

Kinetika Kimia

Studi/kajian tentang laju reaksi

<http://fpmipa.upi.edu/>

- Pengertian Laju reaksi
- Pengukuran Laju
- **Penentuan Hk. Laju**
- Pengaruh Temperatur pada Laju reaksi
- Mekanisme Reaksi
- Catalysis

Rate Law; Integration form

$$\frac{d[A]}{dt} = -k[A]^0$$

Orde 0

A → produk

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

$$[A] - [A]_0 = -kt$$

$$[A] = [A]_0 - kt.$$

Plotting $[A]$ vs. t gives a straight line with slope = $-k$.

First Order Reaction; Integration

n = 1 (first order)

$$-\frac{d[A]}{dt} = k[A]$$

A → produk

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

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

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

$$[A] = [A]_0 e^{-kt}$$

First Order Reaction; Integration

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

n = 1 (first order)

A → produk

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

$$y = mx + c$$

Integrated form of the
1st order rate expression



$$[A] = [A]_0 e^{-kt}$$

Kinetika Orde dua; bentuk integrasi

Kinetika Orde 2

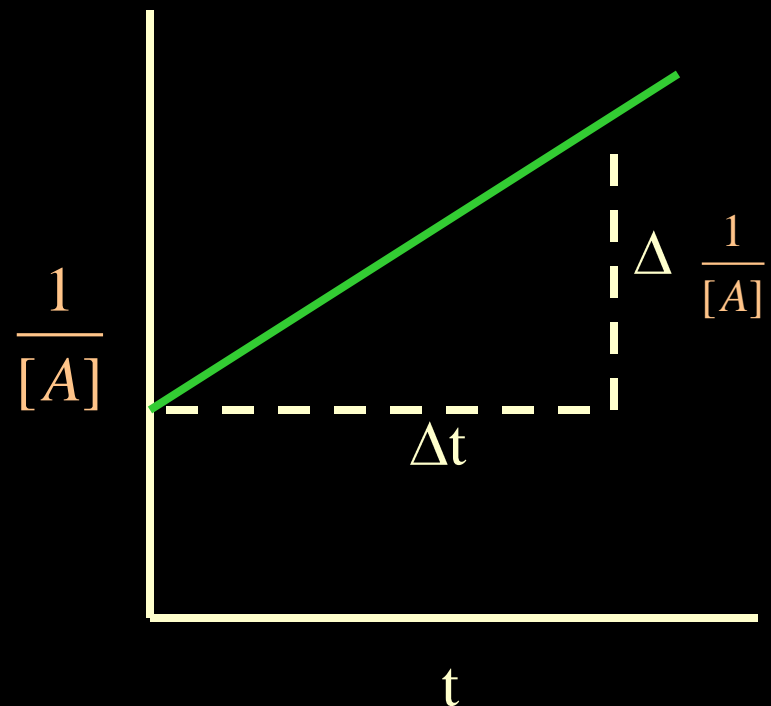
$2A \rightarrow$ produk

Hukum laju: $dA/dt = k[A]^2$

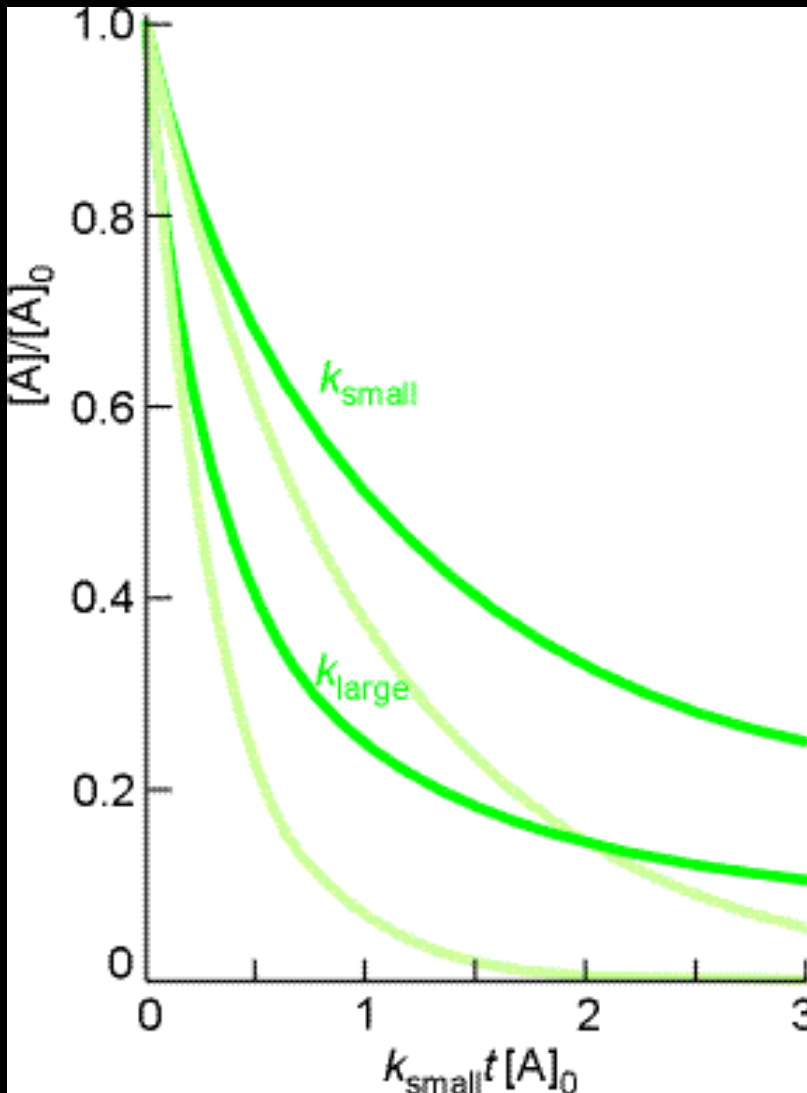
$$\int_{A_0}^A \frac{dA}{[A]^2} = - \int_0^t k dt$$

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

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



Kinetika Orde dua; bentuk integrasi



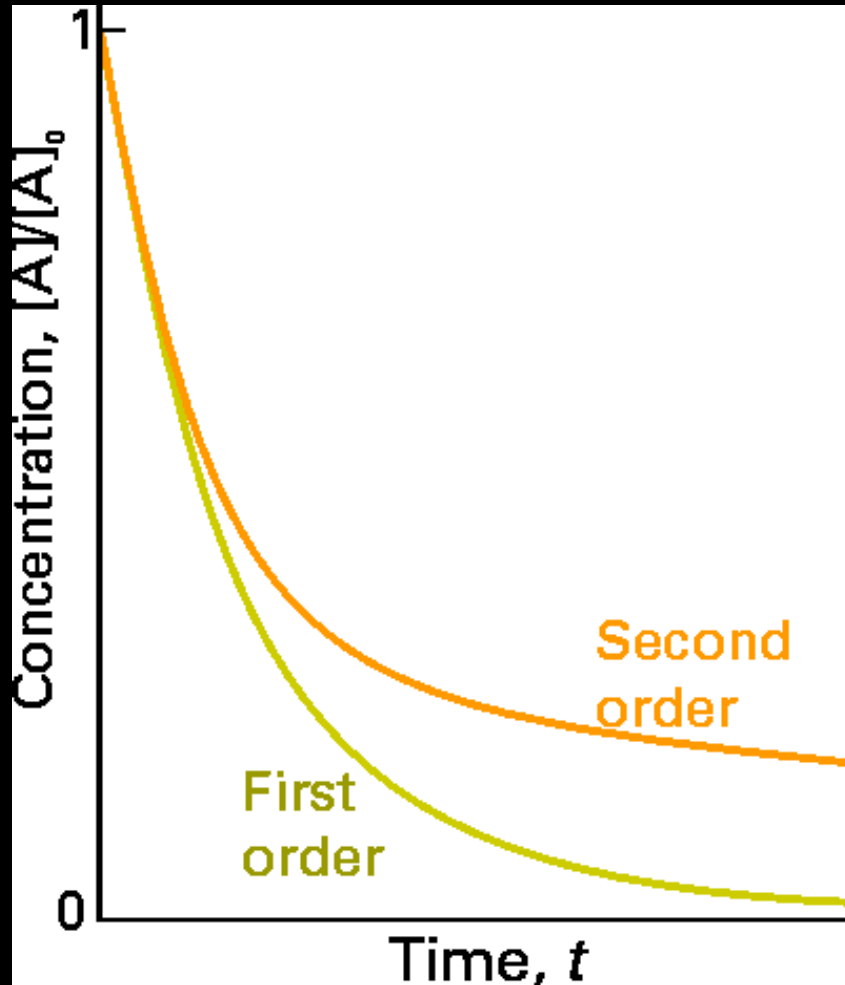
Kinetika Orde 2
 $2A \rightarrow \text{produk}$

