

CHEMISTRY

103

Subject

Final Exam - Chapter Fourteen + 16

تحذير: محاضراتنا (الملخصات) متوفرة فقط لدى:
(1) أكاديمية القصور بفروعها. (2) جمعية التصوير الطبية (مدرج التمريض).

للإستفسار والتسجيل

إربيد

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0795 33 99 34

للضرورة

مدير الأكاديمية

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ساعات ادوام الرسمي

السيث - الخميس 12:30 ظهراً - 11:00 ليلاً
الجمعة 2:00 ظهراً - 11:00 ليلاً

Q.A.J.U.S.



خاص

للفصل الدراسي الأول
2014 - 2013

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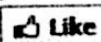
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* جميع التفاعلات تزداد سرعتها مع زيادة درجة الحرارة سواء أكانت ماصة أم طاردة للطاقة

علامة طردية مع سرعة التفاعل

3. Temperature

As temperature increase, increase kinetic energy of molecules, move more rapidly. They collide more frequently and also with higher energy. Rate of reaction increased.

تزيد سرعة التفاعل

عامل مساعد

4. Catalyst

Agents that increase reaction rate without being used up affect the kind of collisions (mechanism). Ex: enzyme natural catalyst for biochemical reaction.

* مواد تضاف للتفاعل فتزيد من سرعة التفاعل دون ان تستهلك في التفاعل ويعمل على زيادة سرعة التفاعل بتقليل طاقة التنشيط

Note: for a collision to lead a reaction, it must occur with energy to stretch bond with a proper length and with suitable orientation for new bonds to form in the proper locations.

تمدد

توصيف مناسب

مجمع

يجب ان يحصل التصادم لا بد ان تمتلك الجزيئات الطاقة

14.1: The Rate of Reaction

هذا ادى مسطاه الحركة يكفي لكير الروابط في المراتب المتعاقبة عند تصادمها ويجب ان يكون اتجاه التصادم مناسباً

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

Reaction rate: the change in the concentration of a reactant or a product with time.

For the general chemical equation:



مراقبة

“We can follow the progress of the reaction by monitoring either the decrease in concentration of the reactant or the increase in concentration of the product”.

For the simple reaction:



We can express the rate of the reaction as:

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

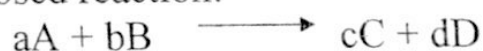
$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

کاهش یافت

“The rate of a reaction may obtain experimentally using spectroscopic methods, electrical methods or by pressure of gases for the reactions involved formation or consumption of gases”.

Reaction Rates and Stoichiometry

In the following proposed reaction:



The rate of reaction can be expressed as one of the following terms, considering the mole coefficient of reactants and products.

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

يصرفه العلاقة بين سرعة التفاعل و ثابت سرعة K و تراكيز
المواد المتفاعلة لتركيزه لتركيزه

14.2: The Rate Law:

Rate law: expresses the relationship of the rate of the reaction to the rate constant and the concentrations of the reactants raised to some powers.

For the general equation:



The rate law of this reaction is expressed as:

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

K: rate constant

“Where m & n specify the relationships between the concentrations of reactants A and B and the reaction rate, they are not equal to the stoichiometric coefficients a & b”.

Reaction order: the sum of the powers to which all reactant concentrations appearing in the rate law are raised.

Ex. If the rate law is:

$$\text{Rate} = k [A]^2 [B] \quad m=2, n=1; \text{ \& } (m+n)=3$$

We say that the reaction is second (2nd) order in A, first (1st) order in B, and third (3rd) order overall.

An exponent 1 means that the rate depends linearly on the concentration of the corresponding reactant. For example, if $m=1$ and [A] is doubled, the rate doubles. If $m=2$ and [A] is doubled, [A]² quadruples and the rate increases by a factor of 4.

Ex.: The reaction of nitric oxide with hydrogen at 1280°C is



Based on the following data for the reaction, determine (a) rate law (b) rate constant.

