

Units of Rate Constant k

What are the units of k?

Assuming time is measured in seconds, the rate of a reaction is always expressed in terms of M/s.

Zero Order

If the reaction is zero order, the rate law is, Rate = k

The units of k must be the same as that of rate, M/s.

First Order

In a first order reaction, the rate law is, Rate = k[A]

In terms of units, this is $M/s = k * M$. The units of k must be 1/s, or s^{-1} .

Second Order

In a second order reaction, the rate law is,

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

In terms of units, this is $M/s = k * M^2$

The units of k must be 1/Ms, or $M^{-1}s^{-1}$.

Question:

For the decomposition of hydrogen peroxide in dilute sodium hydroxide at 20 °C



The average rate of disappearance of H_2O_2 over the time period from $t = 0$ to $t = 516$ min is found to be 8.08×10^{-5} M/min. What is the rate of appearance of O_2 over the same time period?

Answer:

The reaction equation shows that for every two moles of H_2O_2 that react, one mole of O_2 is formed. Therefore the rate of formation of O_2 is half the rate of H_2O_2 consumption.

$$\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \times \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{1}{2} \times \frac{8.08 \times 10^{-5} \text{ M}}{\text{min}} = 4.04 \times 10^{-5} \text{ M / min}$$

Chapter_14_Kinetics_2_7_BV

Problems:

1-The isomerization of methyl isonitrile to acetonitrile in the gas phase at 250 °C $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$

is first order with a rate constant of $3.00 \times 10^{-3} \text{ s}^{-1}$. If the initial concentration of CH_3NC is 0.107M, how much time must pass for the concentration of CH_3NC to drop to 0.0142 M?

2- Consider the table of initial rate for the reaction between hemoglobin (Hb) and carbon monoxide.

Experiment	[HB] ₀ , μmol/L	[CO] ₀ , μmol/L	Initial Rate, μmol/(L · s)
1	2.21	1.00	0.619
2	4.42	1.00	1.24
3	3.36	2.40	2.26

- Order with respect to HB:
- Order with respect to CO:
- Rate law for this reaction:
- Value and units for the rate constant:

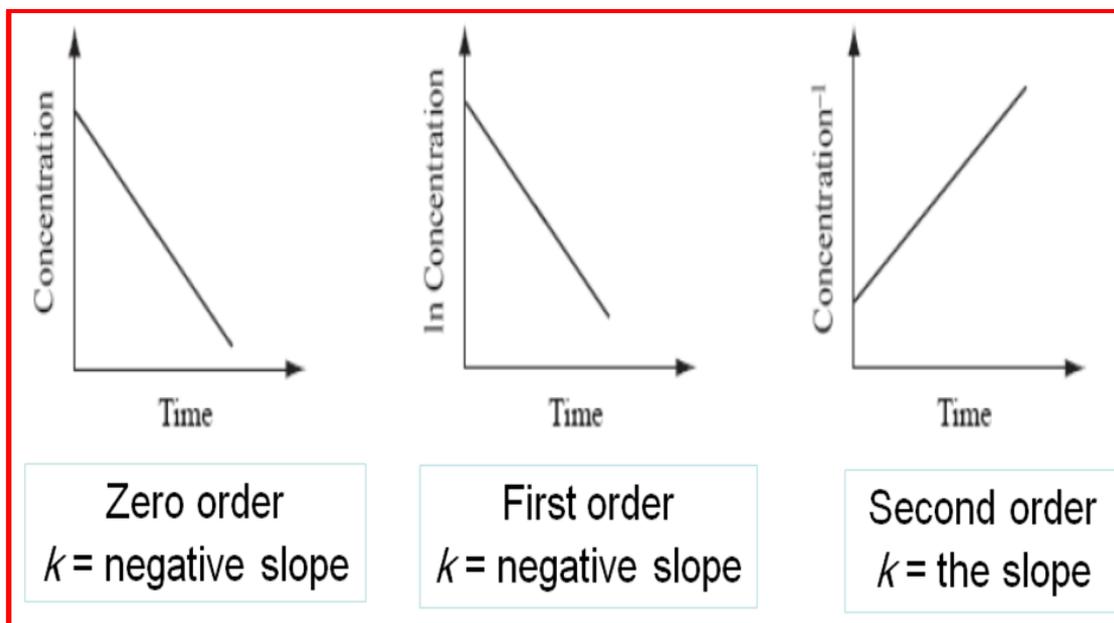
Find the half time of reaction [$t_{1/2}$]

