

Your Teacher !!

Nama	: Agus Setiabudi
Tempat Tgl. Lahir	: Tasikmalaya, 03 Agustus 1968
Pendidikan	: S1 Kimia IKIP Bandung (1987-1991) S2 Kimia ITB, Kimia Fisika, (1995-1998) S3 Delft University of Technology Nederland, Katalisis (1999-2004)

CV

- Apa yang dipelajari dalam Kuliah Kimia Fisika ?
- Apa yang dipelajari dalam Kuliah Termodinamika?
- Apa yang akan dipelajari dalam Kuliah Kinetika?

- Energi yang menyertai perubahan materi
- Membahas mengapa reaksi dapat terjadi atau tidak terjadi, jadi hanya melihat keadaan awal dan keadaan akhir tanpa memperhatikan proses

- Perubahan fisik spt perubahan fasa, sifat koligatif
- Keadaan fisik suatu reaksi spt. Suhu, tekanan
- Aspek fisika dalam sistem kimia dengan menggunakan matematika sbg alat bantu
 - › T,P, V, Energi, Kecepatan reaksi, Kestimbangan

Kimia Fisika

- Cabang ilmu kimia yang menggunakan prinsip dan hukum fisika untuk mempelajari perilaku system kimia
- Menggunakan Matematika sebagai Alat
- It includes the qualitative and quantitative study, both experimental and theoretical, of the general principles determining the behavior of matter, particularly the transformation of one substance into another.

Chemical Kinetics and Thermodynamics

Senyawa Kimia

$$\Delta_f G_{298}^0$$

C ₂ H ₅ OH	-174.78
C ₆ H ₁₂ O ₆	-910.1
CO ₂	-394.36
H ₂ O	-228,57

1. Parameter apa yang menentukan kespontanan reaksi?
2. Apakah reaksi antara C₂H₅OH and O₂ merupakan reaksi yang spontan?

Those question shows you the importance of

Physical Chemistry Topics

➤ Gas Laws

➤ Basic Thermodynamics

➤ Chemical Equilibrium

➤ Phase Equilibrium

➤ **Mult. Phase Equilibrium**

➤ **Electro Chem**

➤ Basic Quantum Chemistry

➤ Atomic Structure and
Chemical Bonding

Thermodynamics

~~Statistical
Mechanics~~

Quantum Chemistry

Radiochemistry

Kinetics

➤ Reaction Rate and Mechanism
(Time as variable)

➤ Introduction to Catalysis

Kinetics vs Thermodynamics

Thermodynamics show *why* a reaction wants to proceed.

Kinetics can explain *how* it proceeds.

The two topics are complementary:
you will need both to understand chemistry.

Thermodynamics vs Kinetics

$$\Delta_f G_{298}^0 H_2O(g) = -228,572 \text{ kJ mol}^{-1}$$

Means that ΔG for the formation of $H_2O < 0$:



Spontaneous ????

Refferensi dan Pelaksanaan Perkuliahan

- 1. Gilbert Castelan, Physical Chemistry,**
- 2. Ira Levine, Physical Chemistry**
- 3. Sumber-sumber Lain**

Urutan dan pendekatan sangat mungkin tidak sesuai dengan buku !!!!!

Chemical Kinetics

A study on reaction rate and mechanism

Introduction

Pengukuran Laju Reaksi

Penentuan Hukum Laju

Pengaruh Temperatur

Mekanisme Reaksi

Catalysis

Kinetics - the rates of chemical reactions

- How fast does a reaction go?
- Does the rate change over time?
- Can it be influenced?
- What does all this say about *how* the reaction proceeds?

