law for a second-order reaction involving one reactant:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k\int_0^t dt \; ; \quad \frac{1}{[\text{A}]_t} - \frac{1}{[\text{A}]_0} = kt \quad (\text{second-order reaction; rate} = k[\text{A}]^2)$$

$$t = \frac{1}{k}\left[\frac{1}{[A]_t} - \frac{1}{[A]_\circ}\right] \qquad \textbf{Second-order reaction}$$

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Or:

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

Q2: A reaction which follows second-order kinetics has a rate constant (k) of 0.0286 $M^{-1}sec^{-1}$. Given a starting concentration of 0.750 M, What is the molarity of the remaining reactant after 19.2 sec?

Solution:

$[A]_0$= 0.750 M (Starting concentration of reactant)

$[A]_t$ = ? (Remaining concentration of reactant)

K= 0.0286 $M^{-1}sec^{-1}$

t = 19.2 sec

$$t = \frac{1}{k}\left[\frac{1}{[A]_t} - \frac{1}{[A]_\circ}\right] \quad ; 19.2 = \frac{1}{0.0286}\left[\frac{1}{[A]_t} - \frac{1}{[0.750M]_\circ}\right]$$

$$\frac{1}{[A]} = \frac{1}{[0.750\ M]} + (0.0286\ M^{-1}s^{-1})(19.2\ s)$$

$$\frac{1}{[A]} = 1.33\ M^{-1} + 0.549\ M^{-1} = 1.88\ M^{-1}$$

$$[A] = 0.532\ M$$

Homework 2

A reaction which follows second-order kinetics has a rate constant k of 0.108 $M^{-1}sec^{-1}$.
Given a starting concentration of 1.75 M, How many seconds are required for the concentration of reactant to reach 0.632 M?

Homework 3

A certain reaction A → products is second order in A. If this reaction is 10 % complete after 20 s, **how long** would it take for the reaction to be 90 % complete?

Answer

A. 180 s, B. 1600 s , C. 440 s, D. 18,000 s, E. 540 s

Integrated Rate Law for third –order reaction

Let us consider a simple third order reaction of the type:

$$3A + B \longrightarrow \text{Products}$$

If [A]=[B], the rate equation and the rate law will express by [A] only.

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \qquad \text{and} \qquad \text{rate} = k[A]^3$$

$$Rate = -\frac{\Delta[A]}{\Delta t} = k\,[A]^3 \qquad or \qquad -\frac{\Delta[A]}{[A]^3} = k\,\Delta t$$

Integrating over time gives the integrated rate law for a third-order reaction involving one reactant:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^3} = -k\int_0^t dt$$

$$t = \frac{1}{2k}\left[\frac{1}{[A]_t^2} - \frac{1}{[A]_o^2}\right]$$

Third –Order reaction

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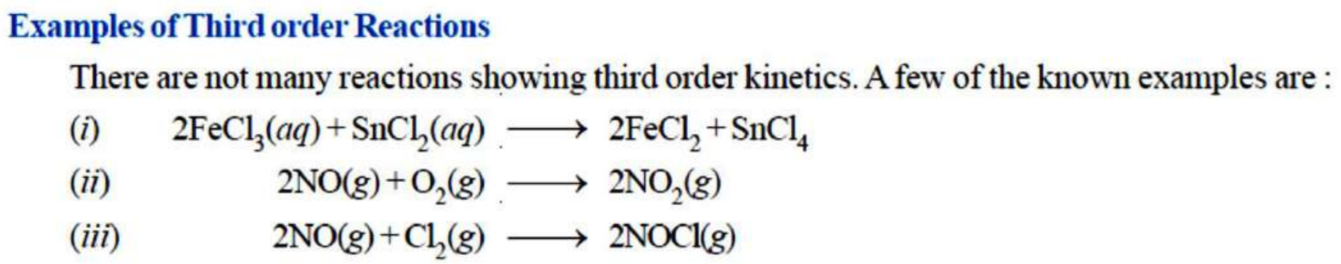


Examples of Third order Reactions

There are not many reactions showing third order kinetics. A few of the known examples are :

(*i*) $2FeCl_3(aq) + SnCl_2(aq) \longrightarrow 2FeCl_2 + SnCl_4$

(*ii*) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(*iii*) $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$

Integrated Rate Law for Zero-order reaction

For a general **zero-order reaction**, setting **the two rate expressions equal to each other gives:** $\mathbf{A \longrightarrow Product}$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} \quad \text{and} \quad \text{rate} = k[A]^0 = k\,x1 = k$$

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^0 = k \qquad \text{or} \qquad -\Delta[\text{A}] = k\Delta t$$

Integrating over time gives the integrated rate law for a zero-order reaction:

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

$$[\text{A}]_t - [\text{A}]_0 = -\text{kt} \qquad \textbf{Zero-order reaction}$$

Example: The catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface

The decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \xrightarrow{Pt} 2N_2(g) + O_2(g)$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate, so the order of reaction will be zero order.

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k$$

تحلل N_2O على سطح البلاتين (Pt) لإنتاج N_2 وO_2 ، والذي يحدث في درجات حرارة تتراوح من 200 درجة مئوية إلى 400 درجة مئوية.

بدون سطح البلاتين (المساحة السطحية الفعالة) ، يتطلب التفاعل درجات حرارة أكبر من 700 درجة مئوية ،
ولكن ما بين 200 درجة مئوية و 400 درجة مئوية ، العامل الوحيد الذي يحدد مدى سرعة تحلل N_2O هو مقدار سطح Pt المتاح (وليس كمية Pt).
طالما يوجد ما يكفي من N_2O للتفاعل مع سطح Pt بأكمله ، فإن مضاعفة تركيز N_2O أو مضاعفته أربع مرات لن يكون له أي تأثير على سرعة التفاعل لذلك يعتبر هذا التفاعل مثال للمرتبة الصفرية

HALF–LIFE OF A REACTION ($t_{1/2}$)

Half-life period is the time required for the concentration of a reactant to decrease to half its initial value.

➢ First-Order Reactions

We can derive an expression for the half-life of a first-order reaction from the integrated rate law, which is:

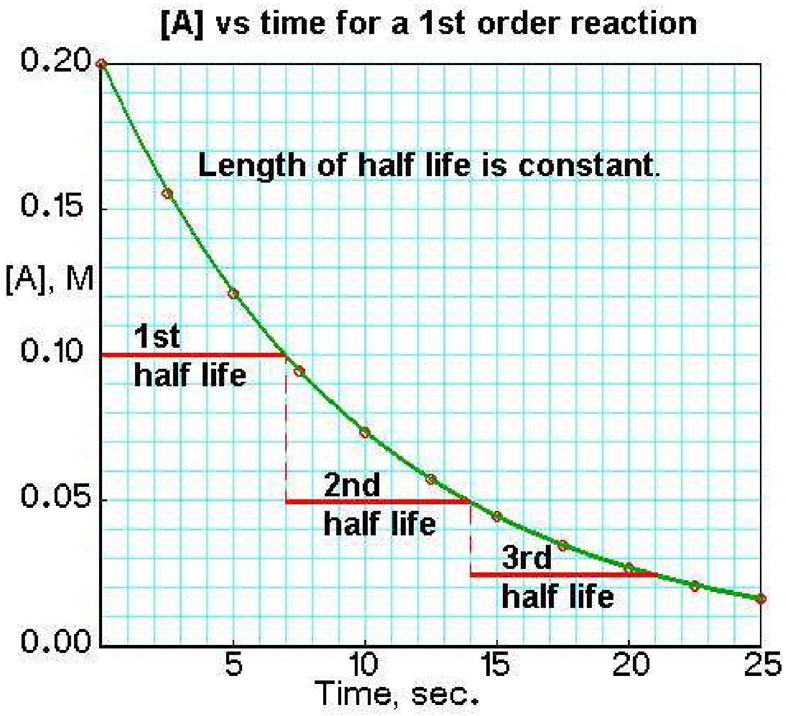
$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = kt$$

By definition, after one half-life, $t = t_{1/2}$, and $[\mathrm{A}]_t = \frac{1}{2}[\mathrm{A}]_0$. Substituting and canceling $[\mathrm{A}]_0$ gives

$$\ln \frac{\cancel{[\mathrm{A}]_0}}{\frac{1}{2}\cancel{[\mathrm{A}]_0}} = kt_{1/2} \qquad \text{or} \qquad \ln 2 = kt_{1/2}$$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

For a first-order reaction, the time it takes to reach one-half the starting concentration is a constant and, thus, independent of reactant concentration.



➢ Second-Order Reactions

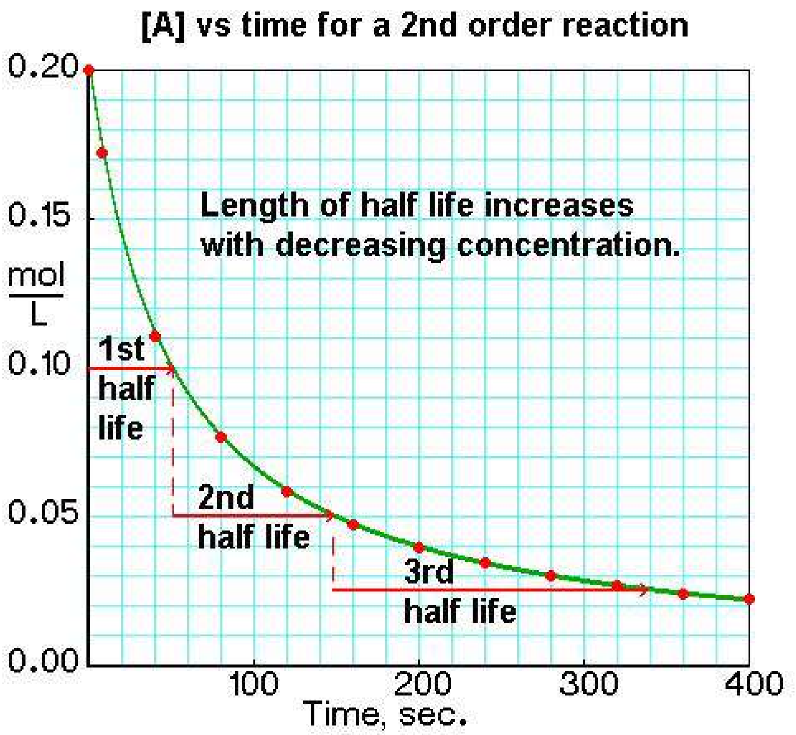
In contrast to the half-life of a first-order reaction, the half-life of a second-order reaction does depend on reactant concentration:

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

The half-life is inversely proportional to the initial reactant concentration.

A second-order reaction with (a high initial reactant concentration has a shorter half-life),

With (a low initial reactant concentration has a longer half-life).



➢ Third –Order Reaction

In contrast to the half-life of a first-order reaction, the half-life of a third-order reaction does depend on the second power of the reactant concentration:

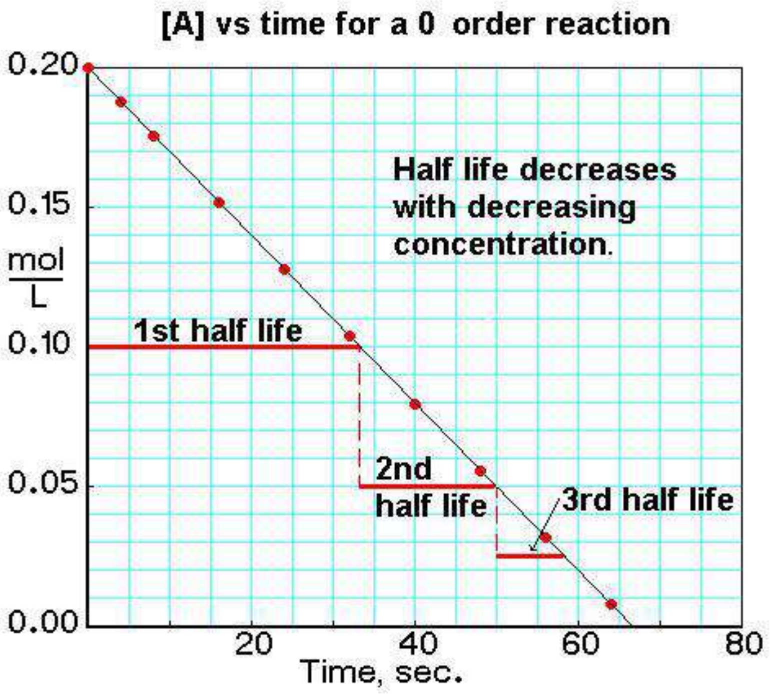
$$t_{\frac{1}{2}} = \frac{3}{2k[A]_o^2}$$

➢ Zero-Order Reactions

In contrast to the half-life of a second-order reaction, the half-life of a zero-order reaction is directly proportional to the initial reactant concentration:

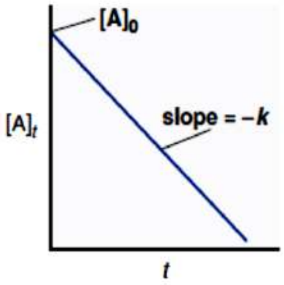
$$t_{1/2} = \frac{[A]_o}{2k}$$

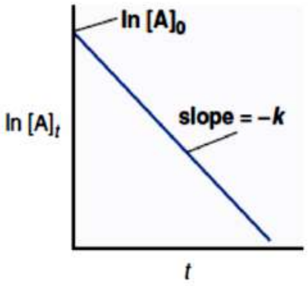
If a zero-order reaction begins with a high reactant concentration, it has a longer half-life than, if it begins with a low reactant concentration.

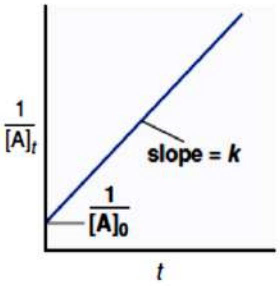


The Summery

	Zero Order	First Order	Second Order
Rate law	rate = k	rate = $k[\mathrm{A}]$	rate = $k[\mathrm{A}]^2$
Units for k	mol/L·s	1/s	L/mol·s
Half-life	$\dfrac{[\mathrm{A}]_0}{2k}$	$\dfrac{\ln 2}{k}$	$\dfrac{1}{k[\mathrm{A}]_0}$
Integrated rate law in straight-line form	$[\mathrm{A}]_t = -kt + [\mathrm{A}]_0$	$\ln [\mathrm{A}]_t = -kt + \ln [\mathrm{A}]_0$	$1/[\mathrm{A}]_t = kt + 1/[\mathrm{A}]_0$
Plot for straight line	$[\mathrm{A}]_t$ vs. t	$\ln [\mathrm{A}]_t$ vs. t	$1/[\mathrm{A}]_t$ vs. t
Slope, y intercept	$-k$, $[\mathrm{A}]_0$	$-k$, $\ln [\mathrm{A}]_0$	k, $1/[\mathrm{A}]_0$







Q: **Iodine-123 is used to study thyroid gland function. This radioactive isotope breaks down in a first-order process with a half-life of 13.1 h. What is the rate constant for the process?**

Solution:

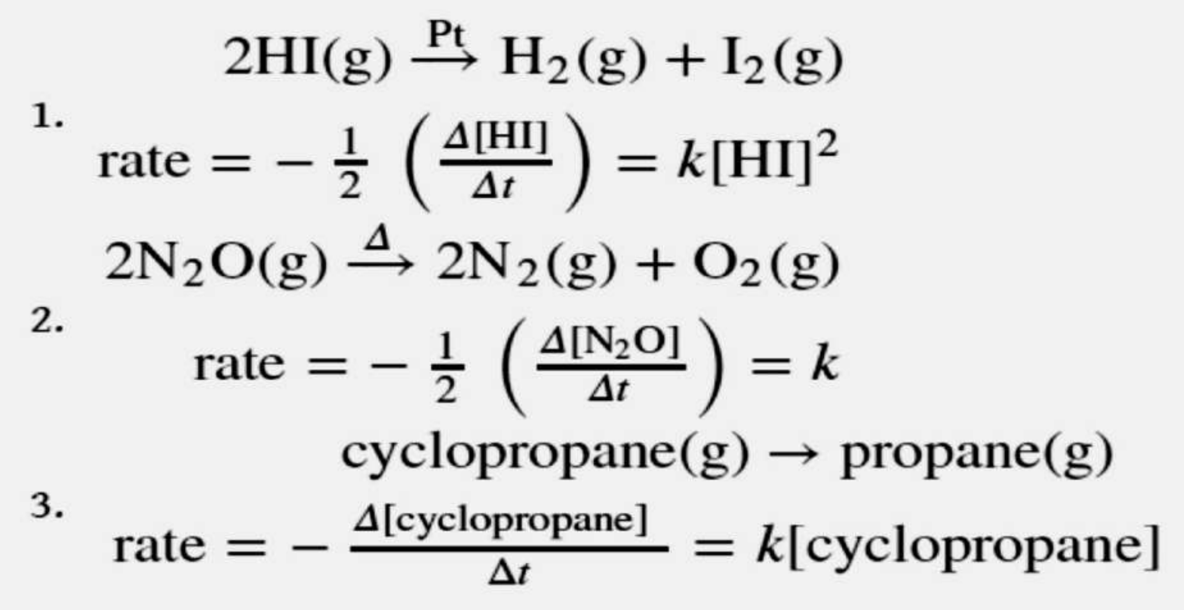
$t_{\frac{1}{2}} = 0.693/ k$

$k = 0.693 / 13.1\mathrm{h} = 0.05290\ \mathrm{h}^{-1}$

Problems and Solutions

Q1:

We present three reactions and their experimentally determined differential rate laws. **For each reaction**, give **the units of the rate constant**, give **the reaction order with respect to each reactant**, give **the overall reaction order**, and **predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled** ?