This terms refer to the time which required to consume the half amount of reactant. Thus to find that we can suppose the value of $x=1/2a$ and t replace by $t_{1/2}$:

<u>The order</u>	<u>rate law</u>	<u>half time</u>
n = 0	$x = k_0 t$	$t_{1/2} = a/2k_0$
n = 1	$\ln (a/a-x) = k_1 t$	$t_{1/2} = 0.693/k$
n = 2	$1/ (a-x) = k_2 t + 1/a$	$t_{1/2} = 1/a k_2$

Mathematical treatment of rate law

You can derive the integrated rate law equations using $[y = mx + b]$



ينبغي الانتباه الى العلاقة بين سرعة التفاعل او ثابت سرعة التفاعل والتركيز من حيث العلاقة الرياضية فيما لو كانت مباشرة او بدلالة اللوغارتم او معكوس التركيز ومدلولاتها على قيمة ثابت السرعة مع الزمن.

المعادلات التكاملية بدلالة الضغوط الجزئية

تفاعلات الغازات تقتضي استخدام القانون العام للغازات $PV = nRT$ وهنا يمكن ان نستبدل التراكيز للمواد المتفاعلة بالضغوط الجزئية وبالاعتماد على قانون دالتون للضغوط الجزئية) والذي ينص على ان الضغط الكلي لمزيج من الغازات يساوي مجموعة الضغوط الجزئية)

$$P_t = \sum P_i$$

وفي نفس الوقت

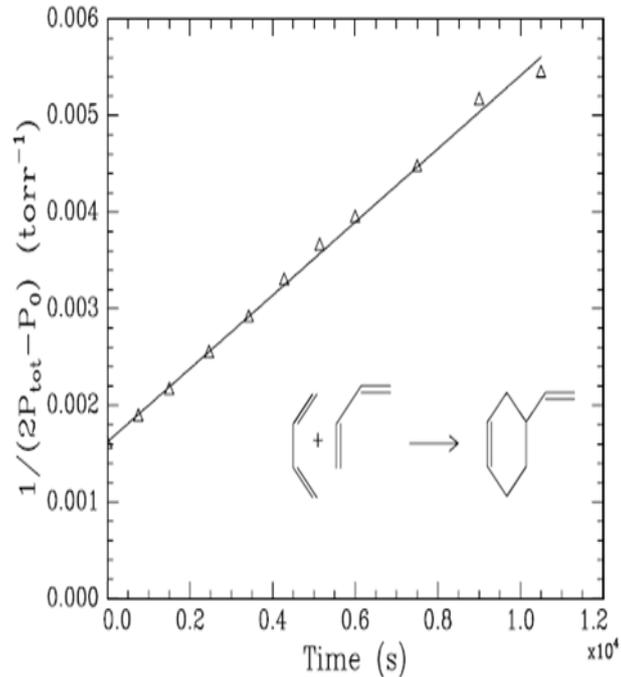
$$P_0 = a \text{ and } P = x \text{ thus } a - x = P_0 - P$$

ملاحظة : المثال المحلول الاتي يتضمن تفاعل غازي يتم متابعة سير التفاعل من خلال التغير في ضغط الضغط الكلي للغازات الناتجة من التفاعل فيصبح المزيج عبارة عن ضغط المادة المتفاعلة وضغط المواد الناتجة . لذلك سنلاحظ معاملات رياضية بسيطة لايجاد الضغط بعد فترات زمنية مختلفة.

Specific problem:

Butadiene, C_4H_6 , dimerizes in a Diels-Alder condensation to yield a substituted cyclohexene, C_8H_{12} . Given the data on the 400 K gas phase reaction below, show that the dimerization occurs as a second order process and find the rate constant.

Time (s)	Tot. Press. (torr)
0	626
750	579
1500	545
2460	510
3425	485
4280	465
5140	450
6000	440
7500	425
9000	410
10500	405



The complication here is that we are given the *total* pressure rather than the *reactant* pressure as a function of time.

The reactant pressure is related to the total pressure through the stoichiometry of the reaction $2 \text{C}_4\text{H}_6 \rightarrow \text{C}_8\text{H}_{12}$.