Introduction

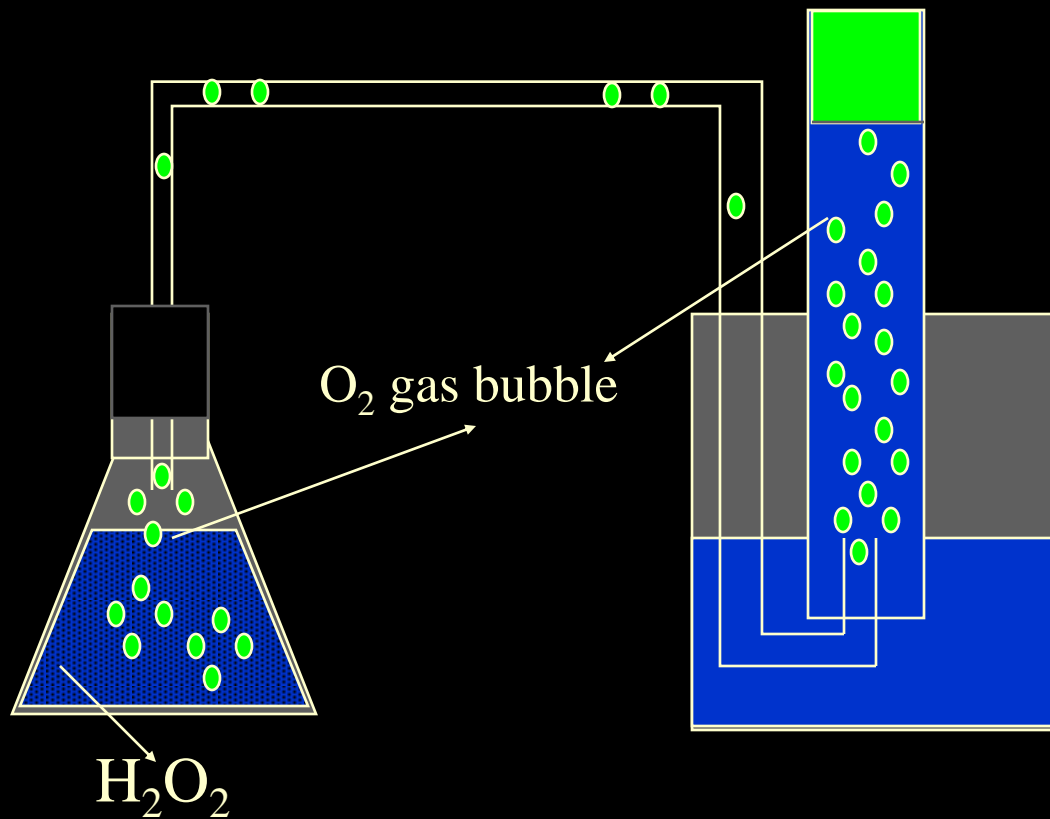
- What is reaction rate ?
- How to determine?