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

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

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

2ND ORDER RATE LAWS 5.2



The most prominent difference between 1st and 2nd orders is the rate at low concentration of A, much slower for 2nd order

2nd order decay processes die out long before they would have if they were 1st order decays,

especially important to the atmosphere, as many pollutants disappear by 2nd order laws

Contoh Soal

- Data reaksi dimerisasi $2A \rightarrow A_2$ suatu senyawa nitril oksida, ditunjukkan pada tabel berikut:

[A]/(mmol/L)	68,0	50,2	40,3	33,1	28,4	22,3	18,7	14,5
t/min	0	40	80	120	160	240	300	420

Tentukan orde reaksinya, dengan metode yang telah di pelajari!



Kinetika Orde dua; bentuk integrasi

- Bentuk lain dari reaksi orde 2 adalah

$$r = k[A][B].$$

More difficult to integrate !!!

Untuk Reaksi: $aA + bB \rightarrow \text{produk}$

$$\frac{1}{a} \frac{d[A]}{dt} = -k[A][B]$$

$$\frac{1}{a [A][B]} d[A] = -k dt$$

Persamaan ini memiliki 3 variable: [A], [B], dan t

Kinetika Orde dua; bentuk integrasi

$$\frac{1}{a} \frac{d[A]}{[A][B]} = -k dt$$

Supaya persamaan dapat diintegrasikan [B] harus dieliminasi dengan menghubungkannya dg [A]

perbandingan [A] dan [B] yang bereaksi :

$$\frac{\Delta[A]}{\Delta[B]} = \frac{a}{b}$$

atau

$$\frac{b}{a} = \frac{([B]_0 - [B])}{([A]_0 - [A])}$$

sehingga

$$[B] = [B]_0 - \frac{b}{a}[A]_0 + \frac{b}{a}[A]$$

Kinetika Orde dua; bentuk integrasi

$$\frac{1}{a} \frac{d[A]}{[A][B]} = -kdt$$

Integrasi persamaan hk laju :

$$\frac{1}{a} \int_1^2 \frac{1}{[A] \left([B_0] - \frac{b}{a}[A_0] + \frac{b}{a}[A_0] \right)} d[A] = - \int_1^2 kdt$$

Integrasi persamaan hk laju menghasilkan :

$$\frac{1}{a[B_0] - b[A_0]} \ln \frac{\left(\frac{B}{B_0} \right)}{\left(\frac{A}{A_0} \right)} = kt$$

Penentuan Hukum Laju Cara Waktu paruh

Berlaku untuk persamaan laju $r = k[A]^n$

- Orde 0
- $[A] = [A]_0 - kt$.