1.
$$2HI(g) \xrightarrow{Pt} H_2(g) + I_2(g)$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[HI]}{\Delta t}\right) = k[HI]^2$$

2.
$$2N_2O(g) \xrightarrow{\Delta} 2N_2(g) + O_2(g)$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = k$$

3.
$$\text{cyclopropane}(g) \rightarrow \text{propane}(g)$$
$$\text{rate} = -\frac{\Delta[\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]$$

Solution:

1.

$$2\mathrm{HI}(g) \xrightarrow{\mathrm{Pt}} \mathrm{H_2}(g) + \mathrm{I_2}(g)$$

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{HI}]}{\Delta t}\right) = k[\mathrm{HI}]^2$$

1- A) **$[HI]^2$** will give units of **(moles per liter)^2**.

For ***the reaction rate*** to have units of ***moles per liter per second***, ***the rate constant*** must have reciprocal units ***[1/(M·s)]:*** **Rate (M/s) = k $[HI]^2$ = k $[M]^2$**

$$k = \frac{\mathrm{M/s}}{\mathrm{M}^2} = \frac{1}{\mathrm{M \cdot s}} = \mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$$

B) The exponent in the rate law is 2, so the reaction is second order in HI. And the reaction is also second order overall.

C) If the concentration of HI is doubled, the reaction rate will quadruple.

2.

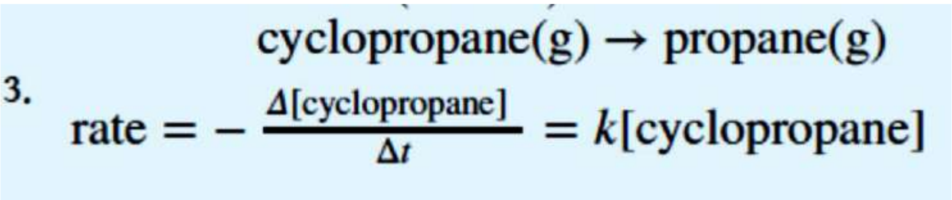
$$2\mathrm{N_2O}(g) \xrightarrow{\Delta} 2\mathrm{N_2}(g) + \mathrm{O_2}(g)$$

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[\mathrm{N_2O}]}{\Delta t}\right) = k$$

2. A) Because **no concentration** term appears in the rate law, the rate constant **(k)** must have M/s units for the reaction rate to have M/s units**.**

B) The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

C) Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.



3.

$$\text{cyclopropane}(g) \rightarrow \text{propane}(g)$$

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

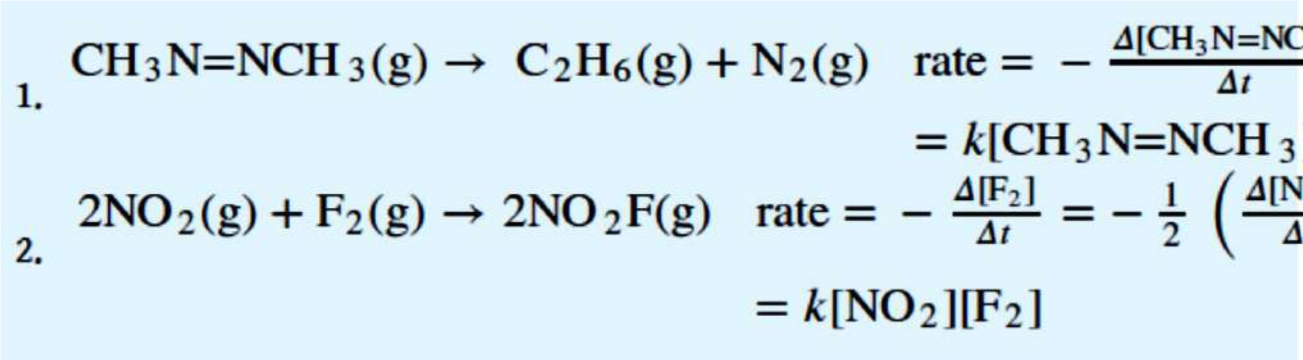
3. A) The rate law contains only one concentration term raised to the first power. Hence **the rate constant must have units** of reciprocal **seconds (s^{-1})** to have units of **(mol/L.s)** for the reaction rate:

K= Rate / [cyclopropane] = M.s^{-1} / M = s^{-1}

B) The only concentration in the rate law is that of cyclopropane, and its exponent is **1**. This means that the reaction **is first order in cyclopropane**. So the reaction is also **first order overall**.

C) **Doubling the initial cyclopropane concentration will doubles the reaction rate.**

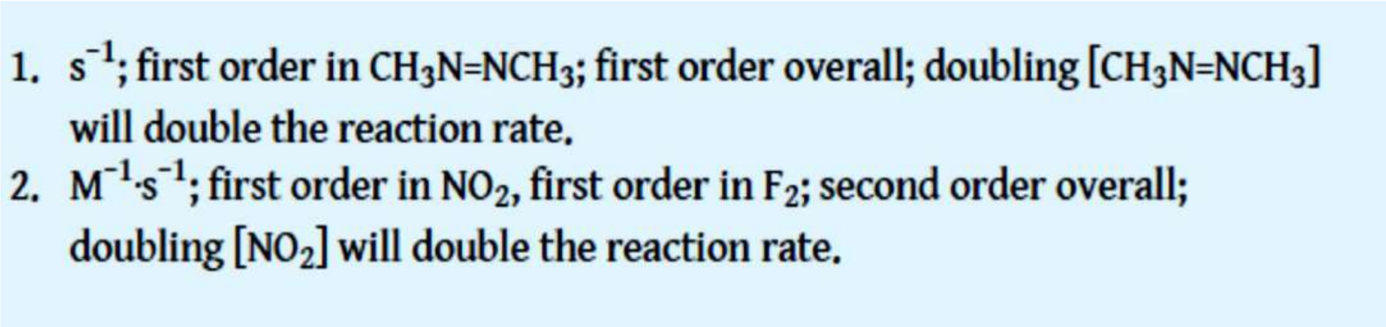
Q2: Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.



1. $CH_3N{=}NCH_3(g) \rightarrow C_2H_6(g) + N_2(g)$ rate $= -\dfrac{\Delta[CH_3N{=}NCH_3]}{\Delta t}$
$= k[CH_3N{=}NCH_3]$

2. $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$ rate $= -\dfrac{\Delta[F_2]}{\Delta t} = -\dfrac{1}{2}\left(\dfrac{\Delta[NO_2]}{\Delta t}\right)$
$= k[NO_2][F_2]$

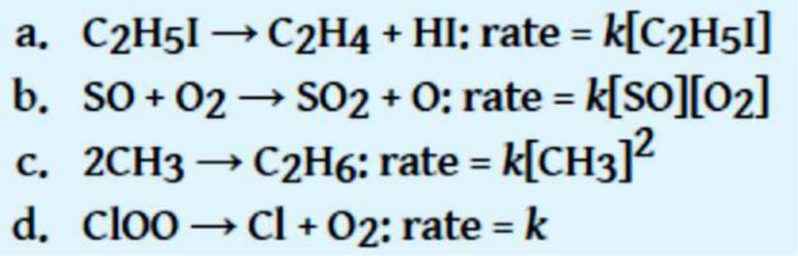
Solution:



1. s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.
2. $M^{-1}{\cdot}s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling $[NO_2]$ will double the reaction rate.

Q3:

Predict how the reaction rate will be affected by **doubling the concentration of the first species in each equation**?



a. $C_2H_5I \rightarrow C_2H_4 + HI$: rate = $k[C_2H_5I]$

b. $SO + O_2 \rightarrow SO_2 + O$: rate = $k[SO][O_2]$

c. $2CH_3 \rightarrow C_2H_6$: rate = $k[CH_3]^2$

d. $ClOO \rightarrow Cl + O_2$: rate = k

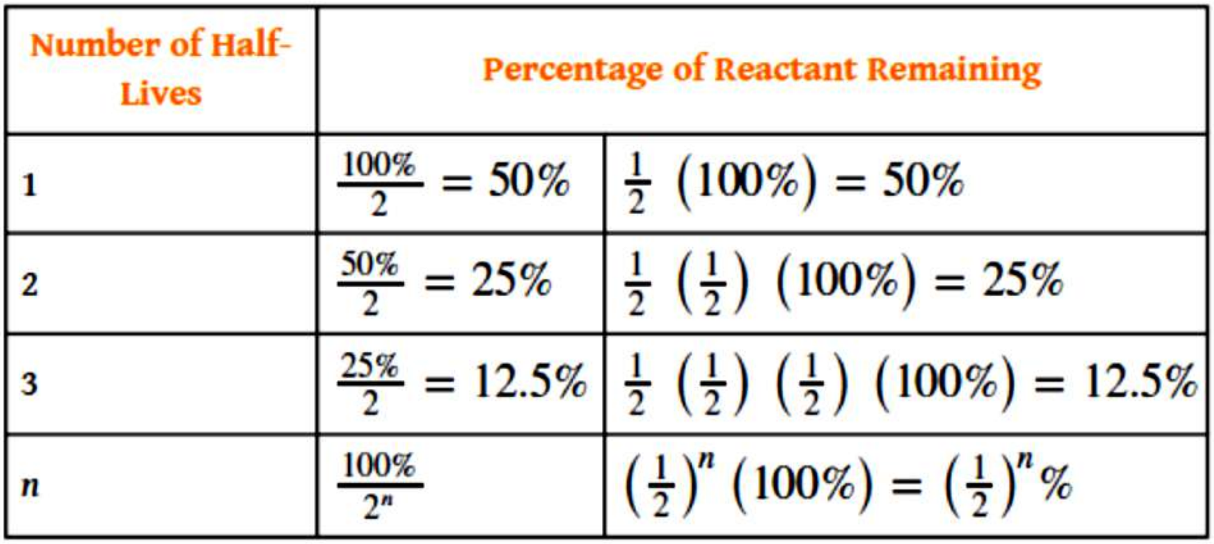
Solution

a – Doubles the reaction rate

b- Doubles the reaction rate

c- Quadruples the reaction rate

d- The reaction rate will not be affected



Number of Half-Lives	Percentage of Reactant Remaining	
1	$\frac{100\%}{2} = 50\%$	$\frac{1}{2}\left(100\%\right) = 50\%$
2	$\frac{50\%}{2} = 25\%$	$\frac{1}{2}\left(\frac{1}{2}\right)\left(100\%\right) = 25\%$
3	$\frac{25\%}{2} = 12.5\%$	$\frac{1}{2}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)\left(100\%\right) = 12.5\%$
n	$\frac{100\%}{2^n}$	$\left(\frac{1}{2}\right)^n\left(100\%\right) = \left(\frac{1}{2}\right)^n\%$

As you can see from this table, the amount of reactant left after *n half-lives* of a first-order reaction is $(1/2)^n$ times the initial concentration.

Q4:

The anticancer drug cisplatin hydrolyzes in water with a rate constant of $1.5 \times 10^{-3}\ \mathrm{min}^{-1}$ at pH 7.0 and 25°C. Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cisplatin has a concentration of 0.053 M, what will be the concentration of cisplatin after 5 half-lives?

Solution:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3}\ \mathrm{min}^{-1}} = 4.6 \times 10^{2}\ \mathrm{min}$$

Note:

Multiply the initial concentration by 1/2 to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.

After 5 half-lives (about 38 h), the remaining concentration of cisplatin will be as follows:

$[A]_t = (1/2)^5 \times 0.053\mathrm{M} = 0.053/32 = 0.0017\mathrm{M}$

Q5:

Cleavage of **C_2H_6** to produce two **$CH_3\cdot$ radicals** is a gas-phase reaction that occurs at 700°C. This reaction is first order, with **$k = 5.46 \times 10^{-4}$ s^{-1}**. **How long** will it take for the reaction to go to **15% completion**? To **50% completion**?

Solution :

$$[A]_0 - [A]_t = X$$

$$100 - [A]_t = 15.0 \quad \longrightarrow \quad [A]_t = 100 - 15.0 = 75.0 \text{ M}$$

$$t = \frac{1}{k} \ln \frac{[A]_\circ}{[A]_t} =$$

$$t = (1/\ 5.46 \times 10^{-4})\ (\ln(100/75)) = 1831.5018 \text{ x } 0.2877 = 37.8307 \text{ s}$$

And the same steps for 50% completion

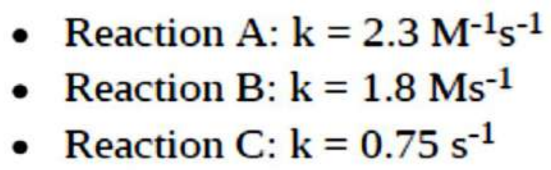
Q6

1. Using the integrated form of the rate law, determine the **rate constant k** of a **zero-order** reaction if **the initial concentration of substance A is 1.5 M** and **after 120 seconds** the concentration of substance **A is 0.75 M**.

2. Using the substance from the previous problem, what is the half-life of substance A if its original concentration is 1.2 M?

3. If the original concentration is reduced to 1.0 M in the previous problem, does the half-life decrease, increase, or stay the same? If the half-life changes what is the new half-life?

4. Given are the rate constants k of three different reactions:



- Reaction A: $k = 2.3\ M^{-1}s^{-1}$
- Reaction B: $k = 1.8\ Ms^{-1}$
- Reaction C: $k = 0.75\ s^{-1}$

   Which reaction represents a zero-order reaction?

5. True/False: If the rate of a zero-order reaction is plotted as a function of time, the graph is a straight line where \(rate = k\ ).

Solutions:

1- $[A]_t - [A]_0 = - k\,t$

$[A]_t - [A]_0 / t = -k$

$(0.75\ M - 1.5\ M) / 120s = -k$

$K = 0.00625\ M/s$

2- $t_{1/2} = [A]_0 / 2k = 1.2\ M / 2 \times 0.00625\ M/s = 96\ s$

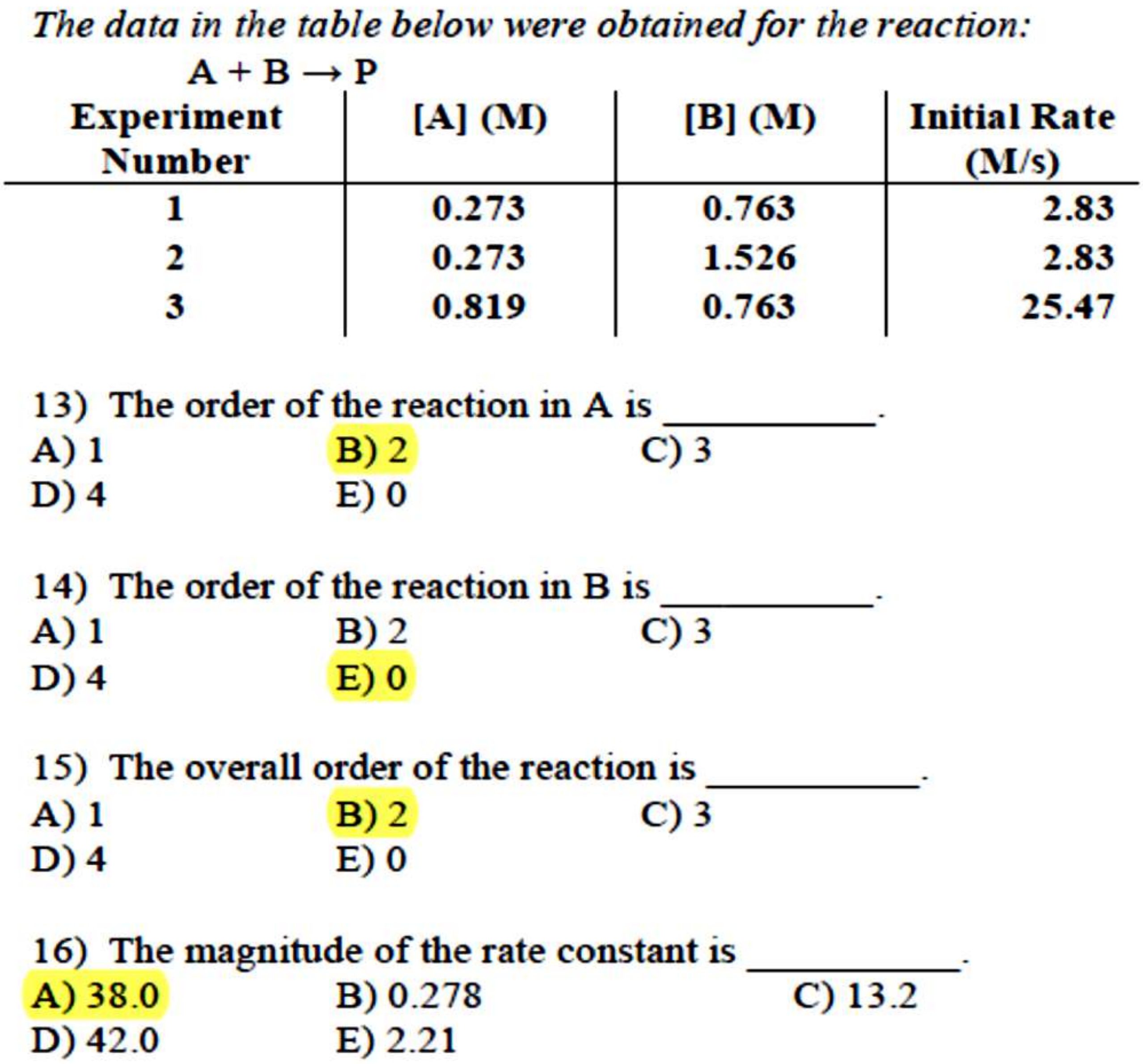
3- Since this is a **zero-order reaction**, the **half-life is dependent on the concentration**. In this instance, **the half-life is decreased when the original concentration is reduced to 1.0 M. The new half-life is 80 seconds**.

