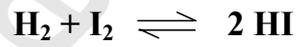
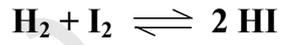
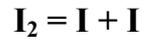


الباب الثالث عشر الحركية الكيميائية

الباب الثالث عشر
الحركية الكيميائية



سرعة التفاعل الكيميائي :

:

" "



A

A

B A

$$\Delta T = T_1 - T_2$$

$$\Delta C = C_1 - C_2$$

:

$$V = - \frac{C_2 - C_1}{\tau_2 - \tau_1} = \frac{\Delta C}{\Delta \tau}$$

V

dτ

dC

$$V = \pm \frac{dC}{d\tau}$$

$$dC/d\tau < 0$$

: Order of chemical reaction مرتبة أو درجة التفاعلات الكيميائية

:

:

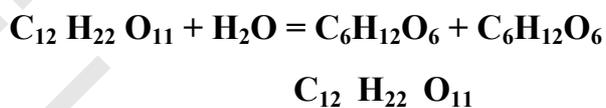
. **Molecularity of reaction**

:

. **Order of chemical reaction**

-1

:

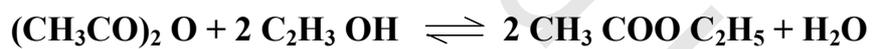


Trimolecular

. **First order reaction**

:

-2



$$\frac{dx}{dt} = KC \times C$$

$$dx / dt = kC_1$$

- 339 -

-3

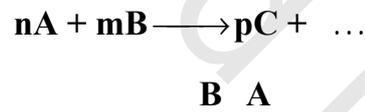
First

Unimolecular

order

-4

- = k [A]
- „ = k [A]² or k [A] [B]
- „ = k [A]³ or k [A]² [B] or k [A] [B] [C]



B A

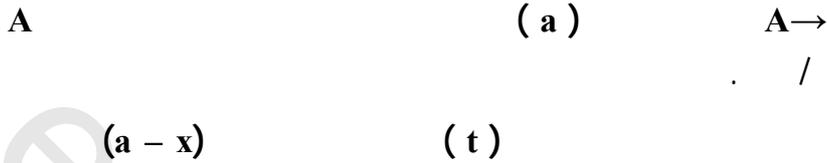
$\frac{dx}{dt}$

$$\frac{dx}{dt} = k [A]^n [B]^m = K. [AB]^{m+n}$$

(n+m)

(n+m)

: First Order Reactions تفاعلات المرتبة الأولى



$$\frac{dx}{dt} = k(a-x); \frac{dx}{dt} = k(a-x) = :$$

$$\frac{dx}{a-x} = k dt ; dt = \frac{dx}{(a-x)}$$

(2.303)

$$\int \frac{dx}{a-x} = k \int dt$$

$$\therefore kt = \int \frac{dx}{(a-x)} = -\log_e (a-x) + \text{«C»}$$

$$\therefore \log_e (a-x) = kt - C$$

$$x = \quad t =$$

$$\dots 0 - \frac{1}{k} \log_e a = C \therefore C = \frac{1}{k} \log_e a$$

$$) x \quad (\quad) t$$

$$t = -\frac{1}{k} \log_e (a-x) + \frac{1}{k} \log_e a = \frac{1}{k} \log_e \frac{a}{a-x}$$

OR $k = \frac{1}{t} \log_e \frac{a}{a-x}$; $kt = \log_e \frac{a}{a-x}$

$$k = \frac{1}{t} \log_{10} \frac{a}{a-x} + \log_{10} e = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

. Unimolecular Reaction

$$x = 0.5 a$$

$$k = \frac{1}{t} \log \frac{a}{0.5a} = \frac{1}{t} \log 2$$

$$t = \frac{1}{k} \log 2$$

. (a)

(t) ∴

m

$$\therefore k = \frac{1}{t} \log \frac{ma}{m(a-x)}$$

$$t = \frac{1}{k} \log \frac{a}{a-x}$$

: Reaction of the Second Order تفاعلات المرتبة الثانية

:



(a)

: (t)

(a - x)

$$\therefore \frac{dx}{dt} = k(a-x)(a-x) = k(a-x)^2$$

$$\therefore \frac{dx}{(a-x)^2} = k dt$$

:

k

$$\frac{dx}{(a-x)^2} = \int dt$$

$$\frac{1}{a-x} = kt + C$$

$$C = \frac{1}{a} \quad : \quad x = 0 ; t = 0$$

$$\therefore \frac{1}{a-x} = kt + \frac{1}{a} \quad \text{or} \quad \frac{1}{a-x} - \frac{1}{a} = kt$$

$$\therefore \frac{a-a+x}{a(a-x)} = kt \quad \text{or} \quad \frac{x}{a(a-x)} = kt$$

$$\text{or} \quad \frac{1}{t} \times \frac{x}{a(a-x)} = k$$

:

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

$x = a - t$

K

:

:

$b - a$

$$\frac{dx}{dt} = k(a-x)(b-x)$$

:

$$k = \frac{1}{t(a-x)} \log_e \frac{b(a-x)}{a(a-x)}$$

:

$$x = 0.5a$$

$$k = \frac{1}{t} \frac{x}{a(a-x)}$$

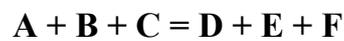
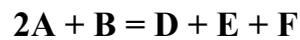
$$k = \frac{1}{t} \times \frac{0.5a}{a \times 0.5a} = \frac{1}{at}$$

$$t = \frac{1}{ka}$$

$$t = \frac{1}{a}$$

: Third Order Reactions تفاعلات المرتبة الثالثة

:



(t)

(a)

.(a - x)

$$\frac{dx}{dt} = k(a - x)^3 :$$

$$\int \frac{dx}{(a - x)^2} = kdt \int k$$

$$\frac{1}{2(a - x)^2} = kt + C \quad (\quad)$$

$$: \quad x = 0 \quad t = 0$$

$$C = \frac{1}{2a^2} \quad \therefore \frac{1}{2(a - x)^2} = kt + \frac{1}{2a^2}$$

$$kt = \frac{1}{2(a - x)^2} - \frac{1}{2a^2}$$

$$k = \frac{1}{2t} \left(\frac{1}{(a - x)^2} - \frac{1}{a^2} \right) = \frac{1}{t} \times \frac{x(2a - x)}{2a^2(a - x)^2}$$

ملاحظات على تفاعلات المرتبة الثالثة :

$$x = 0.5a$$

$$k = \frac{1}{t} \times \frac{x(2a - x)}{2a^2(a - x)^2}$$

$$\therefore kt = \frac{0.5a \cdot 1.5a}{2a^2 \cdot 0.5a \cdot 0.5a} \text{ or } t = \frac{1}{k} \frac{0.5}{a^2} = \frac{1.5}{k} \frac{1}{a^2} \quad \therefore t = \frac{1}{ka^2}$$

تفاعلات المرتبة صفر : Zero order reactions

$$. x = kt + I \quad dx/dt = k :$$

x

k

: Detemination of the order of Reactions تحديد رتبة التفاعل

: Integration Method () (1)

K

:

600	312	157	72	3	الزمن (دقيقة)
0.0228	0.0348	0.0512	0.0656	0.0916	(a - x) بالجرام جزيء

:

k

:

$k = \frac{1}{t} \frac{a}{a(a-x)}$	$a = 0.0916$ $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$	x	a - x	
0.0601	0.00462	0.036	0.0656	72
0.0558	0.00370	0.0404	0.0512	157
0.0551	0.00308	0.0568	0.0348	312
0.0549	0.00231	0.0688	0.0228	500

k

:

(2)

initial concentration

$(n - 1)$

$t_2 \quad t_1$

$n \quad a_2 \quad a_1 \quad :$

$$\therefore t_1 \propto \frac{1}{a_1^{n-1}}, \quad t_2 \propto \frac{1}{a_2^{n-1}}, \quad \therefore t_2/t_1 = \frac{a_1^{n-1}}{a_2^{n-1}} \quad t_2/t_1 = \left(\frac{a_1}{a_2}\right)^{n-1}$$

$:$ n

$:$

340.5

288

102

140

$:$

$:$

$$288 = a_2 \quad 340.5 = a_1$$

- 348 -

$$. 240 = t_2 \quad 102 = t_1 :$$

$$\left(\frac{340.5}{288}\right)^{n-1} = \frac{140}{102} \quad t_2/t_1 = \left(\frac{a_1}{a_2}\right)^{n-1} :$$

$$(n-1) \times \log \frac{340.5}{288} = \log \frac{140}{102}$$

$$(n-1) \times 0.0727 = 0.1375 \quad \therefore n = 2.89$$

(t)

(p)

250	500	750	p-mm.
950	235	105	t-(min)

$$: \quad a_2 = 500 : a_1 = 750$$

$$t_2 = 235 \quad t_1 = 105$$

$$\left(\frac{a_1}{a_2}\right)^{n-1} = t_2/t_1 \quad \text{or} \quad \left(\frac{750}{500}\right)^{n-1} = 235/105$$

$$(n-1) \log 1.5 = \log 235/105$$

$$0.1741 (n-1) = 0.3499 \quad n = 2.9$$

$$t_2 = 950 \quad t_1 = 235$$

$$a_1 = 500 \quad a_2 = 250$$

$$\therefore \left(\frac{500}{250}\right)^{n-1} = 950/235$$

$$(n-1) \log 2 = \log 950 - \log 235$$

$$0.3010 (n-1) = 0.9099$$

: Alternative method

(3)

(a) (t)

$$t \cdot a = t \propto \frac{1}{a}$$

$$t \cdot a^2 = t \propto \frac{1}{a^2}$$

37.5	79	707	الضغط الابتدائي (مم)
83	84	84	زمن نصف التغير (ثانية)

(t)

p (mm)	450	400	350	300	250
t (second)	75.5	85	97	112.5	136

(a) (p)

(t) ()

 $p \times t =$

p	450	400	350	300	250
t	75.5	85	97	112.5	136
= p × t	33975	34000	34950	33750	34000

$$p \times t$$

: Graphical Method (4)

$$(t) \quad (x) \quad \frac{dx}{dt} \quad (\theta)$$

$$dx/dt = \tan \theta$$

$$(a-x) \quad (a-x)^2 \quad (a-x) \quad \text{unimolecular} \quad (a-x)^3$$

: (5)

$$dc_2/dt = kC_2^n \quad dc_1/dt = kC_1^n$$

$$dc_1/dt \cdot dc_2/dt = [C_1/C_2]^n \quad n$$

$$\log \frac{dc_1}{dt} - \log \frac{dc_2}{dt} = n (\log C_1 - \log C_2)$$

$$\text{or } n = \frac{\log(dc_1/dt) - \log(dc_2/dt)}{\log C_1 - \log C_2}$$

Ostwald's Isolation Method : (6)

active mass



A

n

B

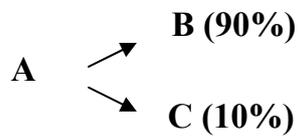
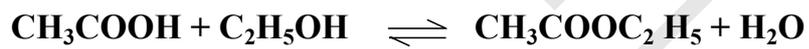
B

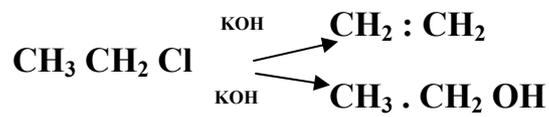
A

(m) A

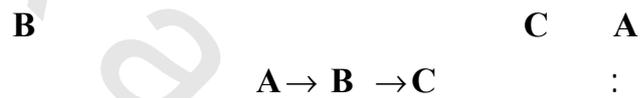
(n + m) :

