Chemical Kinetics الكيمياء الحركية

المصادر الانكليزية المعتمدة لدراسة المادة:

1-P.W.Atkinus " physical chemistery" oxford landon 1980, 1990, 1998, 2004, 2014.

2-P.W.Atkinus " solution man ual for physical chemistery" oxford landon 2014.

3-F.Danial and R.A. Al berty "physical chemistery"Wily New Yourk (1967, 1990, 2001, 2012)

المصادر العربية:

١ـ الكيمياء الحركية لطلبة كلية التربية تاليف الدكتور عمار هاني الدجيلي والدكتور نوري يوسف خليفة ١٩٨٨ .

٢ـ الكيمياء الفيزيائية تاليف الدكتور صفاء العمري ونوري يوسف خليفة ١٩٨٩ .

Chemical kinetics: the study of *reaction rate*, in addition to the conditions affecting speed and the mechanism of the reaction

We study in chemical reactions:

Reaction rate: changes in a concentration of a product or a reactant per unit time. Mathematically

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

[ ] → concentration

Δ → change

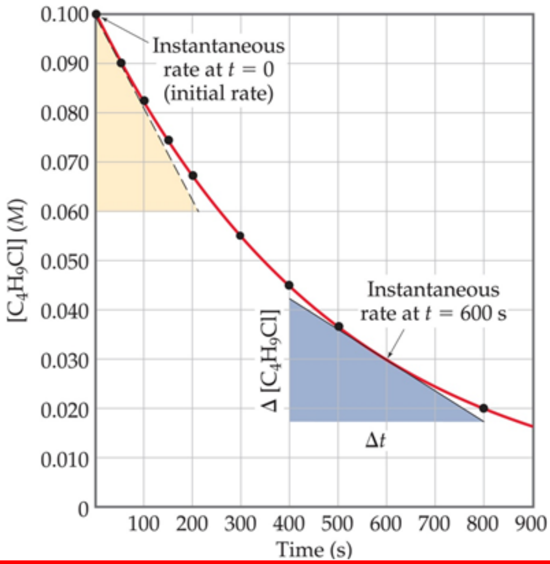
We use the experiments data for the forming of Butanol from butane chloride when studies the change of concentration for butane chloride with the time.

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

The **average rate** of the reaction is the change in concentration divided by the change in time:

$$average\ rate = \frac{\Delta [C_4H_9]}{\Delta t} = \frac{0.1000 - 0.0905\ M}{50.0 - 0.0\ s}$$

Time, t(s)	$[C_4H_9Cl]$ (M)
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0



Average Rate (M/s)
1.9×10^{-4}
1.7×10^{-4}
1.6×10^{-4}
1.4×10^{-4}
1.22×10^{-4}
1.01×10^{-4}
0.80×10^{-4}
0.560×10^{-4}

-Note that the average rate decreases as the reaction proceeds.

-This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

يمكن ملاحظة ان سرعة استهلاك المتفاعل تساوي سرعة تكون الناتج:

$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Example: find the ratios between the rate of reactant and product for the reaction:

$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$$

Answer:

$$rate = -\frac{\Delta [H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta [HI]}{\Delta t}$$

The reaction

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3$$

proceeded in a closed autoclave of the volume $V = 5\,\mathrm{dm}^3$. In the course of 1 s, 0.01 moles of nitrogen reacted.

a) Estimate the rates of consumption of nitrogen and hydrogen, the rate of formation of ammonia, and the rate of the reaction.

b) Find out how these rates will change if we write the reaction in the form

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3\,.$$

Solution

a) **The change in the concentration of nitrogen is**

$\Delta c_{N2} = \Delta n_{N2}/V = -0.01/5 = -0.002$ mol dm^{-3}.

The rate of consumption of nitrogen is

$$r_{N_2} = -\frac{\mathrm{d}\,c_{N_2}}{\mathrm{d}\,\tau} \doteq -\frac{\Delta c_{N_2}}{\Delta \tau} = -\frac{-0.002}{1} = 0.002\ \mathrm{mol\,dm^{-3}\,s^{-1}}$$

According to

$$r = -\frac{1}{a}\frac{\mathrm{d}\,c_A}{\mathrm{d}\,\tau} = -\frac{1}{b}\frac{\mathrm{d}\,c_B}{\mathrm{d}\,\tau} = \cdots \frac{1}{s}\frac{\mathrm{d}\,c_S}{\mathrm{d}\,\tau} = \frac{1}{t}\frac{\mathrm{d}\,c_T}{\mathrm{d}\,\tau}$$

$r_{N2} = r = 0.002$ mol dm^{-3} s^{-1}

$r_{H2} = 3\,r = 0.006$ mol dm^{-3} s^{-1}

$r_{NH3} = 2\,r = 0.004$ mol dm^{-3} s^{-1}

b) For the same reaction written in the form

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$$

The rate of reaction will be double, the rates r_{N2} , r_{H2} , r_{NH3} will not change

Kinetic equation

A differential equation representing the relation between the concentrations of substances and time.

$$r_A = -\frac{d\,c_A}{d\,\tau} = f(c_A, c_B, \ldots, c_S, c_T, \ldots)$$

The rate of formation of the product or the rate of reaction appearing on the left side of the equation. By solving kinetic equations we obtain the time dependence of the reactants concentrations. The “simple” reaction refer to for such a chemical reaction whose kinetic equation has the form:

$$r_A = -\frac{d\,c_A}{d\,\tau} = k_A\, c_A^{\alpha} c_B^{\beta} \ldots$$

where A, B,. . . are the reactants. The exponent **α** is called the order of reaction with respect to component A, **β** is the order of reaction with respect to B, etc.

The sum of the exponents n = α + β + . . . is called the (overall) order of reaction.