4- Reaction B represents a zero-order reaction because the units are in M/s. Zero-order reactions always having rate constants that are represented by (mol /L.s) .

Higher order reactions, however, require the rate constant to be represented in different units.

5-True. When using the rate function with n equal to zero in zero-order reactions. Therefore**, rate is equal to the rate constant k.**

Q7:



The data in the table below were obtained for the reaction:

A + B → P

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.273	0.763	2.83
2	0.273	1.526	2.83
3	0.819	0.763	25.47

13) The order of the reaction in A is ___________.

A) 1 [✓ B) 2] C) 3

D) 4 E) 0

14) The order of the reaction in B is ___________.

A) 1 B) 2 C) 3

D) 4 [✓ E) 0]

15) The overall order of the reaction is ___________.

A) 1 [✓ B) 2] C) 3

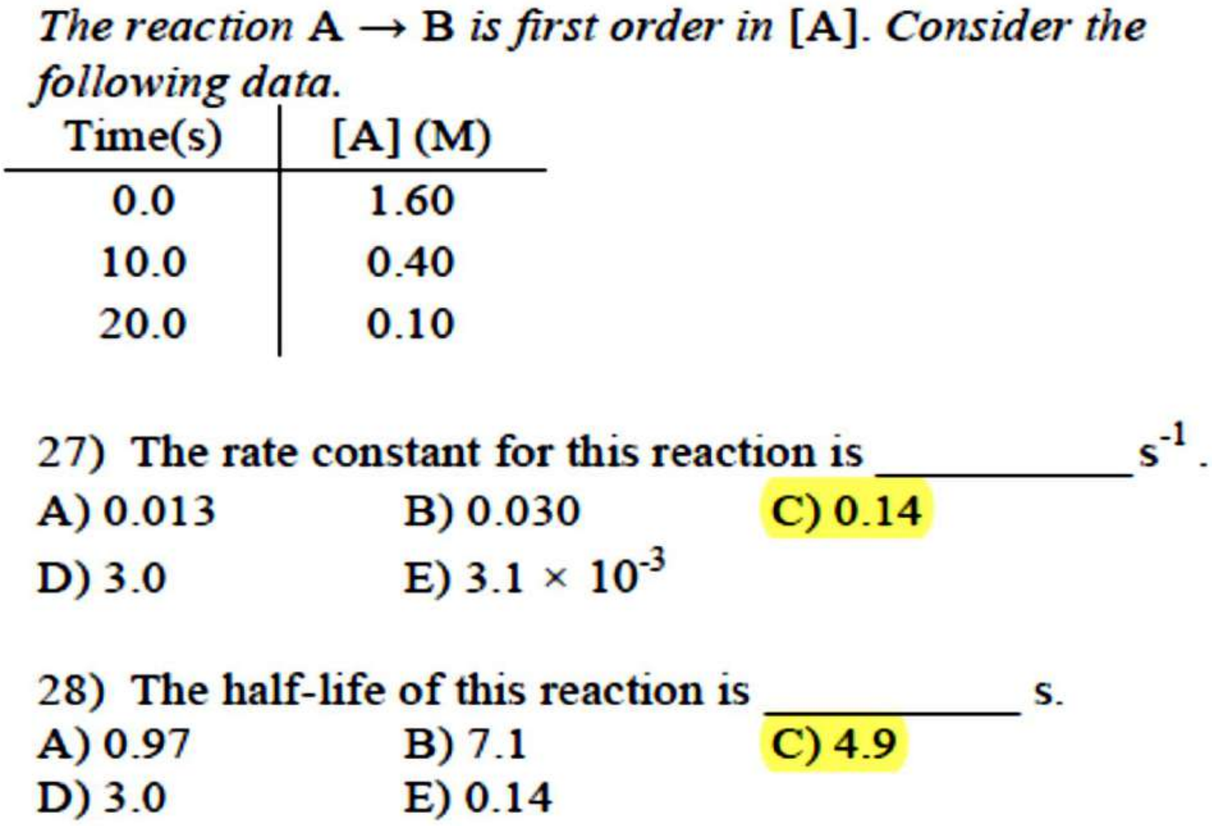
D) 4 E) 0

16) The magnitude of the rate constant is ___________.

[✓ A) 38.0] B) 0.278 C) 13.2

D) 42.0 E) 2.21

Q8:



The reaction **A → B** *is first order in* **[A]**. *Consider the following data.*

Time(s)	[A] (M)
0.0	1.60
10.0	0.40
20.0	0.10

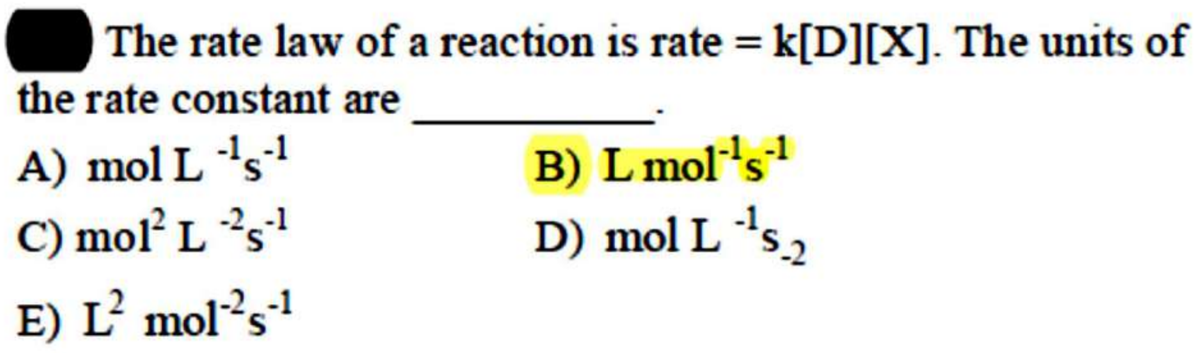
27) The rate constant for this reaction is ___________ s^{-1}.

A) 0.013
B) 0.030
[✓ C) 0.14]
D) 3.0
E) 3.1×10^{-3}

28) The half-life of this reaction is ___________ s.

A) 0.97
B) 7.1
[✓ C) 4.9]
D) 3.0
E) 0.14

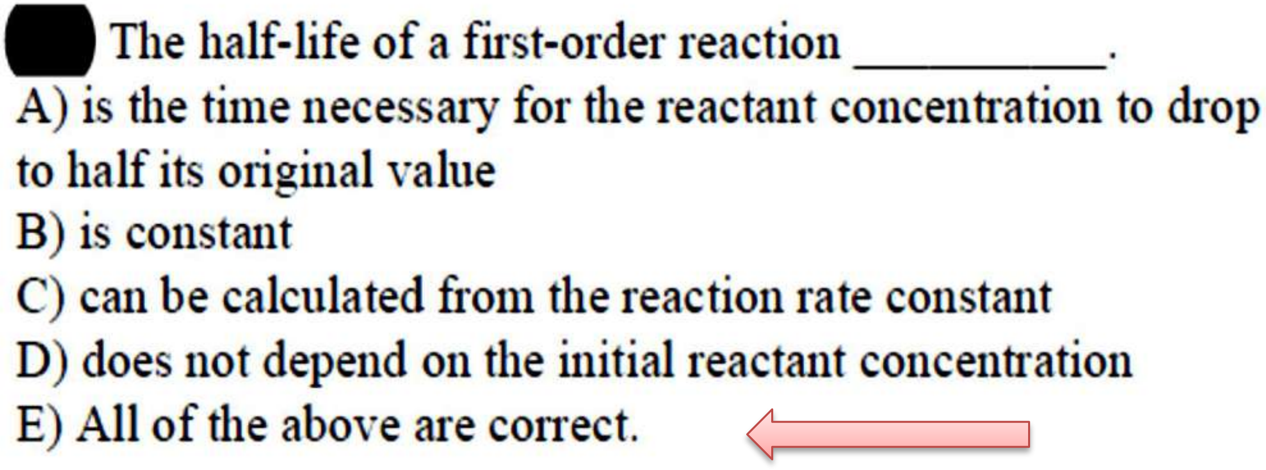
Q9:



[redacted] The rate law of a reaction is rate = k[D][X]. The units of the rate constant are ___________.

A) mol $L^{-1}s^{-1}$
B) L $mol^{-1}s^{-1}$
C) mol^2 $L^{-2}s^{-1}$
D) mol $L^{-1}s_{-2}$
E) L^2 $mol^{-2}s^{-1}$

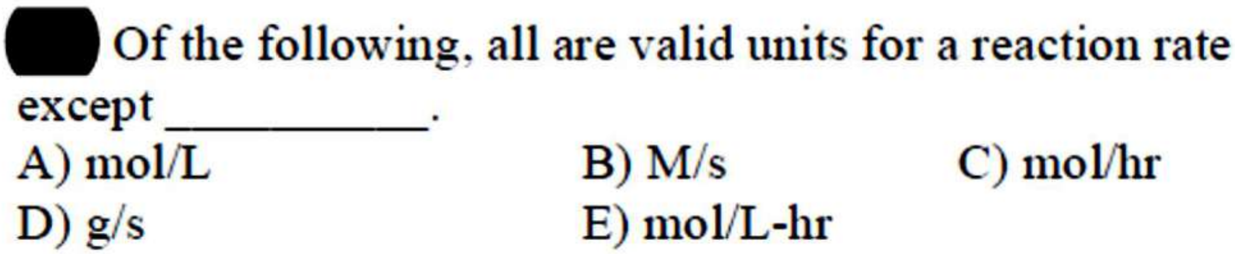
Q10:



[redacted] The half-life of a first-order reaction ___________.

A) is the time necessary for the reactant concentration to drop to half its original value
B) is constant
C) can be calculated from the reaction rate constant
D) does not depend on the initial reactant concentration
E) All of the above are correct. ←

Q11:



[redacted] Of the following, all are valid units for a reaction rate except ___________.

A) mol/L
B) M/s
C) mol/hr
D) g/s
E) mol/L-hr

Q12:

[redacted] Which one of the following is <u>not</u> a valid expression for the rate of the reaction below?

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O$$

A) $-\frac{1}{7}\frac{\Delta[O_2]}{\Delta t}$

B) $\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$

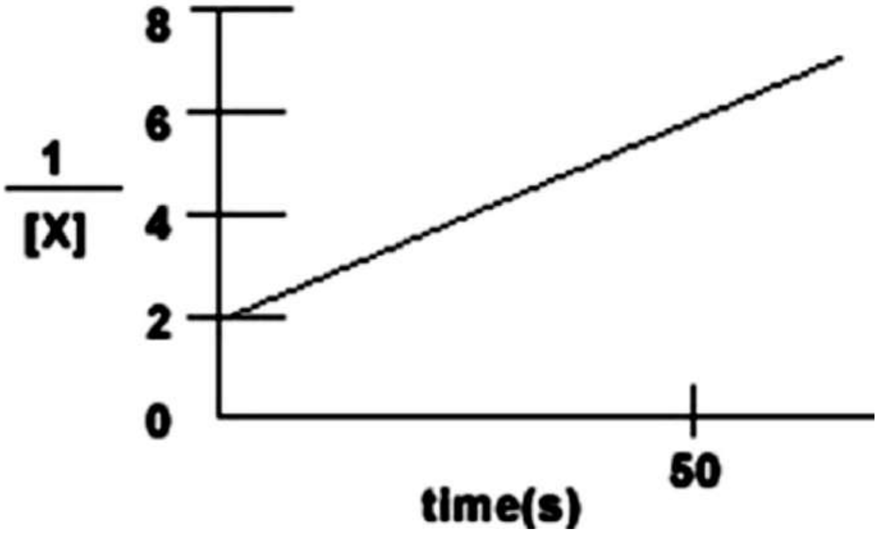
C) $\frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$

D) $-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t}$

E) All of the above are valid expressions of the reaction rate.

Q13:

For the reaction **$X + Y \rightarrow Z$**, the reaction rate is found to depend only upon **the concentration of X**. A plot of **1/X** verses **time** gives a straight line:



What is the rate law for this reaction?

A. rate = k [X]
B. rate = k $[X]^2$
C. rate = k [X][Y]
D. rate = k $[X]^2[Y]$

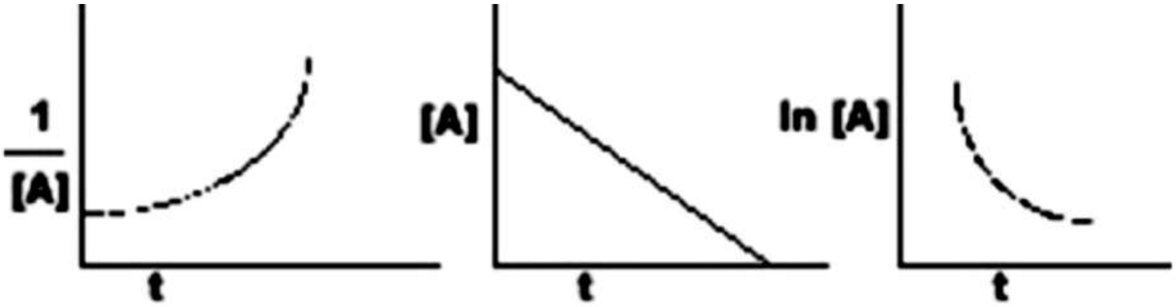
Q14:

For a second - order reaction, the half-life is equal to:

A. $t_{1/2} = 0.693/k$.
B. $t_{1/2} = k/0.693$.
C. $t_{1/2} = 1/k[A]_o$.
D. $t_{1/2} = k$.
E. $t_{1/2} = [A]_o/2k$

Q15:

The graphs below all refer to the same reaction. What is the order of this reaction?



A. zeroth order
B. first order
C. second order
D. unable to predict

Q16:

For the chemical reaction A → C, a plot of $1/[A]_t$ versus time was found to give a straight line with a positive slope. What is the order of reaction?

A. zeroth
B. first
C. second
D. Such a plot cannot reveal the order of the reaction.

Q17:

For what order reaction does the half-life get longer as the initial concentration increases?

A. [✓ Zeroth order]
B. First order
C. Second order
D. none of them because half-life is always independent of the initial concentration

Q18:

In the reaction, $2N_2O \rightarrow 2N_2 + O_2$, oxygen and nitrogen gases are formed at the same rate (mol/L·s) ?

True [✓ False]

Q19:

The rate constant (k) of a first-order reaction, A → products, can be determined from a graph of ln[A] versus t.

[✓ True] False

Q20:

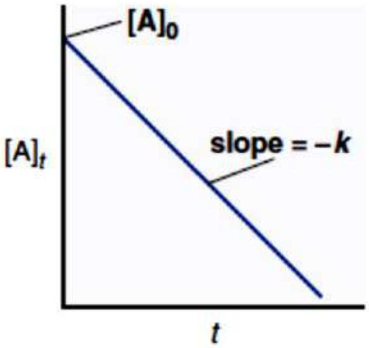
[redacted] How are integrated rate laws used to determine reaction order? What is the order in reactant if a plot of

(a) The natural logarithm of [reactant] vs. time is linear?