Experiment	[NO]	[O ₂]	Initial rate (M/s)
1	0.015	0.015	0.048
2	0.030	0.015	0.192
3	0.015	0.030	0.096
4	0.030	0.030	0.384

Ans.:

(a) Rate law \gggg Rate = $k [\text{NO}]^m [\text{O}_2]^n$

First, keep [O₂] constant

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k (0.030)^m}{k (0.015)^m} = (2)^m$$

$$\frac{0.192}{0.048} = (2)^m$$

$$(2)^2 = (2)^m$$

$$\Rightarrow m = 2$$

Secondly, keep [NO] constant

$$\frac{(\text{Rate})_3}{(\text{Rate})_1} = \frac{k (0.030)^n}{k (0.015)^n} = (2)^n$$

$$\frac{0.096}{0.048} = (2)^n$$

$$(2)^1 = (2)^n$$

$$\Rightarrow n = 1$$

$$\ggggg \text{ Rate} = k [\text{NO}]^2 [\text{O}_2]$$

2nd order in NO, 1st order in O₂ & 3rd order in overall

(b) Rate = $k [\text{NO}]^2 [\text{O}_2]$

\ggggg

$$k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{O}_2]} = \frac{0.048 \text{ M/s}}{(0.015 \text{ M})^2 (0.015 \text{ M})} = 1.4 \times 10^4 \text{ (M}^{-2}\text{.s}^{-1}\text{)}$$

14.3: Relation between Reactant concentration and Time

First (1st) Order Reaction: a reaction whose rate depends on the reactant concentration rose to the first order.

In the following 1st order reaction:



The rate is:

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

Using the natural logarithm in both sides gives:

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

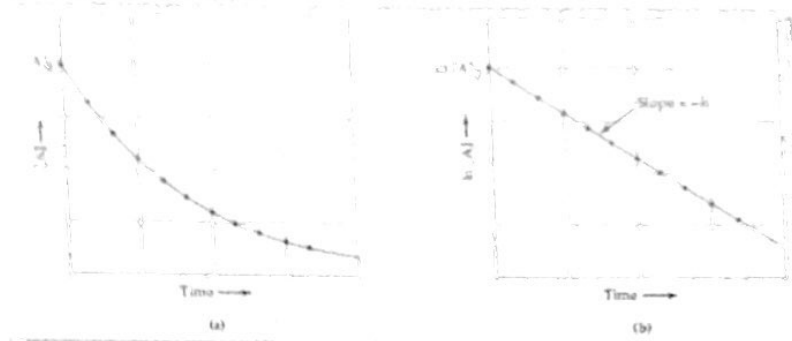
Rearrangement of the above equation gives:

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

$[A]_0$ = concentration of A at time $t = 0$

$[A]_t$ = concentration of A at time $t = t$

Plotting $[A]_t$ versus Time (t):



Ex.: in the following reaction:



This conversion is 1st order reaction with rate constant of $6.7 \times 10^{-4} \text{ s}^{-1}$ at 500°C . If the initial concentration of cyclopropane was 0.25M ,

Calculate:

- The concentration after 8.8 min.
- How long will it take for the concentration of cyclopropane to decrease from 0.25M to 0.15M ?
- How long will it take to convert 70 % of the starting material?

Ans.:

$$\begin{aligned} \text{a) } \ln [A]_t &= \ln [A]_0 - kt \\ \ln [A]_t &= \ln (0.25)\text{M} - (6.7 \times 10^{-4} \text{ s}^{-1})(8.8 \times 60 \text{ s}) \\ \ln [A]_t &= -1.74 \\ &\gg \gg [A]_t = 0.176 \text{ M} \end{aligned}$$

$$\begin{aligned} \text{b) } \ln ([A]_0/[A]_t) &= k \times t \\ \ln (0.25/0.15) &= 6.7 \times 10^{-4} \text{ s}^{-1} \times t \\ 0.511 &= 6.7 \times 10^{-4} \text{ s}^{-1} \times t \\ &\gg \gg t = 762 \text{ s} \end{aligned}$$

c) 70 % of the starting material which means >> 70 % is reacted

$$\gg \gg [A]_0 = 100\% = 1$$

$$[A]_t = 100\% - 70\% = 30\% = 0.30$$

$$\ln ([A]_0/[A]_t) = k \times t$$

$$\ln (1/0.3) = 6.7 \times 10^{-4} \text{ s}^{-1} \times t$$

$$1.204 = 6.7 \times 10^{-4} \text{ s}^{-1} \times t$$

$$\gg \gg \gg t = 1.8 \times 10^3 \text{ s}$$

$$= 1.8 \times 10^3 / 60 = 30 \text{ min}$$

Half-life ($t_{1/2}$):