The constant ***kA*** in the kinetic equation is called the ***rate constant***. It is the function of temperature. The dimension of the rate constant depends on the reaction order. ***Main unit: s^{-1} $(molm^{-3})^{1-n}$***, where n is the order of reaction.

من المتقدم سلفا نجد اننا نبحث في الكيمياء الحركية على العلاقة الرياضية التي تفسر او تضع علاقة بين التركيز للمتفاعل او الناتج مع الزمن بما يعطي تفسيرا كاملا للتفاعل من الناحية الكمية والنوعية من خلال تحديد الميكانيكية المحتملة لحصول التفاعل.

قبل ان نبداء بتصنيف التفاعلات الكيميائية حسب مدلولاتها الرياضية او ما يسمى مرتبتها المؤثرة على سير التفاعل نلحق مجموعة من الاسئلة الاثرائية التي تزيد من فهم العلاقات المذكورة سابقا:

Example" Estimate the **orders** and *rate constant k* from the results observed for the reaction? What is the rate when $[H_2O_2] = [I^-] = [H^+] = 1.0$ M if you have the results for many runs of reaction?"

$$H_2O_2 \quad + \quad 3\,I^- + \quad 2\,H^+ \rightarrow \quad I_3^- + \quad 2\,H_2O$$

Run	H_2O_2	I^-	H^+	Rate M S^{-1}
1	0.010	0.010	0.0050	1.15e-6
2	0.020	0.010	0.0050	2.30e-6
3	0.010	0.020	0.0050	2.30e-6
4	0.010	0.010	0.0100	1.15e-6

Answer:

FROM run 1 and 2 we can divided it to find one of them

$$\frac{1.15e\text{-}6}{2.30e\text{-}6} = \frac{k\,(0.010)^x(0.010)^y(0.0050)^z}{k\,(0.020)^x(0.010)^y(0.0050)^z} \quad \begin{matrix}\leftarrow \text{exprmt 1} \\ \text{----} \\ \leftarrow \text{exprmt 2}\end{matrix} \quad \frac{1}{2}$$

Then X = 1

Question:

Bromide ions and bromate ions react in acid solution to give bromine according to the equation:

$6H^+ + 5Br^- + BrO^{3-} \rightarrow 3Br_2 + 3H_2O$

Rate measurements on four different reaction mixtures gave the following data.

Mixture	$[H^+]$ (mol l^{-1})	$[Br^-]$ (mol l^{-1})	$[BrO_3^-]$ (mol l^{-1})	Relative rate
1	0.45	0.375	0.075	1
2	0.45	0.75	0.075	2
3	0.9	0.375	0.075	4
4	0.45	0.375	0.15	4

(a) What is the rate expression for the reaction?

(b) What is the order of the reaction with respect to each of the reactants?

(c) What is the overall order of the reaction?

(d) Explain why the rate equation and the overall equation are different.

1) Chemical kinetics is the branch of chemistry which deals with the study of:
a) Speed or rate of chemical reaction.
b) The factors affecting the rates of the reaction.
c) The mechanism by which the reactions proceed.
d) All of these. ((ANSWER : All of these))
2) The unit of the rate of reaction is:
a) mol L^{-1} min $^{-1}$
b) mol $^{-1}$ L min^{-1}
c) Both a and b
d) none of these.

((**ANSWER : mol L^{-1} min $^{-1}$**))
3) The rate of reaction depends upon the molar concentration of reactants which:
a) Keep on increasing with passage of time.
b) Keep on decreasing with passage of time.
c) Remains same with passage of time.
d) Does not depend upon the time.
((**ANSWER : Keep on decreasing with passage of time.**

4) The factors on which the rate of reaction depends is:
a) Temperature.
b) Presence of catalyst.
c) Presence of light.
d) All of these. ((**ANSWER : All of these.**

Given the following data for this reaction:

$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

EXPT	$[NH_4^+]$	$[NO_2^-]$	RATE
1	**0.010 M**	**0.020 M**	**0.020 M/s**
2	**0.015 M**	**0.020 M**	**0.030 M/s**
3	**0.010 M**	**0.010 M**	**0.005 M/s**

Find the rate law for the reaction.
For simple reaction:

A + B → products

The rate of the forward reaction at any time can be related to the concentration of A

And B at different time which can be expressed as follows:

rate α [A][B]
when substituted the Proportion mark α we obtain the equation:
rate = k[A][B]
where k is the rate constant.
In more general terms, for a simple reaction:

nA + mB → products

rate = $k[A]^n[B]^m$
This equation is *the rate law.* The quantities n and m are termed the orders with respect to the reactants A and B respectively. The overall order of reaction is given as the sum of the powers of the concentration terms that occur in the rate equation, i.e. in the above example the overall order is $n + m$.

من هذا يمكن ان نصنف التفاعلات حسب المرتبة الى التصنيفات الاتية:

Rate law	Order of reaction
rate $\alpha[A]^0$	0
rate $\alpha\ [A]^1$	1
rate $\alpha\ [A]^2$	2
rate $\alpha[A]^1[B]^1$	2
rate $\alpha\ [A]^1[B]^2$	3

Example
Calculate the rate constant for the reaction between nitrogen monoxide and oxygen:

$$2NO + O_2 \rightarrow NO_2$$

Experiment	Initial concentrations (mol l^{-1})		Initial rate of NO_2 formed (mol l^{-1} s^{-1})
	[NO]	[O_2]	
1	2.0×10^{-5}	4.0×10^{-5}	1.4×10^{-10}
2	2.0×10^{-5}	8.0×10^{-5}	2.8×10^{-10}
3	4.0×10^{-5}	4.0×10^{-5}	5.6×10^{-10}