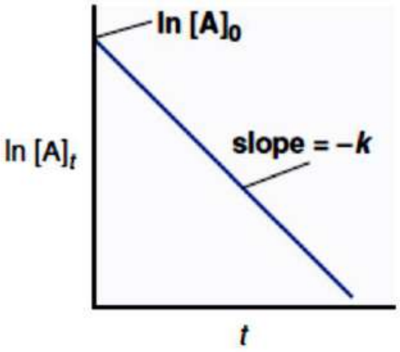
(b) The inverse of [reactant] vs. time is linear?

(c) [Reactant] vs. time is linear?

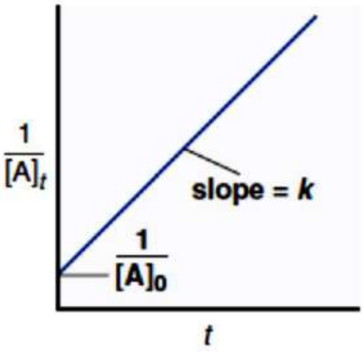
(d) The inverse of [reactant]^2 vs. time is liner ?



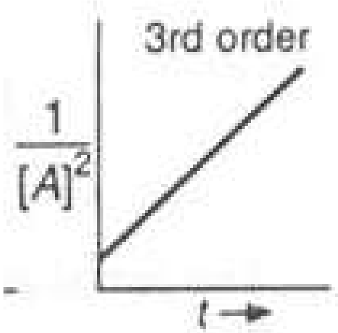
Zero Order



First Order



Second Order



Third Order

HOW TO DETERMINE THE *nth* ORDER OF A REACTION:

There are at least five different methods to determine the *nth* order of a reaction:

1. **Using integrated rate equations**
2. **Graphical method**
3. **Using half-life period**
4. **The Differential method(Van't Hoff's differential method)**
5. **Ostwald's Isolation method**

In this lecture we will explain two of them:
The half-live method and the Van't Hoff's differential method.

(3) Using half-life period:

For calculation the *nth* order of reaction. We know that half-life period for a first order reaction is independent of the initial concentration, [A].
We also know:

$$\text{half-life} \propto \frac{1}{[A]} \quad \text{for 2nd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^2} \quad \text{for 3rd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^{n-1}} \quad \text{for } n\text{th order reaction}$$

Substituting values of initial concentrations and half-life periods from the two experiments, we have:

$$(t_{0.5})1 \propto \frac{1}{[A_1]_o^{n-1}} \qquad \text{and} \qquad (t_{0.5})2 \propto \frac{1}{[A_2]_o^{n-1}}$$

$$\frac{(t_{0.5})2}{(t_{0.5})1} = \left[\frac{A1}{A2}\right]_0^{n-1} \quad \Longrightarrow \quad \boxed{ln\,\frac{(t_{0.5})2}{(t_{0.5})1} = (n-1)\ln\left[\frac{A1}{A2}\right]_0}$$

SOLVED PROBLEM:

In the reduction of nitric oxide, 50% of reaction was completed in 147 seconds when initial pressure was 288mm Hg and in 108 seconds initial pressure was 336 mm Hg. Find the order of the reaction?

SOLUTION

$$\ln \frac{(t_{0.5})2}{(t_{0.5})1} = (n-1)\ln\left[\frac{A1}{A2}\right]_0$$

$$n-1 = \frac{\ln\frac{(t_{0.5})2}{(t_{0.5})1}}{\ln\left[\frac{A1}{A2}\right]_0} = \frac{\ln\frac{(108)}{(147)}}{\ln\frac{(288)}{(336)}} = \frac{-0.308}{-0.154} = 2$$

n =2+1=3 , the reaction is of the third-order

* * *

(4) The Differential method (Van't Hoff's differential method):

According to this method, *the rate of a reaction (R) of the nth order* is proportional to the *nth power of concentration*.

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

$R_1 = k[A_1]^n$

$R_2 = k[A_2]^n$

$$\frac{R_1}{R_2} = \left[\frac{A_1}{A_2}\right]^n \qquad \text{or} \qquad \ln\frac{R_1}{R_2} = n\ln\left[\frac{A_1}{A_2}\right]$$

Theories of Chemical Kinetics

1- **Collision Theory**
2- **Transition State Theory**

1- Collision theory of reaction rates:

According to this theory, a chemical reaction takes place only by collisions between the reacting molecules. But not all collisions are effective. Only a small fraction of the collisions produce a reaction.

The two main conditions for a collision between the reacting molecules to be productive are:

(1) The colliding molecules must posses sufficient kinetic energy to cause a reaction.

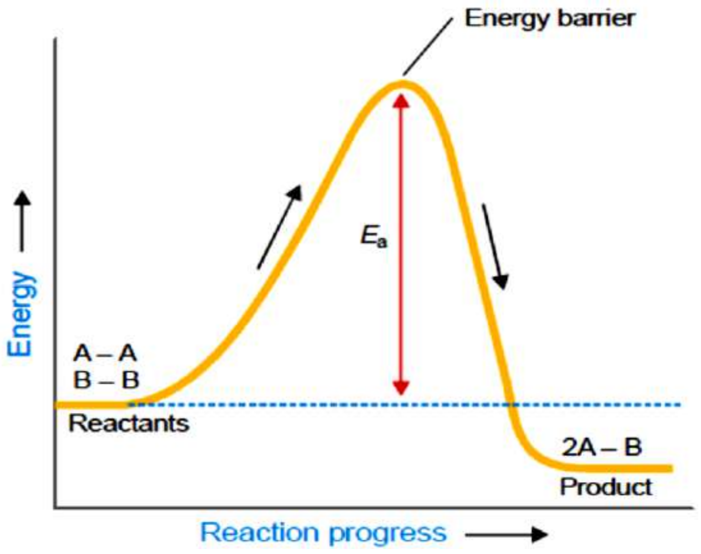
(2) The reacting molecules must collide with proper orientation

****

(1) The colliding molecules must posses sufficient kinetic energy to cause a reaction:

$$A-A \ + \ B-B \longrightarrow 2A-B$$

A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and forming new bonds in the product molecules. The energy for the breaking of bonds comes from the kinetic energy possessed by the reacting molecules before the collision.



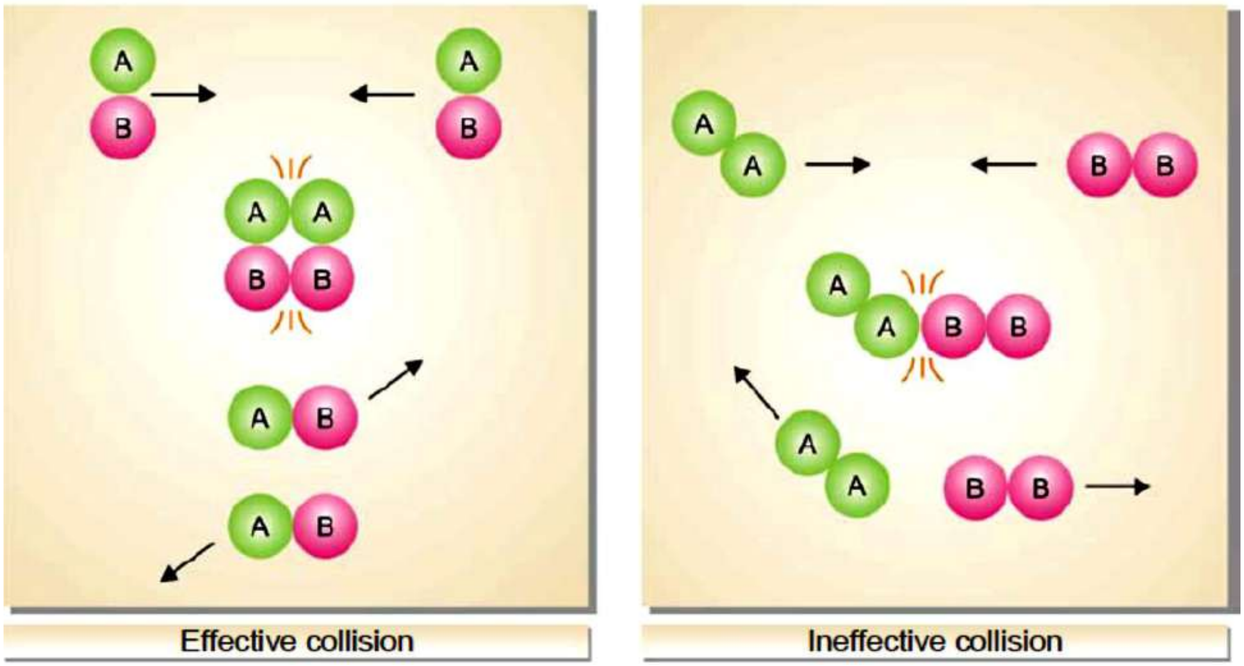
The activation energy, Ea, is the minimum energy necessary to cause a reaction between the colliding molecules. Only the molecules that collide with a kinetic energy greater than Ea, are able to get over the barrier and react. The molecules colliding with kinetic energies less than Ea fail to surmount the barrier. The collisions between them are unproductive and the molecules simply bounce off one another.

(2) The reacting molecules must collide with proper orientation

The reactant molecules must collide with favorable orientation.
The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bonds.

.

Only the molecules colliding with kinetic energy greater than Ea and with correct orientation can cause reaction.



Effective collision

Ineffective collision

Orientations of reacting molecules A_2 and B_2 which lead to an effective and ineffective collision.

Collision Theory and Reaction Rate Expression:

Taking into account the two postulates of the collision theory, the reaction rate for the elementary process:

$$A + B \longrightarrow C + D$$

Is given by the expression:

Rate = f x p x z

Where:

f = fraction of molecules which possess sufficient energy to react;

؛

p = probable fraction of collisions with effective orientations, and

z = collision frequency.

****

Temperature Dependence of Reaction Rate and Arrhenius Equation:

The kinetic energy of a gas is directly proportional to its temperature.
So ***the temperature of a system is increased, more and more molecules will acquire necessary energy greater that Ea to cause productive collisions***. ***This increases the rate of the reaction***.

In 1889, Arrhenius suggested as simple ***relationship between the rate constant,*** **k*****, for a reaction*** **and** ***the temperature of the system.***

$$K= Ae^{-Ea/RT} \quad \ldots\ldots\ldots\ldots \textit{Arrhenius equation}$$

A = An experimentally determined quantity (Arrhenius constant)
Ea = The activation energy,
R = The gas constant,
T = Kelvin temperature

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

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

Calculation of *Ea* Using Arrhenius Equation:

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

$$\uparrow \qquad\qquad \uparrow \qquad\qquad \uparrow$$

$$y \;=\; mx \;+\; b$$

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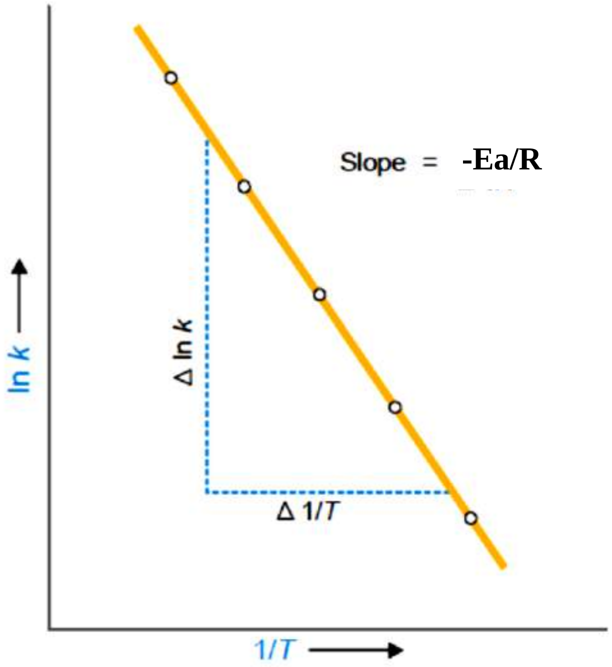
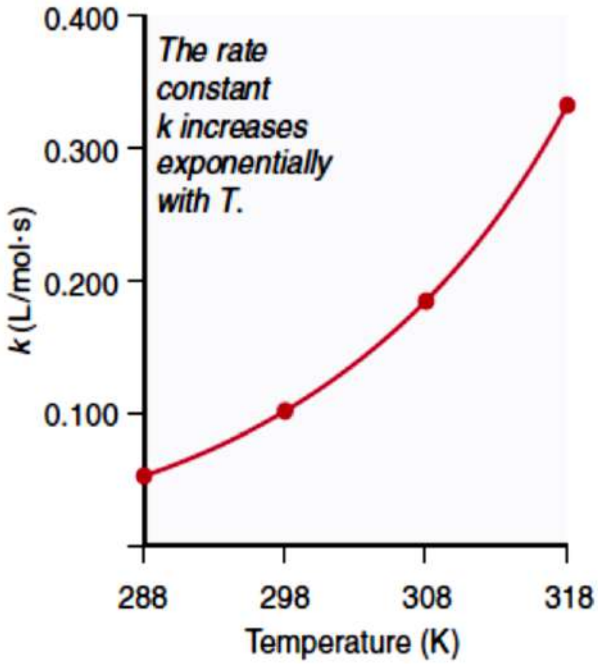
You can see from the equation is that of ***a straight line***, **y = mx + b**.

The two variables in this equation are ***(1n k) and (1/T). From the slope of the line, we can calculate the value of Ea.***





SOLVED PROBLEM. The values of the rate constant (k) for the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ were determined at several temperatures. A plot of ln k *versus* $1/T$ gave a straight line of which the slope was found to be -1.2×10^4 K. What is the activation energy of the reaction ?

SOLUTION

We know that

$$\text{Slope} = -\frac{E_a}{R}$$

$$E_a = -R \times (\text{slope})$$

Substituting the values, we have

$$E_a = (-8.314\ \text{JK}^{-1}\ \text{mol}^{-1})(-1.2 \times 10^4\ \text{K})$$

$$= 1.0 \times 10^5\ \text{J mol}^{-1}$$

Thus the activation energy for the reaction is $\mathbf{1.0 \times 10^5\ J\ mol^{-1}}$

Calculation of (Ea) from the Values of k (k_1 and k_2) at Two Temperatures (T_1 and T_2):

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

The values of (k_1 and k_2) measured at (T_1 and T_2) can be used to find (Ea).

SOLVED PROBLEM.

The gas-phase reaction between methane (CH_4) and diatomic sulphur (S_2) is given by the equation*:*

$$CH_4\,(g)+2S_2\,(g)\longrightarrow CS_2\,(g)+2H_2S\,(g)$$

At 550°C the rate constant (k) for this reaction is (1.1) *l* mol^{-1} *sec* and at 625°C the rate constant (k) is (6.4) *1* mol^{-1} *sec*. Calculate Ea for this reaction.

SOLUTION

k_1 = 1.1 1itre mol^{-1} sec. $T_1 = 550 + 273 = 823$ K

k_2 = 6.4 1itre mol^{-1} sec. $T_2 = 625 + 273 = 898$ K

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

$$\ln\left(\frac{6.4}{1.1}\right)=\frac{E_a}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{823\,\mathrm{K}}-\frac{1}{898\,\mathrm{K}}\right)$$

$$E_a=\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823\,\mathrm{K}}-\frac{1}{898\,\mathrm{K}}\right)}$$

$$=\mathbf{1.4\times10^5\ J/mol}$$

SIMULTANEOUS REACTIONS

Sometimes there are some side reactions accompanying the main chemical reaction. Such reactions are known as **complex reactions** ***as these do not take place in a single step***. In other words, ***such complex reactions proceed in a series of steps instead of a single step and the rate of overall reaction is in accordance with the stoichiometric equation for that reaction***. Generally, following types of complications occur:

، تستمر هذه

التفاعلات المعقدة في سلسلة من الخطوات بدلاً من خطوة واحدة وتكون سرعة التفاعل الكلي وفقًا لمعادلة

الكيميائية المتكافئة المتوازنة لهذا التفاع

(1) Consecutive reactions

(2) Parallel reactions

(3) Reversible or opposing reactions

(1) Consecutive Reactions

The reactions in which the final product is formed through one or more intermediate steps are called **consecutive reactions**. These are also known as sequential reactions. ***In such reactions the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction***. Various step reactions can be written for the overall reaction as shown below:

	A	$\xrightarrow{k_1}$	B	$\xrightarrow{k_2}$	C
Initial conc.	$[A]_0$		0		0
Conc. after time *t*	[A]		[B]		[C]

- In the above reaction **the product [C] is formed from the reactant [A] through intermediate [B]**.
- In this reaction **each stage has its own different rate constants k1 for the first step and k2 for the second step**.
- The **overall rate of reaction depends upon the magnitude of these two rate constants.**
- The **initial concentration** and **concentration after time t** are shown below each species in above reaction under consideration.