Substitusi t dengan $t_{1/2}$ dan $[A]$ dengan $\frac{1}{2}[A]_0$

$$\frac{1}{2}[A]_0 = [A]_0 - kt_{1/2}$$

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

Penentuan Hukum Laju Cara Waktu paruh

- Orde 1

$$\ln \left(\frac{A}{A_0} \right) = -kt$$

Substitusi t dengan $t_{1/2}$ dan [A] dengan $\frac{1}{2}[A]_0$

$$\ln \left(\frac{A_0}{2 A_0} \right) = -kt_{1/2}$$

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

Penentuan Hukum Laju Cara Waktu paruh

- Orde 2

$$\frac{1}{A} = \frac{1}{A_0} + kt$$

Substitusi t dengan $t_{1/2}$ dan [A] dengan $\frac{1}{2}[A]_0$

$$\frac{1}{\frac{1}{2}A_0} = \frac{1}{A_0} + kt_{1/2}$$

$$\frac{1}{A_0} = kt_{1/2}$$

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

Penentuan Hukum Laju Cara Waktu paruh

Untuk reaksi orde n:

$$\frac{dA}{dt} = -k [A]^n$$

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

$$\frac{[A]^{-n+1} - [A]_0^{-n+1}}{-n+1} = -k t \quad \times (1-n)[A]_0^{n-1}$$

$$\left(\frac{[A]}{[A]_0} \right)^{-n+1} = 1 + [A]_0^{n-1} (n-1)kt \quad \text{ut. } n \neq 1$$

Untuk $[A] = \frac{1}{2} [A]_0$ dan $t = t_{1/2}$

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)[A]_0^{n-1} k} \quad \text{ut. } n \neq 1$$

Experimental Determination of Rate Law

Isolation Method:

- All reactant is made excessive, except a reactant under investigation

For the reaction: $m\text{A} + n\text{B} \rightarrow \text{product}$

If A and B are dilutes solution: $r = k[\text{A}]^x[\text{B}]^y$

If the reaction is proceed in excess of B:

$$r = k[\text{A}]^x$$

- This reaction order obtained is called pseudo-order

The various pseudo- orders can be put together to give the overall order.

Determination of Rate Law

Initial Rate Methods:

- The rate is measured at the beginning of reaction with some variations in reactant initial concentrations:

Exercise:

For the reaction $2A + B + C \rightarrow \text{product}$, the initial reaction as a function of initial concentration is shown as follow

($c^0 = 1 \text{ mol/dm}^3$):

Expt. nr	1	2	3	4
$[A]_0/c^0$	0,20	0,60	0,20	0,60
$[B]_0/c^0$	0,30	0,30	0,90	0,30
$[C]_0/c^0$	0,15	0,15	0,15	0,450
$100 r_0 / (c^0 / \text{s})$	0,60	1,81	5,38	1,81

Contoh soal (1)

Dekomposisi fasa gas asetaldehid telah dipelajari pada temperatur 791 K. Hasil pengukuran dari dua percobaan adalah:

Konsentrasi awal/(mol/L)	$9,72 \times 10^{-3}$	$4,56 \times 10^{-3}$
Waktu paruh/detik	328	572

Tentukan orde reaksi dan konstanta laju reaksinya!

Contoh soal (1)

Untuk reaksi $A + B \rightarrow C + D$, eksperimen dengan:

$[A_0] = 400 \text{ mmol/L}$, dan $[B_0] = 4 \text{ mmol/L}$ menghasilkan data

t/s	0	120	240	360	~
$[C] \times 10^1 / \text{mmol.L}^{-1}$	0	2,00	3,00	3,5	4,00

Pada $[A_0] = 4 \text{ mmol/L}$, dan $[B_0] = 400 \text{ mmol/L}$ menghasilkan data

t/s	0	69	206	485	~
$[C] \times 10^1 / \text{mmol.L}^{-1}$	0	2,00	3,00	3,5	4,00

Tentukan hukum laju dan konstanta laju

Exercise E7.6

- The half-life of a substrate in a certain enzyme-catalyzed first order reaction is 138 s. How long is required for the initial concentration of substrate, which was 1.28 mmol/L, to fall to 0.040 mmol/L?