Example: Your Laboratory Experiment



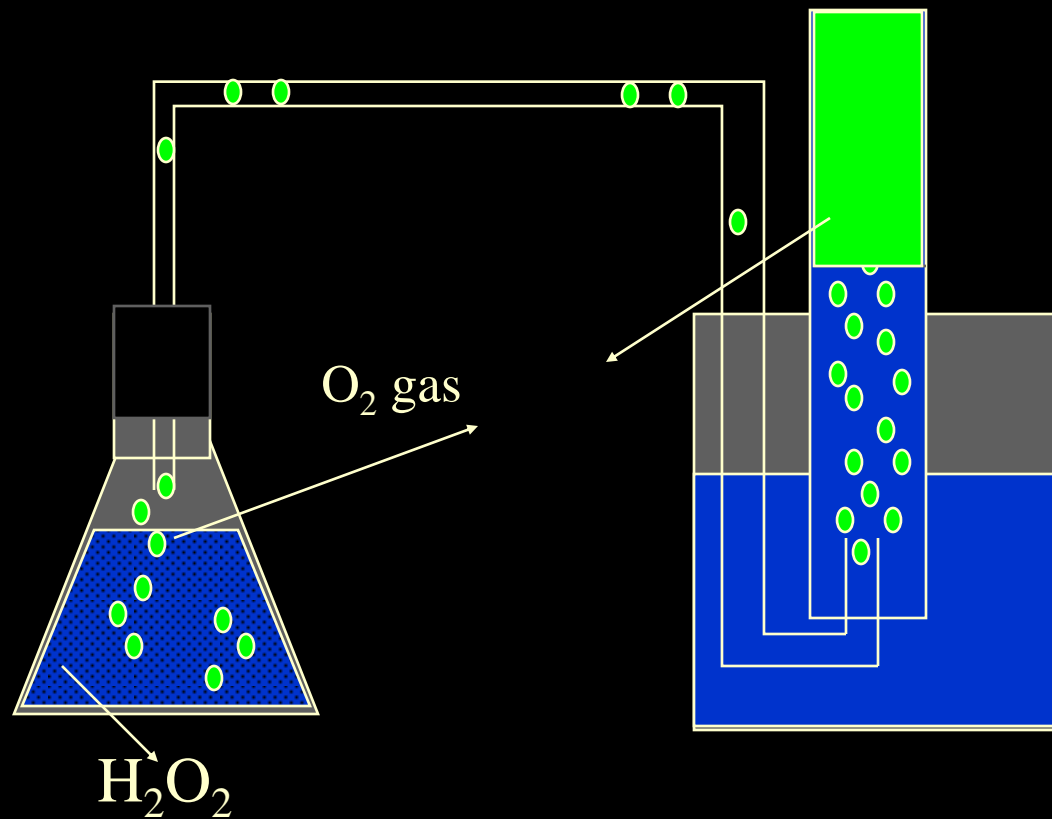
Pengukuran dan Penentuan Laju Reaksi

Our Laboratory Practice:



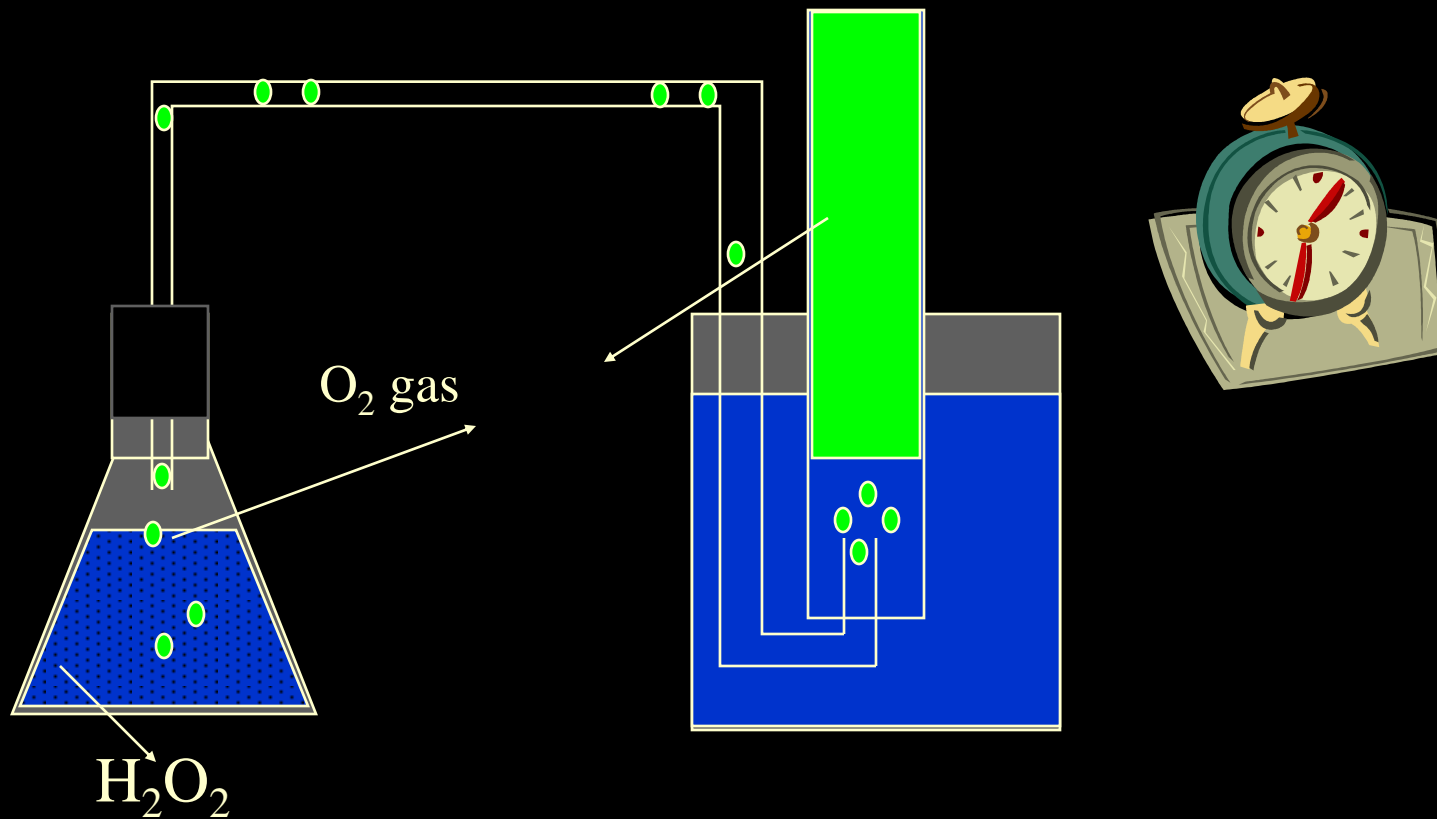
Pengukuran dan Penentuan Laju Reaksi

Our Laboratory Practice:



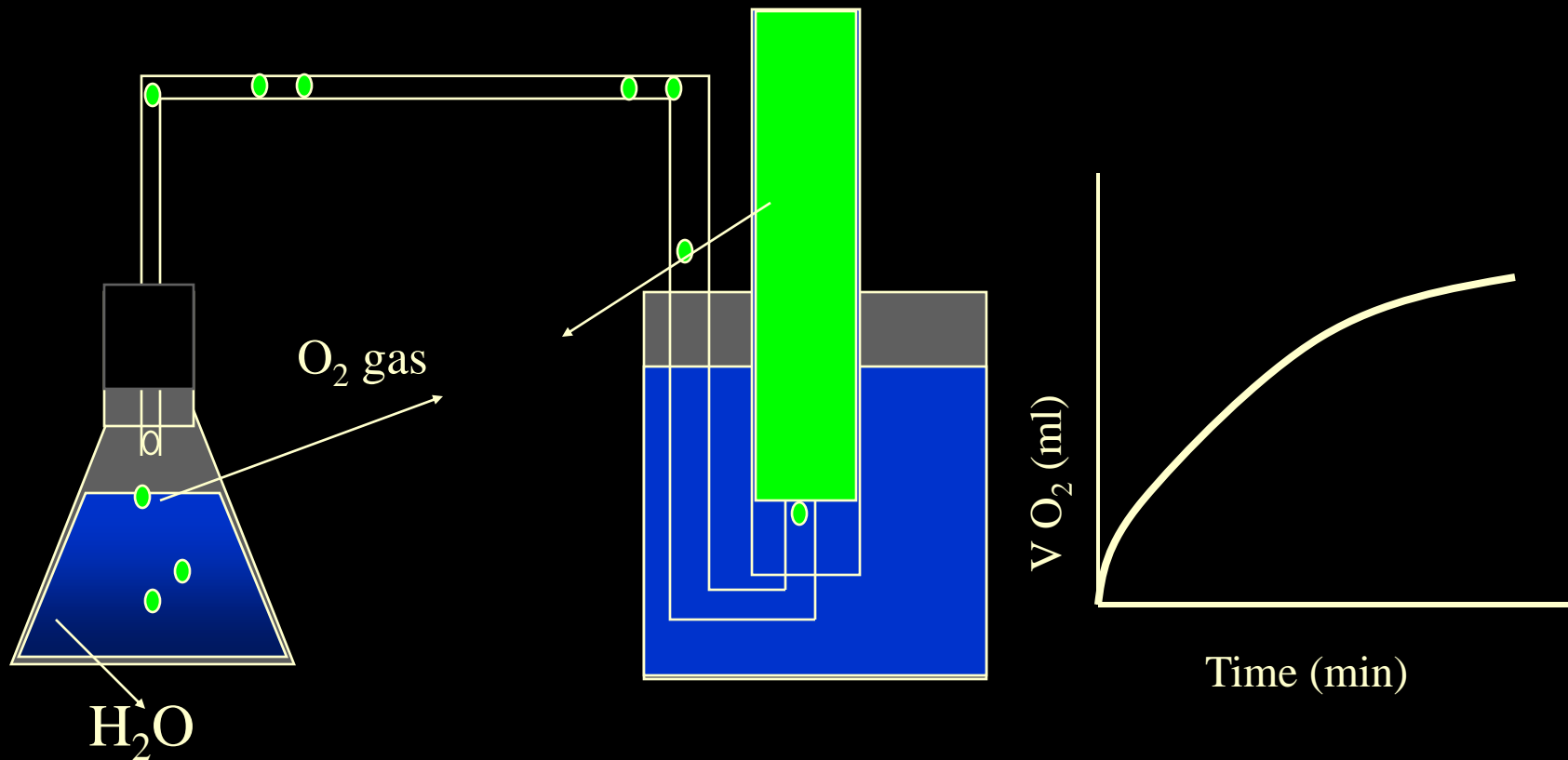
Pengukuran dan Penentuan Laju Reaksi

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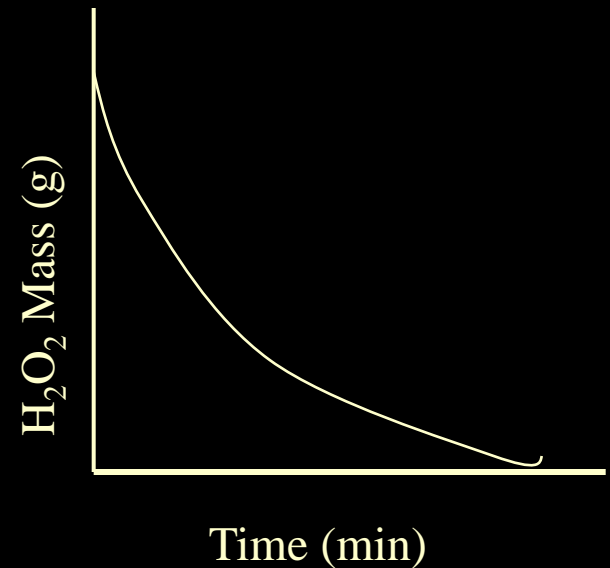
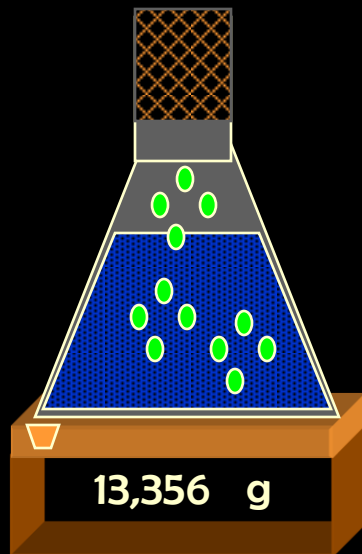