It is clear that

$$[\mathrm{A}]_0 = [\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}]$$

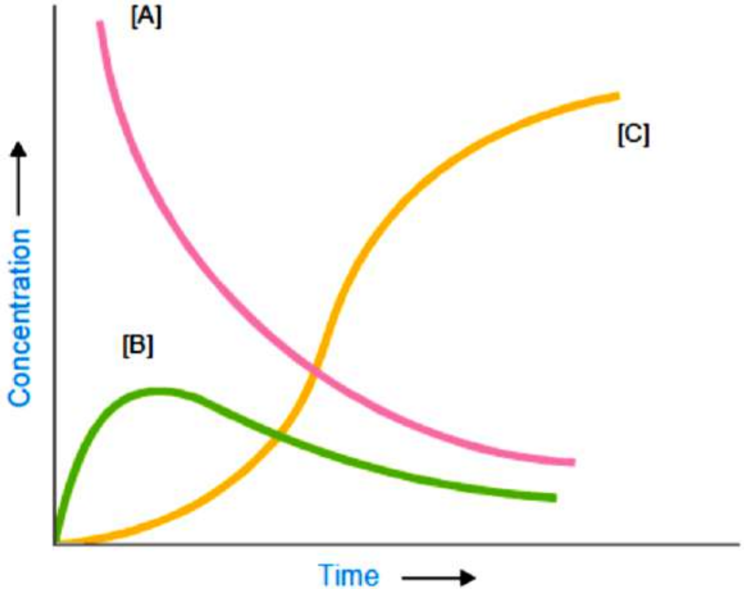
The differential rate expressions are

$$\frac{-d[\mathrm{A}]}{dT} = k_1[\mathrm{A}]$$

$$\frac{d[\mathrm{B}]}{dT} = k_1[\mathrm{A}] - k_2[\mathrm{B}]$$

and

$$\frac{d[\mathrm{C}]}{dT} = k_2[\mathrm{B}]$$



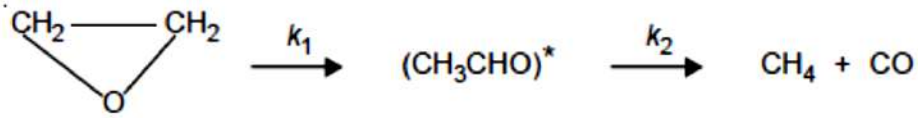
It is clear that ***the concentration of [A] decreases exponentially*****,** ***the concentration of [B] first increases and then decreases*** **and that of** ***[C] increases (from zero) with time and finally attains the value equal to $[A]_0$ (initial concentration A)*** **when all [A] has changed into the final product [C].**

Examples of First Order Consecutive Reactions

(*a*) Decomposition of dimethyl ether is gaseous phase

$$CH_3COCH_3 \xrightarrow{k_1} CH_4 + HCHO \xrightarrow{k_2} H_2 + CO$$

(*b*) Decomposition of Ethylene oxide

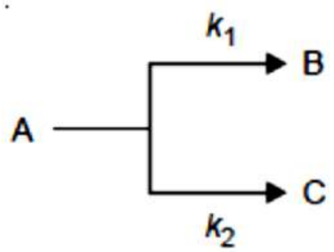


(*c*) Any radioactive decay of the type

$$^{218}_{84}Po \xrightarrow{-\alpha} {}^{214}_{82}Pb \xrightarrow{-\beta} {}^{214}_{83}Bi \xrightarrow{-\beta} {}^{214}_{84}Po$$

(2) Parallel or Side Reactions

In these reactions *the reacting substance follows two or more paths to give two or more products*. The ***preferential rate*** of such may be changed by varying the conditions like **pressure, temperature or catalyst**. The reaction in which **the maximum yield of the products is obtained is called *the main reaction* while the other reaction (or reactions) is called *side or parallel reactions*. For example:**



In the above reaction:

- The **reactant [A] gives two products [B] and [C] separately** in **two different reactions with rate constants k1 and k2** respectively.
- If **k1 > k2** : the reaction **A $\longrightarrow$ B will be the major reaction**; and **A $\longrightarrow$ C will be the side or parallel reaction**.

  Let us assume that both these reactions are of **first order** and **concentration of A is [A] at the time (t)**.

  The differential rate expressions are:

$$r_1 = \frac{-d[\mathrm{A}]}{dT} = k_1[\mathrm{A}] \qquad ...(i)$$

and
$$r_2 = \frac{-d[\mathrm{A}]}{dT} = k_2[\mathrm{A}] \qquad ...(ii)$$

The **total rate** of disappearance of A is given by:

$$\begin{aligned}\frac{-d[\mathrm{A}]}{dT} &= r_1 + r_2 = k_1[\mathrm{A}] + k_2[\mathrm{A}]\\ &= (k_1 + k_2)[\mathrm{A}]\\ &= k'[\mathrm{A}] \qquad ...(iii)\end{aligned}$$

Where:

k′ = **The firs-order rate constant**.

k′ = k1 + k2 ***(of two side reactions).***

Integrating equation (iii), we get:

$$\int \frac{-d[\mathrm{A}]}{dT} = \int k'[\mathrm{A}]$$

applying the limits $[\mathrm{A}_0]$ & $[\mathrm{A}]_t$ and 0 & t, we have

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{-d[\mathrm{A}]}{dt} = k' \int_0^t dt$$

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = k't + (k_1 + k_2)t \qquad ...(iv)$$

Where:

$[\mathrm{A}]_0$ = ***The initial concentration of the reactant A***

[A]t = ***Concentration of A at time t***.

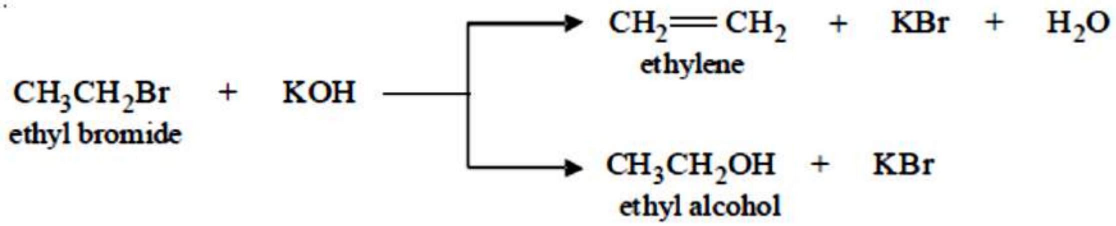
The ratio of the rates of two side reactions is ***obtained by dividing equations (i) by (ii):***

$$\frac{r_1}{r_2} = \frac{k_1[\mathrm{A}]}{k_2[\mathrm{A}]} = \frac{k_1}{k_2} \qquad ...(v)$$

***From equations* (iv) *and* (v) *we can calculate the individual rate constant k1 and k2*.**

Examples of Parallel or Side Reactions

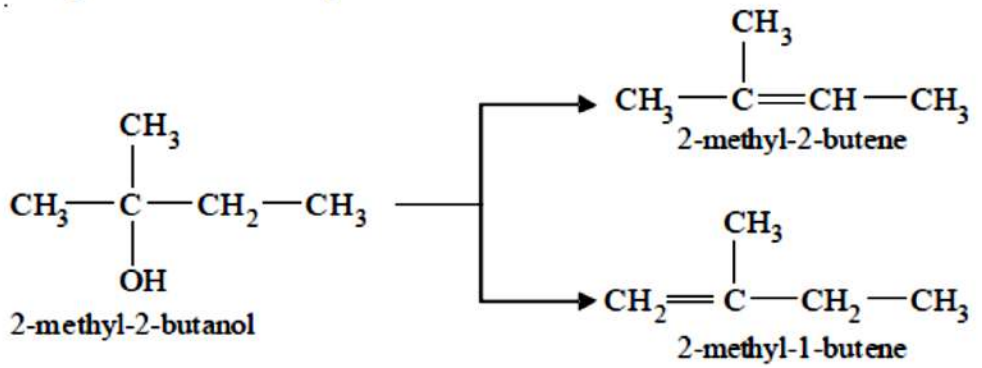
(*a*) Reaction of ethyl bromide with potassium hydroxide



$$CH_3CH_2Br + KOH \rightarrow CH_2{=}CH_2 + KBr + H_2O$$

$$CH_3CH_2Br + KOH \rightarrow CH_3CH_2OH + KBr$$

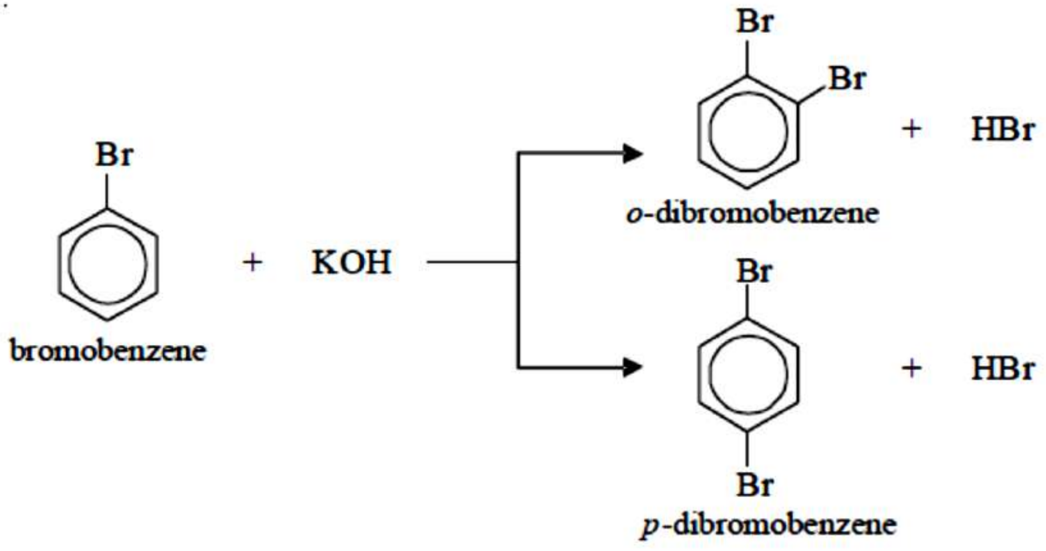
(*b*) Dehydration of 2-methyl–2–butanol



$$CH_3-C(CH_3)(OH)-CH_2-CH_3 \rightarrow CH_3-C(CH_3){=}CH-CH_3$$

$$CH_3-C(CH_3)(OH)-CH_2-CH_3 \rightarrow CH_2{=}C(CH_3)-CH_2-CH_3$$

(*c*) Bromination of bromobenzene



(3) Reversible or Opposing Reactions

In reversible or opposing reactions the products formed also react to give back the reactants. Initially, the rate of forward reaction is very large which decreases with passage of time and **the rate of backward or reverse reaction is zero which increases with passage of time**. **A stage is reached when two rates become equal**.

This situation is called **the chemical equilibrium**. ***It is dynamic in nature*** i.e., ***all the species are reaching at the rate at which they are being formed.***

A reaction of this type may be represented as:

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

	A	B
Initial concentration	$[A]_0$	0
Conc. after time t	$[A]$	$[B]$

Where:

k_f , k_b = **The rate constants of the forward and backward reactions, respectively.**

So:

Rate of Reaction = Rate of forward reaction – Rate of backward reaction

$$\frac{-d[A]}{dt} = \frac{d[B]}{dt} = k_f[A] - k_b[B] \qquad ...(i)$$

If:

$[A]_0$ = The initial concentration of A

X = The concentration (moles) of product in time (t)

$[A]_t = [A]_0 - X$, and $[B] = X$

Substituting these in equation (i), we get:

$$\frac{dx}{dt} = k_f([A]_0 - x) - k_b x \qquad ...(ii)$$

At equilibrium $$\frac{dx}{dt} = 0$$

Hence $$k_f([A]_0 - x_{eq}) = k_b x_{eq} \qquad ...(iii)$$

$X_{eq.}$ = The concentration of the product at equilibrium.

From equation (iii) we have:

$$k_b = k_f\left(\frac{[A]_0 - x_{eq}}{x_{eq}}\right)$$

Substituting the value of k_b in equation (ii), we get:

$$\frac{dx}{dt} = k_f([A]_0 - x) - k_f\left(\frac{[A]_0 - x_{eq}}{x_{eq}}\right)x$$

Integrating this equation between the limits t = 0, X= 0 and t = t, X = Xeq,

$$\int_{0}^{x} \frac{dx}{x_{eq} - x} = k_f \frac{[\mathrm{A}_0]}{x_{\mathrm{eq}}} \int_{0}^{t} dt$$

$$= -\ln (x_{\mathrm{eq}} - x) + \ln x_{\mathrm{eq}} = k_f \frac{[\mathrm{A}]_0\, t}{x_{\mathrm{eq}}}$$

Or:

$$\ln \frac{x_{\mathrm{eq}}}{x_{\mathrm{eq}} - x} = k_f \frac{[A]_0}{x_{\mathrm{eq}}}\, t$$

So we can find the value of (k_f) from $[A]_0$, X_{eq} and X at time t.

From the value of k_f the value of k_b can be calculated by using the relation.

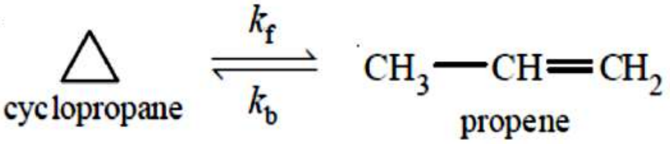
$$k_b = k_f \left(\frac{[\mathrm{A}_0] - x_{\mathrm{eq}}}{x_{\mathrm{eq}}} \right)$$

Examples of Opposing Reactions

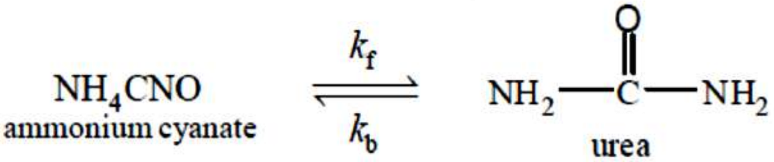
(*a*) Dissociation of hydrogen iodides

$$2HI \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2 + I_2$$

(*b*) Isomerisation of cyclopropane into propene

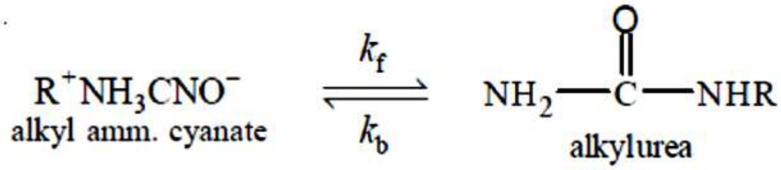


(*c*) Isomerisation of ammonium cyanate into urea in aqueous solution.



$$\underset{\text{ammonium cyanate}}{NH_4CNO} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{urea}}{NH_2—\overset{\overset{\displaystyle O}{\|}}{C}—NH_2}$$

(*d*) Isomerisation of alkyl ammonium cyanate into substituted urea in aqueous solution



$$\underset{\text{alkyl amm. cyanate}}{R^+NH_3CNO^-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{alkylurea}}{NH_2—\overset{\overset{\displaystyle O}{\|}}{C}—NHR}$$

(*e*) Reaction between gaseous CO and NO_2

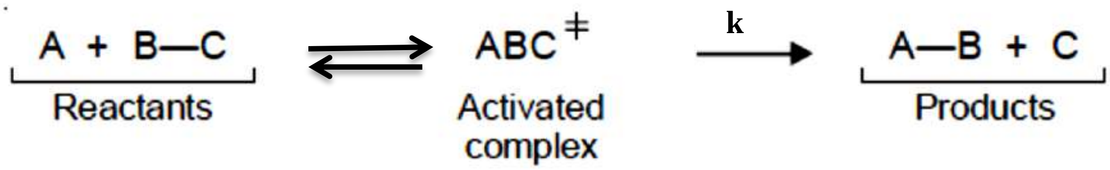
$$CO(g) + NO_2(g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CO_2(g) + NO(g)$$

TRANSITION STATE THEORY

The **transition state** or **activated complex theory** was developed by Henry Erying (1935).

- This theory is also called the **absolute rate theory** because with its help it is possible to get **the absolute value of the rate constant**.
- **The transition state theory assumes that simply** a collision between the reactant molecules does not really causes a reaction.
- During the collision, **the reactant molecules form a transition state or activated complex which has higher energy than both the reactants and the products (for this reason that the theory is called Transition stat theory). The activated complex is in equilibrium with the reacting molecules and the rate of reaction is given by the rate of decomposition of the complex to form the products.**

Thus,



(≠) is used to identify the activated complex.