: Reversible Reactions : التفاعلات العكسية





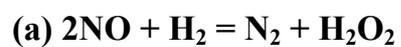
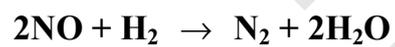
: Successive reactions التفاعلات المتتالية

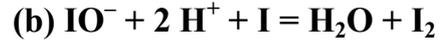
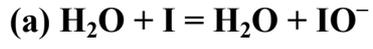
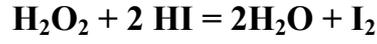


(b)

C A

: -1





تحديد سرعة التفاعل عملياً :



0.5

0.3

0.2

0.1

1

100

(3 : 1)

HCl

$$T_{\infty} - T_2 \quad T_{\infty} - T_1$$

N/2

N/2

:

-2

N/20

(60)

50

1

3

N/20

10

N/20

(x)

a

(a - x)



:

$$K = 2.303/t \log_{10} x/a (a - x)$$

. t x a

k

: Catalysis الحفز

:

:

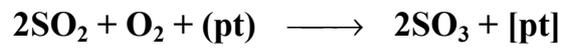
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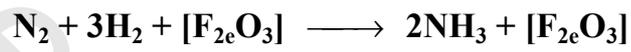
()

:

-1



-2



-3

المميزات العامة للتفاعلات التي تسري في وجود عامل حافز :

:

-1

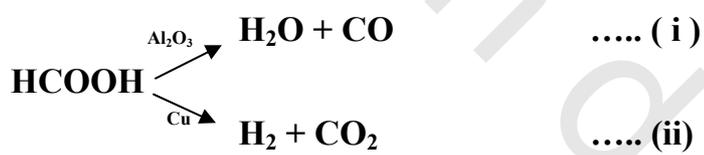
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2.5



-3

-4



: Catalytic poisoning

-7

: Activation of Catalyat

-8

**Promotor or Activator
Activation**

: Autocatalysis

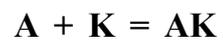
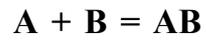
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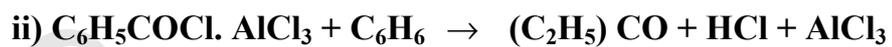
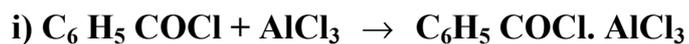
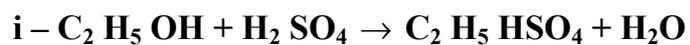
عامل الحفز السالب :

النظريات التي تفسر ميكانيكية الحفز :

-1



($AK + B = AB + K$) :



: The adsorption theory : -2

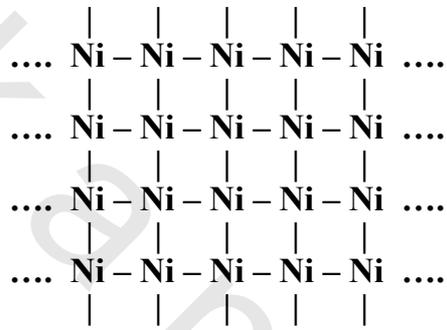
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⋄

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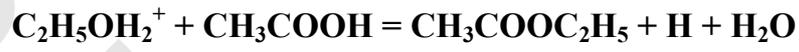
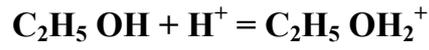
-4

X

XH



:



(taken by water)

الإنزيمات كعوامل حافزة :

مميزات الإنزيمات كعوامل حافزة :

:

-1

-2

-3

(°40 – 30)

-4

-5

-6

-7

* * *

"الأسئلة"

-1

-2

-3

-4

-5

-6

()

()

()

-7

-8

-9

-10

-11

* * *