Pengukuran dan Penentuan Laju Reaksi

Our Laboratory Practice:



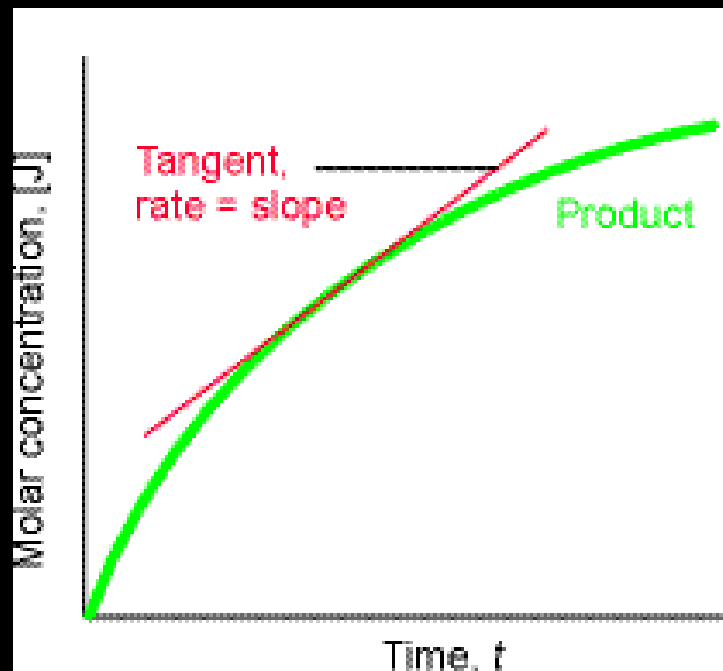
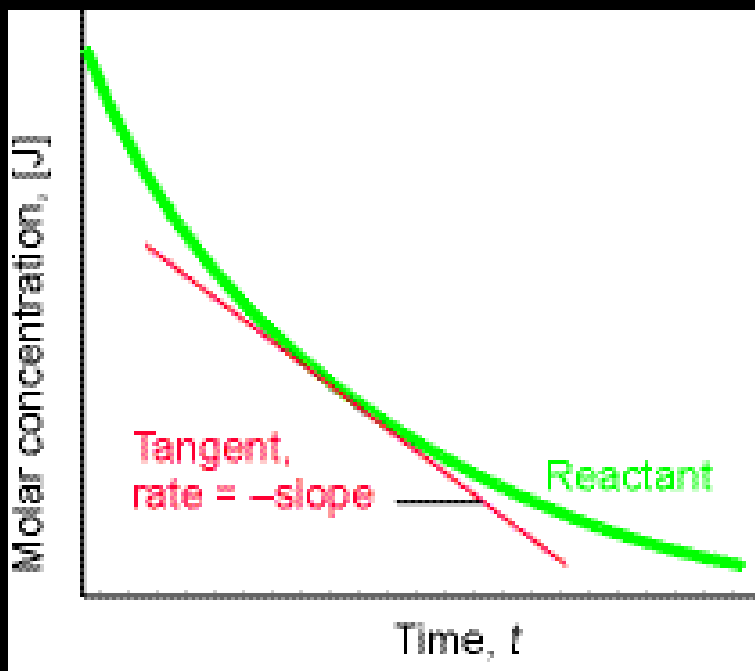
Pengukuran dan Penentuan Laju Reaksi