The rate constant (k) for any reaction is:

$$(rate\ constant)\quad k = \frac{RT}{Nh}\mathrm{K} \quad \text{........(i)}$$

R= Gas constant

h= Planck's constant

N= Avogadro's number

T= Absolute temperature

K= Equilibrium constant for the formation of the activated complex:

$$\mathrm{K} = \frac{[\mathrm{ABC}^{\neq}]}{[\mathrm{A}][\mathrm{BC}]} \quad \text{........ (ii)}$$

From thermodynamics:

$$\Delta G^{\neq} = -RT \ln K$$

$$\ln K = -\Delta G^{\neq} / RT$$

$$K = e^{-\Delta G^{\neq} / RT}$$

$\Delta G^{\neq}$ = the free energy of activation of reaction

Substituting the value of K *(equilibrium constant)* in eq.(i):

$$k = \frac{RT}{Nh} e^{-\Delta G^{\neq} / RT} \quad \text{..........(iii)}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

$$k = \frac{RT}{Nh} e^{-(\Delta H^{\neq} - T\Delta S^{\neq})/ RT}$$

$$k = \frac{RT}{Nh} e^{\Delta S^{\neq}/ R} \cdot e^{-\Delta H^{\neq} / RT} \quad \text{.........(iv)}$$

Eq.(iii), exhibited the significance of the transition state theory:

- The first factor : $\frac{RT}{Nh}$ is constant at constant T
- The rate of reaction depends on the second factor: $e^{-\Delta G^{\neq} / RT}$

{The greater the value of the $\Delta G^{\neq}$ of activation for a reaction, the slower will be the reaction}

- **Comparison with Arrhenius equation:**

$$k = \underbrace{\frac{RT}{Nh} e^{\Delta S^{\neq}/R}}_{A} \cdot \underbrace{e^{-\Delta H^{\neq}/RT}}_{e^{-Ea/RT}}$$

$$k = A \quad e^{-Ea/RT}$$

$E_a = \Delta H^{\neq}$ (**Enthalpy of activation = Energy of activation**)

$$A = \frac{RT}{Nh} e^{\Delta S^{\neq}/R}$$

- **Comparison with Collision theory :**

$$\text{Rate} = F \times P \times Z$$

$$A = PZ$$

$$A = PZ = \frac{RT}{Nh} e^{\Delta S^{\neq}/R}$$

P = probable fraction of collisions with effective orientations

Z = collision frequency.

So:

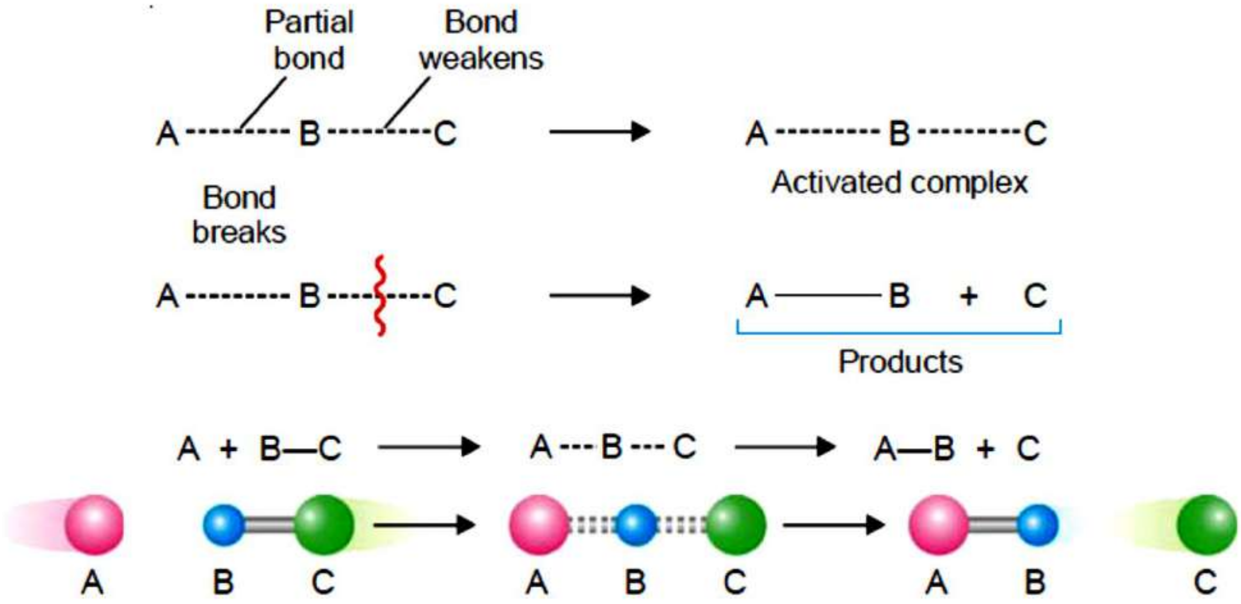
The probability factor (P) is related to the entropy of activation ($\Delta S^{\neq}$)

- **The transition state theory will be summarized as follows:**

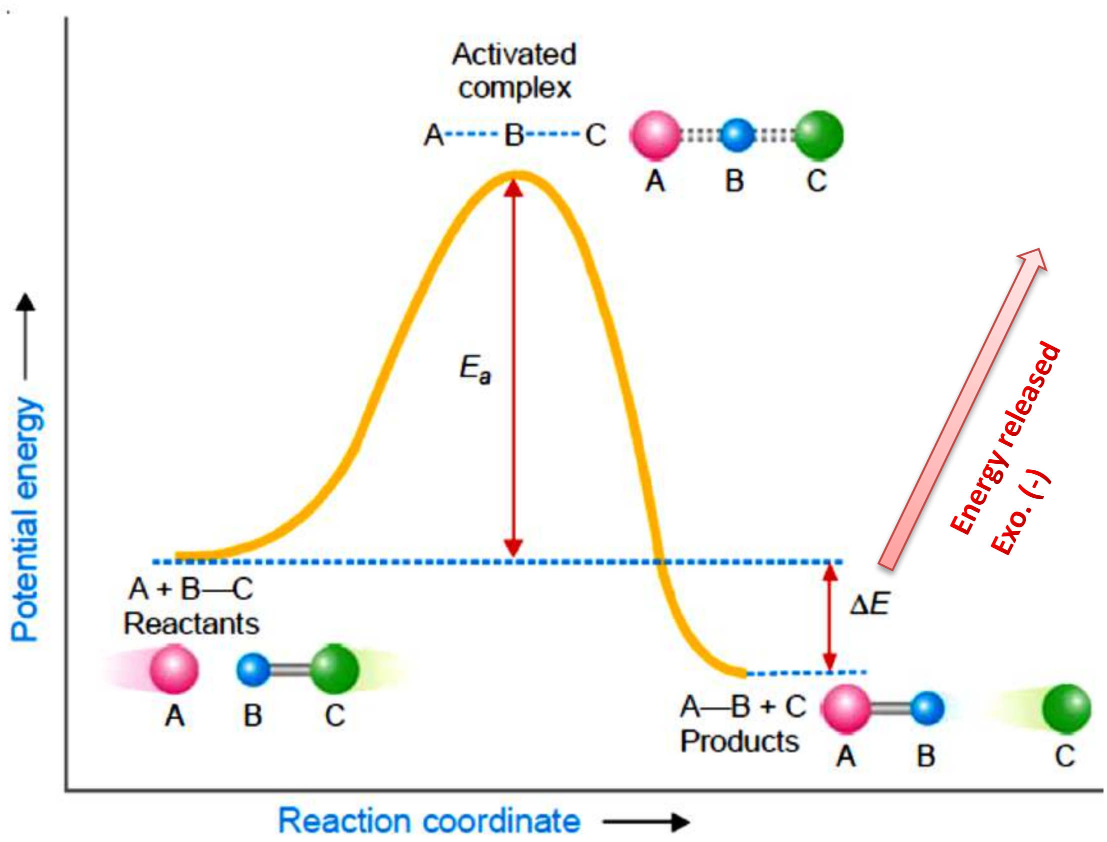
(1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process the kinetic energy of the two molecules is converted into potential energy.

(2) As the molecules come close, the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.

(3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an activated complex or transition state. The activated complex is momentary and decomposes to give the products (A–B + C)



The activated complex theory illustrated by the reaction energy diagram



Change of potential energy during a collision between the reactant molecules for an exothermic reaction(-)

$$\Delta H \text{ (reaction)} = \sum \Delta H \text{ (Products)} - \sum \Delta H \text{ (Reactants)}$$

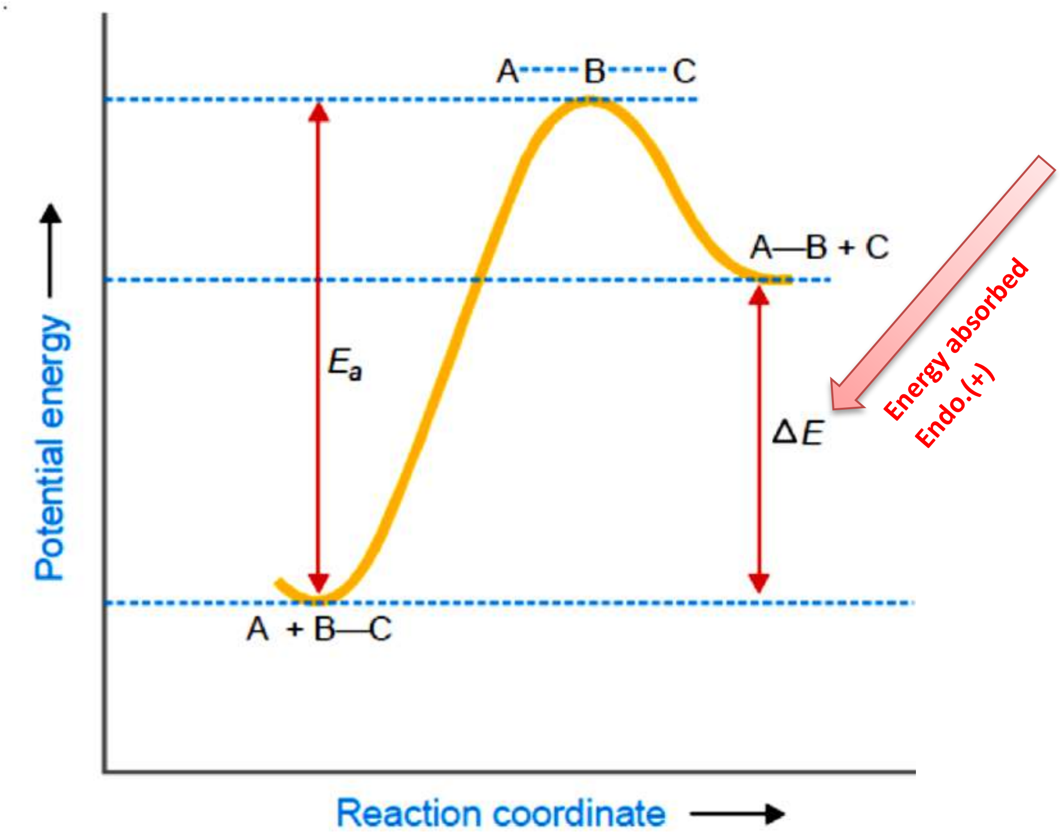
Or

$$\Delta E \text{ (reaction)} = E \text{ (Products)} - E \text{ (Reactants)}$$

$$\Delta H \text{ (Products)} < \Delta H \text{ (Reactants)}$$

$$E \text{ (Products)} < E \text{ (Reactants)}$$

$$\Delta H^{\neq} \text{ (reaction)} = (-) \text{ Exothermic}$$



A potential energy diagram for an endothermic reaction (+).

$$\Delta H\ (\text{reaction}) = \sum \Delta H\ (\text{Products}) - \sum \Delta H\ (\text{Reactants})$$

Or

$$\Delta E\ (\text{reaction}) = E\ (\text{Products}) - E\ (\text{Reactants})$$

$$\Delta H\ (\text{Products}) > \Delta H\ (\text{Reactants})$$

$$E\ (\text{Products}) > E\ (\text{Reactants})$$

ΔH (reaction) = (+) Endothermic ماصًا للحرارة

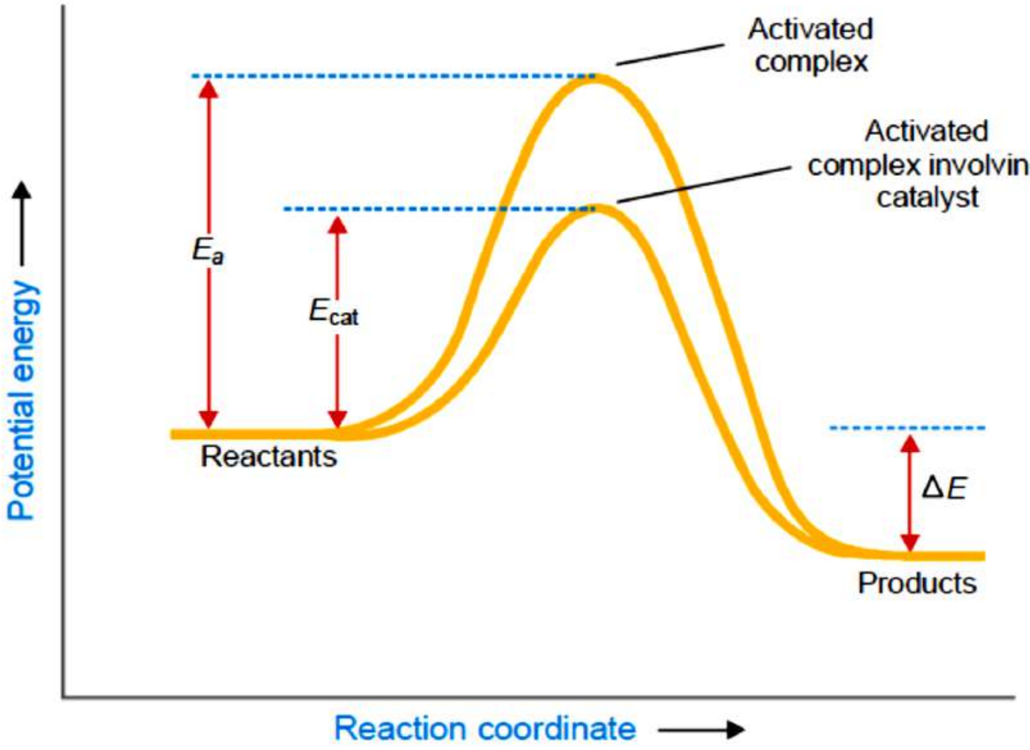
ACTIVATION ENERGY (E_a) AND CATALYSIS:

- The catalyst functions by providing another pathway with lower activation energy (E_{cat})

.

- Thus a much large number of collisions become effective at a given temperature. Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same.

- From the diagram: Although a catalyst lowers the activation energy, the energy difference, ΔE, between products and reactants remains the same.



Energy diagram for a catalyzed and un-catalyzed reaction showing a lowering of activation energy by a catalyst

The Basis of Catalytic Action

A catalyst causes a lower activation energy, which in turn makes the rate constant larger and, thus, the reaction rate higher:

$$\text{Catalyst} \Longrightarrow \text{lower } E_a \Longrightarrow \text{larger } k \Longrightarrow \text{higher rate}$$

- **For a general un-catalyzed reaction, the activation energy is relatively large, so the rate is relatively low:**

:

$$\text{A} + \text{B} \longrightarrow \text{product} \qquad [\text{larger } E_a \Longrightarrow \text{lower rate}]$$

- **For the catalyzed reaction:التفاعل(المحفز) اي مع عامل مساعد**

$$\begin{array}{llll} (1) & \text{A} + \text{catalyst} \longrightarrow & \text{C} & [\text{smaller } E_a \Longrightarrow \text{higher rate}] \\ (2) & \text{C} + \text{B} \longrightarrow & \text{product} + \text{catalyst} & [\text{smaller } E_a \Longrightarrow \text{higher rate}] \end{array}$$

- **Some catalysts function in homogeneous (single-phase) mixtures; others function in heterogeneous (multiphase) mixtures, such as in surface-catalyzed reactions.**

- **Enzyme Catalysis**:
  An enzyme is a biological molecule, such as a high-molecular-mass protein, that functions as a catalyst.
  In enzyme catalysis, the substrate (S) (reactant) binds to ***an active site*** on the enzyme (E) to form a complex (ES) that dissociates into product molecules (P).

$$\begin{array}{lll} (1) & E + S \rightleftharpoons ES & \text{[fast, reversible]} \\ (2) & ES \longrightarrow E + P & \text{[slow; rate-determining]} \end{array}$$

Enzyme activity depends on:

1-the concentrations of substrate

2-enzyme,

3-acidity of the medium,

4- Temperature.