The time required for the concentration of a reactant to decrease to half of its initial concentration " $[A]_t = [A]_0/2$ "

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

Finally;

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

The usefulness of ($t_{1/2}$) is that it gives an estimate of the magnitude of the rate constant (k).
الغالبية العظمى
تقدير
مقدار

Second (2nd)-Order Reactions

The first case: $\text{rate} = k [A]^2$ (predict the unit of k)

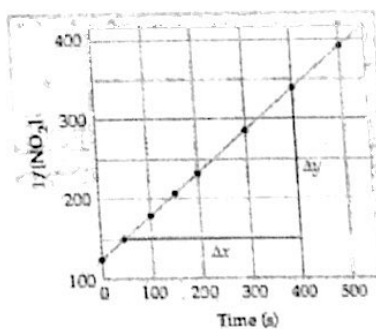
The second case $A + B \longrightarrow \text{product}$

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

We will consider only the first case.

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

>>> Plotting $1/[A]_t$ will give +ve slop = k, & intercept = $1/[A]_0$

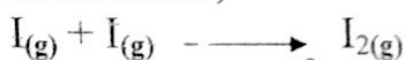


Half-life ($t_{1/2}$):

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

NOTE: the half-life of the second order rate law depends on the initial concentration of a reactant.

Ex.: for the following 2nd order reaction,



This reaction has a high rate constant $7.0 \times 10^9 / \text{M}\cdot\text{s}$ at 23°C . Calculate:

- The concentration of I after 2 min. if the initial concentration was 0.086 M.
- Calculate the $t_{1/2}$ of the reaction if the initial concentration of I is 0.6 M.

Ans.:

a) $1.2 \times 10^{-12} \text{ M}$

b) $2.4 \times 10^{-10} \text{ s}$

Rate Law	Overall Reaction Order	Units for k
Rate = k	Zeroth order	M/s or M s^{-1}
Rate = $k[A]$	First order	$1/\text{s}$ or s^{-1}
Rate = $k[A][B]$	Second order	$1/(\text{M}\cdot\text{s})$ or $\text{M}^{-1} \text{s}^{-1}$

14.4: Activation Energy (E_a) and Temperature Dependence of Rate Constants

النسب بين الكيمياء تنبع من التصادم بين الجزيئات

The Collision Theory of Chemical Kinetics

- Chemical reactions occur as a result of collisions between molecules.
- Not all collisions lead to reactions, some are effective & others are not effective.
- In order to react, the colliding molecules must have a total kinetic energy equal to or greater than the **activation energy (E_a)**

Activation energy (E_a): the minimum amount of energy required to initiate a chemical reaction.

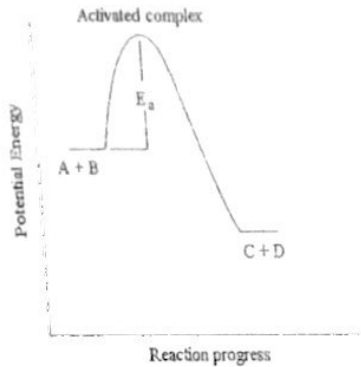
Activated complex: temporary species formed by the reactant molecules as a result of the collision before they form the product

- If the products are more stable than the reactants, then the reaction will be accompanied by a release of heat, the reaction is

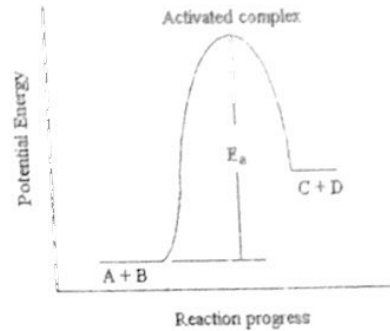
“exothermic”

- If the products are less stable than the reactants, then heat will be absorbed by the reacting mixture from the surrounding and we have an “endothermic” reaction

Exothermic Reaction



Endothermic Reaction



The Arrhenius Equation

- Arrhenius equation expresses the relation between the rate constant and temperature.