Let $2x$ be the pressure of C_4H_6 that has reacted;
then $P(\text{C}_8\text{H}_{12}) = x$, and $P(\text{C}_4\text{H}_6) = P_0 - 2x$, where P_0 is the initial pressure. The total pressure is thus
 $P_{\text{tot}} = P(\text{C}_4\text{H}_6) + P(\text{C}_8\text{H}_{12}) = P_0 - x$, or $x = P_0 - P_{\text{tot}}$.

Consequently, $P(\text{C}_4\text{H}_6) = P_0 - 2(P_0 - P_{\text{tot}}) = 2P_{\text{tot}} - P_0$.

A plot of $1/(2P_{\text{tot}} - P_0)$ vs. time a least squares fit gives the slope of the line as $k = 3.8 \times 10^{-7} \text{ s}^{-1} \text{ torr}^{-1}$.

Recalling that $1 \text{ torr} = (1/760) \text{ atm}$ and assuming ideal gas behavior, we can express k in more conventional units:

$$k = (3.8 \times 10^{-7} \text{ s}^{-1} \text{ torr}^{-1}) \times (760 \text{ torr/1 atm}) \times (82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (400 \text{ K})$$

$$= 9.48 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

$$\text{Thus, } -d[\text{A}]/dt = (9.48 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) [\text{A}]^2.$$

اختبار:

١-جد العلاقة بين الضغط الجزئي والضغط الكلي لتفكك الامونيا؟

٢-لتفاعل تفكك الامونيا اوجد قيمة غاز الهيدروجين والنيتروجين بعد فترات زمنية مختلفة؟

Pseudo - Order Reactions

المرتبة الكاذبة للتفاعل الكيميائي

المقصود بهذا المصطلح امتلاك التفاعل لمرتبة منتحلة او غير حقيقية اخذت مرتبة جديدة بفعل تغيير ظروف التفاعل الكيميائي . على سبيل المثال تفاعل من المرتبة الثانية ياخذ مرتبة اولى عندما يتواجد احد المواد المتفاعلة بتركيز عالي بحيث ان التغير الذي يحصل فيه لا يغير من تركيزة طول فترة التفاعل اي انة من المرتبة صفر لهذا المكون. لهذا يسمى تفاعل من المرتبة الاولى الكاذبة.

It often occurs for second-order reactions that the experimental conditions can be adjusted to make the reaction appear to be first order in one of the reactants and zero order in the other.

Molecularity and Order of Reaction

A chemical reaction that takes place in one with only one step i.e., all that occurs in a single step is called elementary reaction (simple reaction) while a chemical reaction occurring in the sequence of two or more steps is called complicated reaction (complex reaction). The sequence of steps through which a complicated reaction takes place is called reaction – mechanism. Each step in a mechanism is an elementary step reaction.

The molecularity: of an elementary reaction is defined as

The minimum number of molecules, atoms or ions of the reactants(s) required for the reaction to occur and is equal to the sum of the stoichiometric coefficients of the reactants in the chemical equation of the reaction.

In general, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation. or The molecularity of a reaction is the number of reactant molecules taking part in every step of the reaction.

The minimum number of reacting particles that come together or collide in **a rate determining step** to form product or products is called **the molecularity of a reaction**.

For example, decomposition of H_2O_2 takes place in the following two steps:

Step 1:	$H_2O_2 \rightarrow H_2O + [O]$	Slow
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Step 2:	$[O] + [O] \rightarrow O_2$	Fast
Overall Reaction	$H_2O_2 \rightarrow H_2O + 1/2O_2$	

The slowest step is rate-determining. Thus from step 1, reaction appears to be unimolecular.

Note:

- Molecularity is a theoretical concept.
- Molecularity cannot be zero, -ve, fractional, infinite and imaginary.
- Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g.

- $4HBr + O_2 \rightarrow 2H_2O + 2Br_2$
- $2MnI_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

In the first reaction molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions involve two or more steps; each step has its own molecularity not greater than three.

The main differences between molecularity and order of reaction:

Molecularity	Order of Reaction
It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change.	It is the sum of powers of molar concentration of the reacting species in the rate equation of the reaction.
It is always a whole number.	It may be a whole number, zero, fractional,
It is a theoretical concept.	It is experimentally determined.
It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for overall complex reaction.	It is meant for the reaction and not for its individual steps

<http://www.askiitians.com/iit-jee-physical-chemistry/chemical-kinetics/molecularity-of-reaction.aspx>