➢ Summary of the Collision theory and Transition state theory

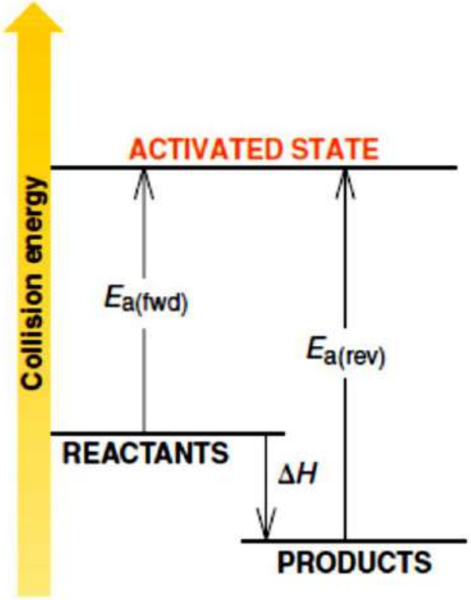
1- Depending on Arrhenius equation:

$$\mathbf{k = Ae^{-Ea/RT}}$$

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

As **T increases**, ***the value of the negative exponent becomes smaller***, which means **k becomes larger**, so **the rate increases**:

$$\text{Higher } T \Longrightarrow \text{larger } k \Longrightarrow \text{increased rate}$$



Molecules must collide with enough energy, **(E_a), to reach an activated state.** ***(This reaction is reversible and is exothermic in the forward direction.)***

$$\mathbf{\Delta H_{rxn} = E_a(fwd) - E_a(rev)}$$

2- *The Effect of Temperature on Collision Energy:*

The ***smaller the activation energy* (Ea)** (or the higher the temperature), ***the larger the fraction of sufficiently energetic collisions***, ***the larger the value of (k)***, and the ***higher the reaction rate(R)***:

$$\text{Smaller } E_a \text{ (or higher } T) \Longrightarrow \text{larger } f \Longrightarrow \text{larger } k \Longrightarrow \text{higher rate}$$

3- The activation energy, Ea, is the minimum energy needed for colliding particles to react.

4- The relative (Ea) values for the forward and reverse reactions depend on whether the overall reaction is exothermic or endothermic.

5- At higher temperatures (T), more collisions have enough energy to exceed Ea.

6- Transition state theory focuses on the change of kinetic energy to potential energy as reactant particles collide and form an unstable transition state.

$$k = \frac{RT}{Nh} e^{-\Delta G^{\neq}/RT}$$

$$k = \frac{RT}{Nh} e^{\Delta S^{\neq}/R} \cdot e^{-\Delta H^{\neq}/RT}$$

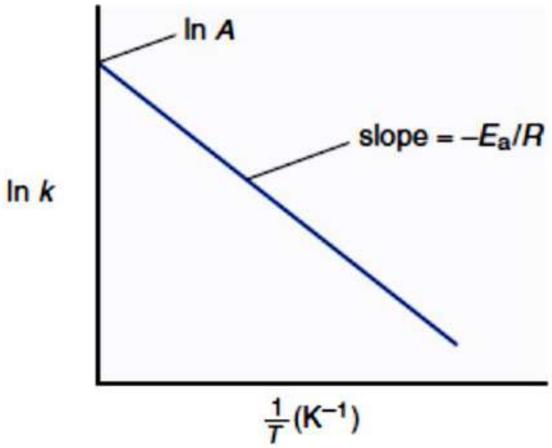
$$\ln K^{\neq} = -\frac{\Delta H^{\neq} - T\,\Delta S^{\neq}}{RT}$$

$K^{\neq}$ = equilibrium constant for the activated complex

- **For first order gas reactions :** **$\Delta H^{\neq} = E_a - RT$**
- **For second order gas reactions:** **$\Delta H^{\neq} = E_a - 2RT$**
- **For third order gas reactions:** **$\Delta H^{\neq} = E_a - 3RT$**

Problems & Slutions

Q1- Graph the relationship between **ln k** and **1/T**. How is the activation energy **(Ea)** determined from this graph?



Q2- The decomposition of hydrogen iodide, 2HI(g) $\longrightarrow$ H_2(g) + I_2(g), has rate constants of $9.51\text{x}10^{-9}$ L/mol .s at 500 K and $1.10\text{x}10^{-5}$ L/mol .s at 600 K. Find Ea.

Solution

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

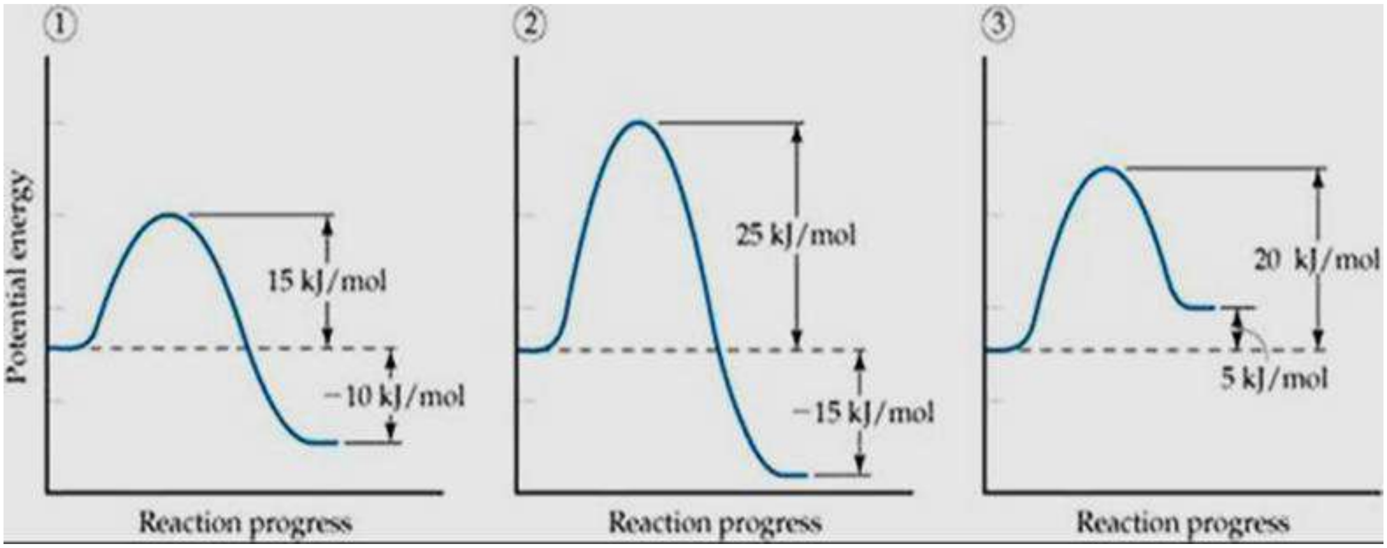
$$E_a = -R\left(\ln \frac{k_2}{k_1}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1}$$

$$= -(8.314\ \text{J/mol·K})\left(\ln \frac{1.10\times10^{-5}\ \text{L/mol·s}}{9.51\times10^{-9}\ \text{L/mol·s}}\right)\left(\frac{1}{600.\ \text{K}} - \frac{1}{500.\ \text{K}}\right)^{-1}$$

$$= 1.76\times10^{5}\ \text{J/mol} = 1.76\times10^{2}\ \text{kJ/mol}$$

Q3- The reaction 2NOCl(g) = 2NO(g) + Cl_2(g) has an Ea of $1.00\text{x}10^{2}$ kJ/mol and a rate constant of 0.286 L/mol.s at 500 K. What is the rate constant at 490 K?

Q4: Consider a series of reactions having these energy profiles:



Rank the reactions from slowest to fastest assuming that they have nearly the same value for the frequency factor A.

Solution

- **The lower the activation energy, the faster the reaction.**
- **The value of ΔE does not affect the rate.**
- **Hence, the order from slowest reaction to fastest is 2 < 3 < 1.**

Q5: Rank the reverse reactions *(from the above energy profiles)* from slowest to fastest?

Solution

- **2 < 1 < 3 because, if you approach the barrier from the right, the (E_a)**
- **(40 kJ/mol) for reverse reaction 2,**
- **(25 kJ/mol) for reverse reaction 1,**
- **(15 kJ/mol)for reverse reaction 3.**

Q6- For the first order hydrolysis reaction of sulfamic acid(H_3NSO_3), $k= 1.16\times10^{-3}$ ($L.mol^{-1}.s^{-1}$) at $90C^{o}$, while Ea= 30500 (cal mol^{-1}). From these data find (a) $\Delta G^{\neq}$, (b) $\Delta H^{\neq}$, (c) $\Delta S^{\neq}$, and (e) $K^{\neq}$ of the reaction?

Solution

$$\Delta H^{\neq} = E_a - RT = 30500 \text{ cal. mol}^{-1} - 1.987 \text{ cal.K}^{-1} \text{.mol}^{-1} \text{x } 363K$$

$$\Delta H^{\neq} = 29800 \text{ cal. mol}^{-1}$$

$$k = \frac{RT}{Nh} e^{-\Delta G\neq / RT} =$$

$$1.16\text{x}10^{-3} = \left(1.987 \text{ cal.K}^{-1} \text{.mol}^{-1}\text{x } 363K / 6.023\text{x}10^{23} \text{ mol}^{-1} \text{x } 6.625\text{x}10^{-27} \text{erg.s}\right) e^{-(\Delta G\neq/1.987 \text{ x } 363)}$$

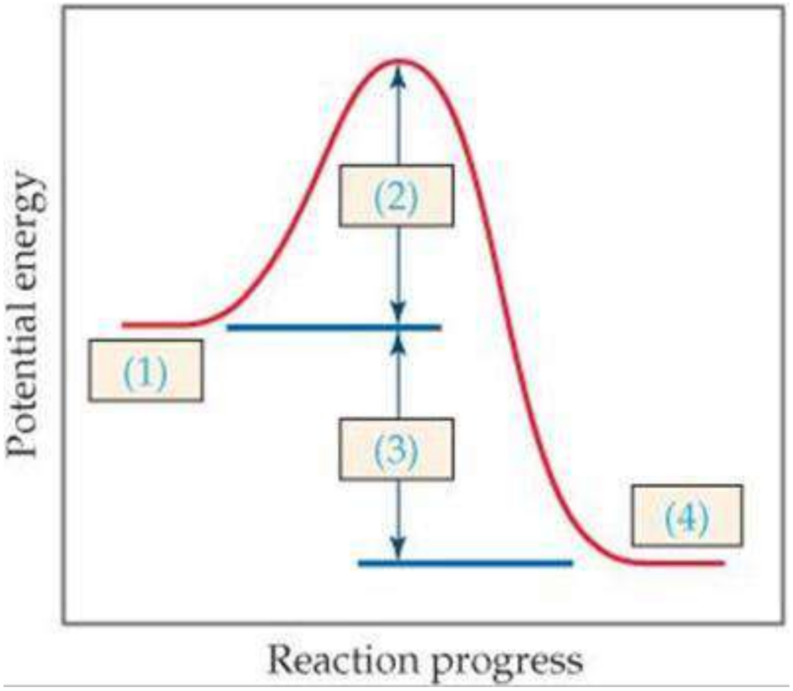
$$\Delta G^{\neq} = 26400 \text{ cal. mol}^{-1}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

$$\Delta S^{\neq} = \Delta H^{\neq} - \Delta G^{\neq} / T = (29800 \text{ cal. mol}^{-1} - 26400 \text{ cal. mol}^{-1})/ 363K = 9.4 \text{ eu. mol}^{-1}$$

$$\ln K^{\neq} = -\frac{\Delta H^{\neq} - T\,\Delta S^{\neq}}{RT} = ?????$$ تحسب من قبل الطالب

Q7: **The following diagram shows the reaction profile of a reaction. Label the components indicated by the boxes.**



Solution

Box(1)= Reactants
Box(2)=E_a
Box(3)=ΔH or ΔE
Box(4)=Products

Q7- **As the temperature of a reaction is increased, the rate of the reaction increases because the ……………………..**

A) Reactant molecules collide less frequently
B) Reactant molecules collide with greater energy per collision
C) Activation energy is lowered
D) Reactant molecules collide less frequently and with greater energy per collision
E) Reactant molecules collide more frequently with less energy per collision

Q8- The **activation energy (Ea) of an un-catalyzed reaction is 95 kJ/mol.** The addition of a catalyst lowers **the activation energy to 55 kJ/mol**. Assuming that the collision factor (A) remains the same, **by what factor will the catalyst increase the rate of the reaction at (a) 25 °C, (b) 125 °C?**

Solution:

a) At T= 25+273=298K

$$\frac{K\ (cat.)}{K\ (un.)} = \frac{Ae^{\frac{-Ea}{RT}}}{Ae^{\frac{-Ea}{RT}}}$$

$$ln\ \frac{K\ (cat.)}{K\ (un.)} = \frac{\frac{-Ea}{RT}}{-\frac{Ea}{RT}} = \frac{55}{95} = 0.58$$

$$\frac{K\ (cat.)}{K\ (un.)} = 1.78$$

b) T= 125+273=?

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Q9- In the Arrhenius equation, **$k = Ae^{-Ea/RT}$** ,…………………. is the frequency factor.

a) k **b) A** **c) e** **d) Ea** **e) R**

Q10- In general, as temperature goes up, reaction rate ………………...

A) Goes up if the reaction is exothermic
B) goes up if the reaction is endothermic
C) Goes up regardless of whether the reaction is exothermic or endothermic
D) Stays the same regardless of whether the reaction is exothermic or endothermic
E) Stays the same if the reaction is first order.

Q11- The activation energy (Ea)for the reaction $CH_3CO \rightarrow CH_3 + CO$ is 71 kJ/mol. How many times greater is the rate constant for this reaction at 170°C than at 150°C?

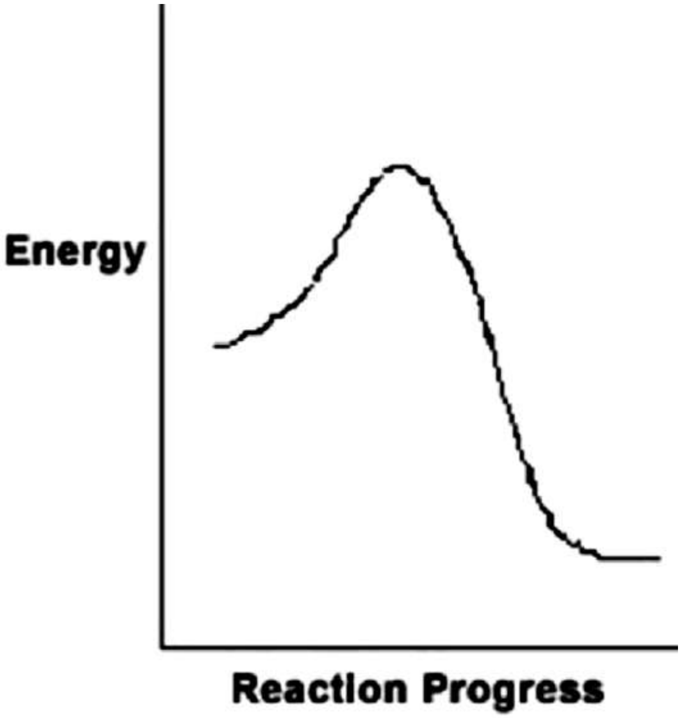
A) 0.40 **B) 1.1** **C) 2.5** **D) 4.0** **E) 5.0**

Solution

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

T1 = 150+273= 423K
T2= 170+273= 443K
ln (k2/k1) = 71x1000J / 8.314[(1/423) - (1/443)]
= 8539.812 (0.00236 - 0.00225)
= 0.9393
k2/k1 = 2.5

Q12- For the chemical reaction system described by the diagram below, which statement is true?



A. The forward reaction is endothermic.

B. The activation energy for the forward reaction is greater than the activation energy for the reverse reaction.

C. At equilibrium, the activation energy for the forward reaction is equal to the activation energy for the reverse reaction.

D. The activation energy for the reverse reaction is greater than the activation energy for the forward reaction.

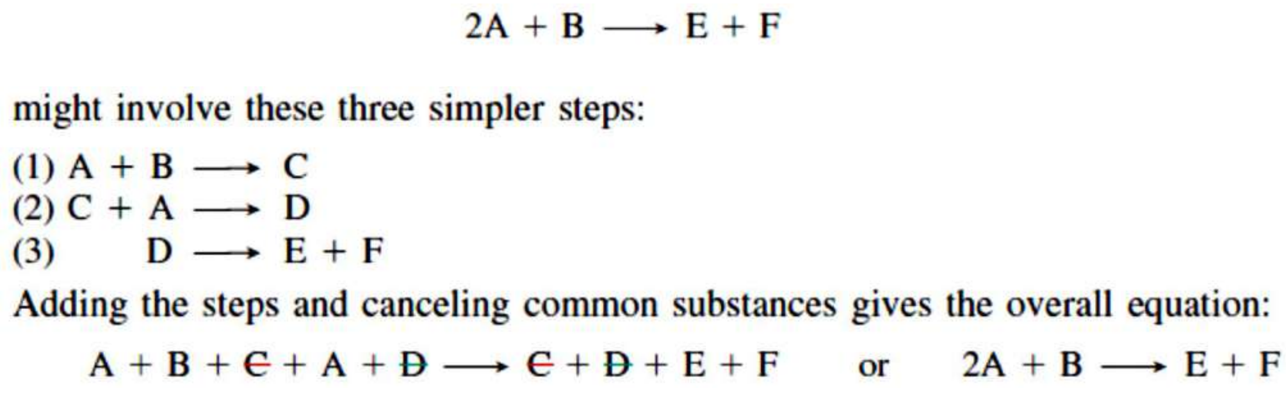
E. The reverse reaction is exothermic

Reaction Mechanisms: the Steps from reactant to product

Most reactions occur through a reaction mechanism, **a sequence of single reaction steps that sum to the overall equation**.