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

- E_a = activation energy (KJ/mol), R = gas constant (8.314 J/K . mol)
- T = absolute temperature, A = frequency factor (collision frequency)

From the relation above:

- Rate constant is directly proportional to A (collision frequency)
- Rate constant decrease with increasing activation energy and vice versa (*activation energy term with minus sign in the equation!!*)
- Rate constant increase with increasing temperature.

Taking the normal logarithm in both sides:

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

- a plot of $\ln k$ versus $1/T$ gives a straight line whose slope is equal to $-E_a/R$ and whose intercept is $\ln A$.
- we can calculate activation energy at different temperatures T_1 and T_2 , or to calculate rate constant if the value of activation energy is given.

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

Ex.: Rate constants for the gas-phase decomposition of hydrogen iodide, $2\text{HI}_{(g)} + \text{I}_{(g)} \longrightarrow \text{H}_{2(g)} + \text{I}_{2(g)}$, are listed in the following table:

t (°C)	T (K)	k ($\text{M}^{-1}\text{s}^{-1}$)
283	556	3.52×10^{-7}
356	629	3.02×10^{-5}
393	666	2.19×10^{-4}
427	700	1.16×10^{-3}
503	781	3.95×10^{-2}

- Find the activation energy (in kJ/mol) using all five data points.
- Calculate E_a from the rate constants at 283°C and 508°C
- Given the rate constant at 283°C and the value of E_a obtained in part b what is the rate constant at 293°C ?

a) The activation energy E_a can be determined from the slope of a linear plot of $\ln k$ versus $1/T$.

$$\gg \gg E_a = 1.87 \times 10^5 \text{ J/mol} = 190 \text{ KJ/mol}$$

b) $K_1 = 3.52 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$, $T_1 = 556 \text{ K}$
 $K_2 = 3.95 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, $T_2 = 781 \text{ K}$

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

gives

$$\ln \left(\frac{3.95 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}}{3.52 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}} \right) = \left(\frac{-E_a}{8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}} \right) \left(\frac{1}{781 \text{ K}} - \frac{1}{556 \text{ K}} \right)$$

$$11.628 = \left(\frac{-E_a}{8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}} \right) \left(\frac{-5.18 \times 10^{-4}}{\text{K}} \right)$$

$$E_a = 1.87 \times 10^5 \text{ J/mol} = 187 \text{ kJ/mol}$$

c) $K_1 = 3.52 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$, $T_1 = 556 \text{ K}$
 $K_2 = \text{????} \text{ M}^{-1} \text{ s}^{-1}$, $T_2 = 781 \text{ K}$
 $E_a = 1.87 \times 10^5 \text{ J/mol}$

$$\ln \left(\frac{k_2}{3.52 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}} \right) = \left(\frac{-1.87 \times 10^5 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}} \right) \left(\frac{1}{781 \text{ K}} - \frac{1}{556 \text{ K}} \right) = 0.715$$

Taking the antilog of both sides gives

$$\frac{k_2}{3.52 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}} = e^{0.715} = 2.04$$

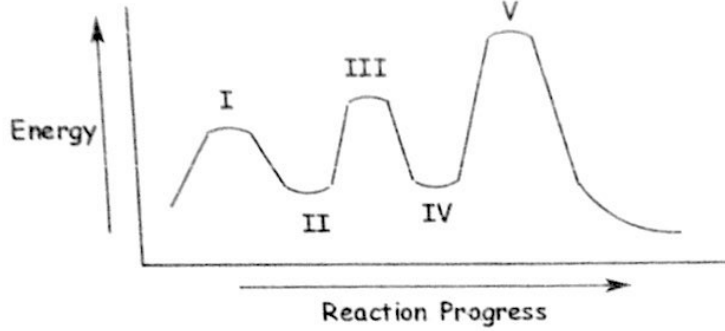
$$k_2 = 7.13 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$$

In this temperature range, a rise in temperature of 10 K doubles the rate constant.

Rate determining step (rds) is the slowest step in reaction

E_a increase >>>> slow step >>> rds

More Energy >>>> less stable



I, III, V: Activated Complexes (Transition State)

II, IV: Intermediates

IV-V: rate determining step (rds) >>> slowest step

اختصاصنا

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