For example:

A possible mechanism for the overall reaction



$$2A + B \longrightarrow E + F$$

might involve these three simpler steps:

(1) $A + B \longrightarrow C$
(2) $C + A \longrightarrow D$
(3) $D \longrightarrow E + F$

Adding the steps and canceling common substances gives the overall equation:

$$A + B + \cancel{C} + A + \cancel{D} \longrightarrow \cancel{C} + \cancel{D} + E + F \quad \text{or} \quad 2A + B \longrightarrow E + F$$

Elementary Reactions and Molecularity:

- **The individual steps that make up a reaction mechanism are called elementary reactions (or elementary steps). Each describes a single molecular event such as: one particle decomposing, two particles combining, and so forth.**

- **An elementary step is characterized by its molecularity, the number of reactant particles in the step.**

  Consider the mechanism for the breakdown of ozone (O_3) in the stratosphere.

  The overall equation is:

$$2O_3(g) \longrightarrow 3O_2(g)$$

A two-step mechanism has been proposed:

(1) $O_3(g) \longrightarrow O_2(g) + O(g)$

(2) $O_3(g) + O(g) \longrightarrow 2O_2(g)$

(1) The first step is *a unimolecular reaction*, one that involves the decomposition or rearrangement of a single particle (O_3).

(2) The second step is *a bimolecular reaction*, one in which two particles (O_3 and O) react.

Because an elementary reaction occurs in one step, its rate law, can be deduced from the reaction stoichiometry, **unlike that for an overall reaction*:***

Reaction order *equals* Molecularity. Therefore, only for **an elementary step, we use the equation coefficients as the reaction orders in the rate law**

Elementary Step	Molecularity	Rate Law
$A \longrightarrow \text{product}$	Unimolecular	$\text{Rate} = k[A]$
$2A \longrightarrow \text{product}$	Bimolecular	$\text{Rate} = k[A]^2$
$A + B \longrightarrow \text{product}$	Bimolecular	$\text{Rate} = k[A][B]$
$2A + B \longrightarrow \text{product}$	Termolecular	$\text{Rate} = k[A]^2[B]$

Problem The following elementary steps are proposed for a reaction mechanism:

(1) $NO_2Cl(g) \longrightarrow NO_2(g) + Cl(g)$

(2) $NO_2Cl(g) + Cl(g) \longrightarrow NO_2(g) + Cl_2(g)$

(a) Write the overall balanced equation.

(b) Determine the molecularity of each step.

(c) Write the rate law for each step.

Solution **(a)** Writing the overall balanced equation:

$$\begin{aligned} NO_2Cl(g) &\longrightarrow NO_2(g) + Cl(g) \\ NO_2Cl(g) + Cl(g) &\longrightarrow NO_2(g) + Cl_2(g) \end{aligned}$$

$$NO_2Cl(g) + NO_2Cl(g) + \cancel{Cl(g)} \longrightarrow NO_2(g) + \cancel{Cl(g)} + NO_2(g) + Cl_2(g)$$

$$2NO_2Cl(g) \longrightarrow 2NO_2(g) + Cl_2(g)$$

(b) Determining the molecularity of each step: The first step has one reactant, NO_2Cl, so it is unimolecular. The second step has two reactants, NO_2Cl and Cl, so it is bimolecular.

(c) Writing rate laws for the elementary steps:

(1) $\text{Rate}_1 = k_1[NO_2Cl]$

(2) $\text{Rate}_2 = k_2[NO_2Cl][Cl]$

The Rate-Determining Step of a Reaction Mechanism

- **All the elementary steps in a mechanism have their own rates.** **One step is usually much slower than the others. This step, called the rate-determining step (or rate-limiting step), limits how fast the overall reaction proceeds.** Therefore, **the rate law of the rate-determining step becomes the rate law for the overall reaction.**

- **The reaction between nitrogen dioxide (NO_2)and carbon monoxide (CO):**

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

If this reaction were an elementary step, … if the mechanism consisted of only one step, the overall rate law :

$$\text{Rate} = k[NO_2][CO] \qquad ?$$

But, as you saw in *the previous solved Problem*

Problem Many gaseous reactions occur in car engines and exhaust systems. One of these is

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \qquad \text{rate} = k[NO_2]^m[CO]^n$$

Use the following data to determine the individual and overall reaction orders:

Experiment	Initial Rate (mol/L·s)	Initial $[NO_2]$ (mol/L)	Initial [CO] (mol/L)
1	0.0050	0.10	0.10
2	0.080	0.40	0.10
3	0.0050	0.10	0.20

Solution

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[NO_2]_2^m[CO]_2^n}{k[NO_2]_1^m[CO]_1^n} = \left(\frac{[NO_2]_2}{[NO_2]_1}\right)^m \quad \text{or} \quad \frac{0.080\ \text{mol/L·s}}{0.0050\ \text{mol/L·s}} = \left(\frac{0.40\ \text{mol/L}}{0.10\ \text{mol/L}}\right)^m$$

This gives $16 = (4.0)^m$, so we have $m = \log 16/\log 4.0 = 2.0$. The reaction is second order in NO_2.

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[NO_2]_3^m[CO]_3^n}{k[NO_2]_1^m[CO]_1^n} = \left(\frac{[CO]_3}{[CO]_1}\right)^n \quad \text{or} \quad \frac{0.0050\ \text{mol/L·s}}{0.0050\ \text{mol/L·s}} = \left(\frac{0.20\ \text{mol/L}}{0.10\ \text{mol/L}}\right)^n$$

We have $1.0 = (2.0)^n$, so $n = 0$. The rate does not change when [CO] varies, so the reaction is zero order in CO.

$$\text{Rate} = k[NO_2]^2[CO]^0 = k[NO_2]^2(1) = k[NO_2]^2$$

The reaction is **second order** overall

Because the experimental data show the rate law is:
Rate = $k[NO_2]^2$……….. Thus, *the overall reaction cannot be elementary*.

A proposed two-step mechanism is

(1) $NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)$ [slow; rate determining]
(2) $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ [fast]

$$\begin{array}{lll}
\text{step 1} & NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO & \text{rate} = k_1[NO_2]^2 \text{ (predicted)} \\
\text{step 2} & \underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2} & \text{rate} = k_2[NO_3][CO] \text{ (predicted)} \\
\text{sum} & NO_2 + CO \xrightarrow{k} NO + CO_2 & \text{rate} = k[NO_2]^2 \text{ (observed)}
\end{array}$$

In this mechanism,

- **NO_3 functions as a reaction intermediate; *a substance formed and used up during the reaction*. Even though it does not appear in the overall balanced equation, a reaction intermediate is essential for the reaction to occur.**

- **Intermediates are less stable than the reactants and products, but unlike much less stable transition states, they have normal bonds and can sometimes be isolated.**

- **Rate laws for the two elementary steps listed above are:**

$$(1)\ \mathrm{Rate}_1 = k_1[NO_2][NO_2] = k_1[NO_2]^2$$

$$(2)\ \mathrm{Rate}_2 = k_2[NO_3][CO]$$

Three key points to notice about this mechanism are:

- **If $k1 = k$, the rate law for the rate-determining step (step 1) becomes identical to the observed rate law.**

- **Because the first step is slow, $[NO_3]$ is low. As soon as any NO_3 forms, it is consumed by the fast second step, so the reaction takes as long as the first step does.**

- **CO does not appear in the rate law (reaction order = 0) because it takes part in the mechanism after the rate-determining step.**

Correlating the Mechanism with the Rate Law

A valid mechanism must meet three criteria:

1. ***The elementary steps must add up to the overall balanced equation.***

2. ***The elementary steps must be reasonable***.

{They should generally involve one reactant particle (unimolecular) or two (bimolecular)}.

3. ***The mechanism must correlate with the rate law, not the other way around.***

Mechanisms with a Slow Initial Step ميكانيكية التفاعل بخطوة أولية بطيئة

- The reaction between NO_2 and CO that we considered earlier has a mechanism with ***a slow initial step***; the first step is **rate-determining.**

- The reaction between nitrogen dioxide (NO_2) and fluorine (F_2) is another example:

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

The experimental rate law is first order in NO_2 and in F_2,

$$\text{Rate} = k[NO_2][F_2]$$

$$2NO_{2(g)} + F_{2(g)} \longrightarrow 2NO_2F_{(g)}$$

And the accepted mechanism is:

$$\text{(1)}\ NO_2(g) + F_2(g) \longrightarrow NO_2F(g) + F(g) \qquad \text{[slow; rate determining]}$$
$$\text{(2)}\ NO_2(g) + F(g) \longrightarrow NO_2F(g) \qquad \text{[fast]}$$

Note that the free fluorine atom (F) is ***a reaction intermediate.***

Let's see how this mechanism *meets the three criteria:*

1. **The elementary reactions sum to the balanced equation:**

$$NO_2(g) + NO_2(g) + F_2(g) + \cancel{F(g)} \longrightarrow NO_2F(g) + NO_2F(g) + \cancel{F(g)}$$
$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

2. **Both steps are bimolecular and, thus, reasonable.**

3. **To determine whether the mechanism is consistent with the observed rate law Rate = k$[NO_2][F_2]$, we first write the rate laws for the elementary steps:**

$$\text{(1) Rate}_1 = k_1[NO_2][F_2]$$
$$\text{(2) Rate}_2 = k_2[NO_2][F]$$

- **Step 1 is the rate-determining step, and with k1 = k, it is the same as the overall rate law Rate = k$[NO_2][F_2]$,** ***so the third criterion is met.***

- **Note that the second molecule of NO_2 is involved after the rate-determining step,** ***so it does not appear in the overall rate law.***

Mechanisms with a Fast Initial Step ميكانيكية التفاعل بخطوة أولية سريعة

If the rate-limiting step in a mechanism is not the initial step, the product of the fast initial step builds up and starts reverting to reactant.

With time, **this fast, reversible step reaches equilibrium, as product changes to reactant as fast as it forms.**

As you'll see, this situation allows us to fit the mechanism to the overall rate law.

- **The oxidation of nitrogen monoxide:**

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

The observed rate law is

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

and a proposed mechanism is

$$\begin{array}{lll} (1) \quad NO(g) + O_2(g) \rightleftharpoons NO_3(g) & & \text{[fast, reversible]} \\ (2)\ NO_3(g) + NO(g) \longrightarrow 2NO_2(g) & & \text{[slow; rate determining]} \end{array}$$

$$NO(g) + O_2(g) + \cancel{NO_3(g)} + NO(g) \longrightarrow \cancel{NO_3(g)} + 2NO_2(g)$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Let's go through the three criteria to see if this mechanism is valid:

- **With cancellation of the reaction intermediate, NO_3, the sum of the steps gives the overall equation, so the first criterion is met.**
- **Both steps are bimolecular, so the second criterion is met.**
- **The mechanism is consistent with the observed rate law— the third criterion is met, rate laws for the elementary steps:**

$$(1) \quad \text{Rate}_{1(\text{fwd})} = k_1[NO][O_2]$$

$$\text{Rate}_{1(\text{rev})} = k_{-1}[NO_3]$$

where k_{-1} is the rate constant and NO_3 is the reactant for the reverse reaction.

$$(2)\ \text{Rate}_2 = k_2[NO_3][NO]$$

But the observed rate law is: **Rate = $k[NO]^2[O_2]$**

$\text{Rate}_{1(\text{fwd})} = \text{Rate}_{1(\text{rev})}$ *or* **k_1 [NO] [O_2] = k-1 [NO_3]**

To express [NO_3] in terms of reactants, we isolate it algebraically:

$$[\mathrm{NO_3}] = \frac{k_1}{k_{-1}}[\mathrm{NO}][\mathrm{O_2}]$$

Then, substituting for [NO_3] in the rate law for the slow step(step 2), we obtain:

$$\mathrm{Rate}_2 = k_2[\mathrm{NO_3}][\mathrm{NO}] = k_2\underbrace{\left(\frac{k_1}{k_{-1}}[\mathrm{NO}][\mathrm{O_2}]\right)}_{[\mathrm{NO_3}]}[\mathrm{NO}] = \frac{k_2k_1}{k_{-1}}[\mathrm{NO}]^2[\mathrm{O_2}]$$

With $k = \frac{k_2k_1}{k_{-1}}$, this rate law is identical to the overall rate law..

Rate = k[NO]^2[O_2]

The Primary Salt Effect in Ionic Reactions

The rate constant of reactions in solution involving either nonelectrolytes or nonelectrolytes and ions are essentially unaffected by the presence of electrolytes.
On the other hand , the velocity constant of reactions between ions are sensitive to variation of the ionic strength of the solution and change with the latter in a manner dependent on the charges of the reacting ions.

To explain the existance of this primary salt effect .

- **Bjerrum postulated that "*reacting ions go to form an activated complex in equilibrium with the reactants and that the rate of reaction is proportional to the concentration of the complex*"**

Any ionic reaction between A^{ZA} and B^{ZB} can be represent by the scheme:

$$\underset{\textit{Reactants}}{A^{ZA} + B^{ZB}} \rightleftharpoons \underset{\textit{activated comples}}{[\,(A.B)^{(ZA+ZB)}]^{*}} \xrightarrow{k'} \text{products}$$

Z_A & Z_B = the charges of the two ions
(Z_A+Z_B) = the charge on the activated complex

- **By applying the Debye - Huckel theory of activity coefficient ,**

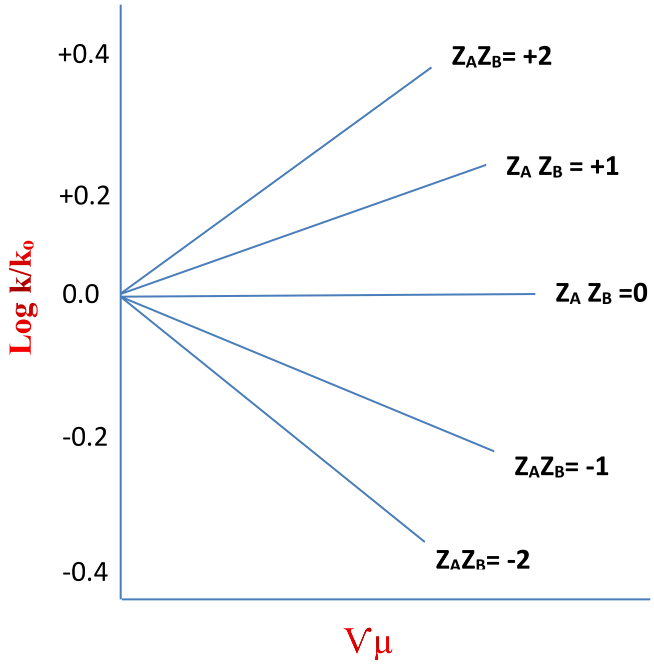
for dilute solutions (k) should vary with the ionic strength (μ), according to the equation:

.

$$\log \frac{k}{k_o} = 2AZ_A Z_B \sqrt{\mu}.$$

A = *Debye- Huckel constant*
$V\mu$ = *the ionic strength,* $\mu = 1/2\sum C_i Z_i^2$
μ = is defined as half the sum of the terms obtainted by multiplying the concentration of each ionic species present in the solution by the square of its valency.

according to the previous equation, a plot of (log k/k_o) against √μ should be linear with a slop equal to (2A Z_AZ_B) , dependent only on the product Z_AZ_B of the charges of the reacting ions.



Primary Salt Effect in Ionic Reactions

The various reactions involving ions may be divided into the following 3 categories:

1- **(Z_AZ_B=0). The reaction between a non-electrolyte and an ion :**

$CH_2ICOOH + CNS^- \longrightarrow CH_2(CNS)COOH + I^-$

(Z_A= 0) (Z_B= -1)

($Z_A.Z_B$)= (0 x -1) =0 , so (Z_AZ_B=0), ***k will not change with μ***

2- **(Z_AZ_B= +). For the reaction :**

$CH_2BrCOO^- + S_2O_3^{-2} \longrightarrow CH_2(S_2O_3)COO^- + Br^-$

(Z_A= -1) (Z_B= -2)

($Z_A.Z_B$)= (-1 x -2) = +2 , so (Z_AZ_B=+2), ***k increases with μ***

3- **(Z_AZ_B= -). For the reaction :**

$[CO(NH_3)_5Br]^{+2} + OH^- \longrightarrow [CO(NH_3)_5OH]^{+2} + Br^-$

(Z_A= +2) (Z_B= -1)

($Z_A.Z_B$)= (+2 x -1) = -2 , so (Z_AZ_B= -2), ***k decreases with μ***

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