Our Laboratory Practice:



Reaction Rate: Definition

Reactant \rightarrow Product



- Rate of reactant consumption $-\frac{d[R]}{dt}$
- Rate of product formation: $\frac{d[P]}{dt}$

Reaction Rate: Definition

- For the reaction:



- B is consumed twice faster than A;
- C is produce three times faster than D.
- To have a numeric value appropriate for overall reaction, a new variable **r** is defined:

$$r = d[D]/dt = 1/3 d[C]/dt$$

$$r = d[A]/dt = 1/2 d[B]/dt$$

Exercise

Exercise

Jika hasil percobaan, pada keadaan STP, untuk reaksi



Adalah sbb

Volume O ₂ /mL (stp):	0	7.5	14.0	28.8	41.2	48.3	57.9
Waktu (menit) :	0	5	10	25	45	65	~

Tentukan:

- Laju reaksi rata-rata penguraian H₂O₂
- Laju reaksi rata-rata antara 10 dan 25 menit
- Laju reaksi awal!
- Laju sesaat pada t = 15 menit

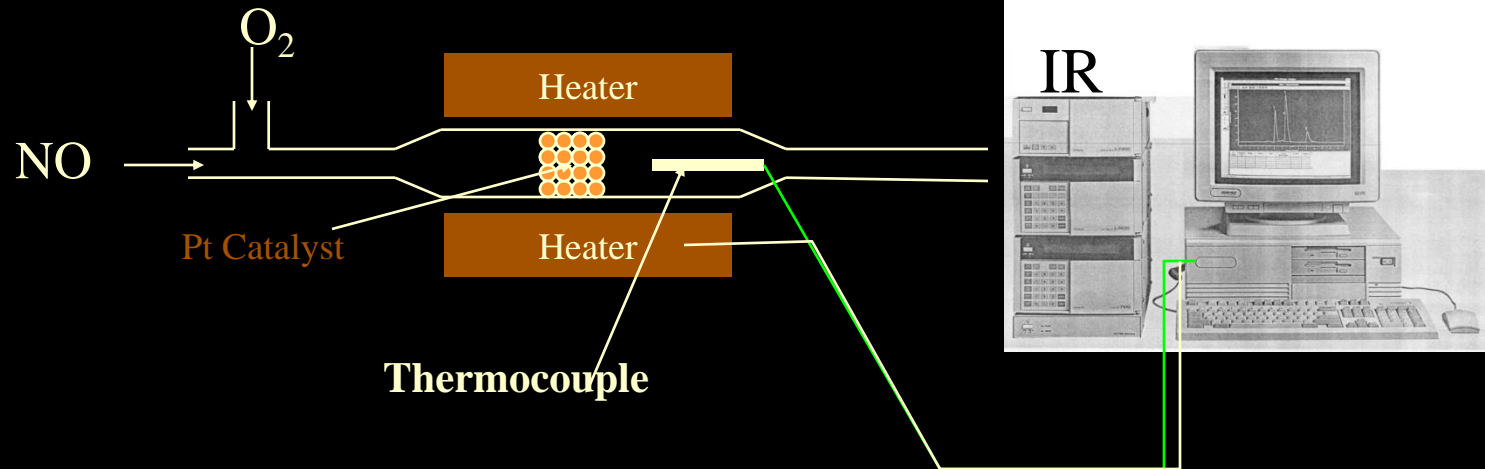
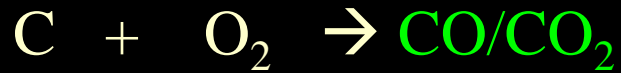
Tugas !!!!

- Jelaskan langkah yang bisa ditempuh untuk mengukur laju reaksi:



Example of Measurement Equipment

Applicable Reaction :



Reaction Rate: Definition and Order

The decomposition of nitrosyl bromide (NOBr) can be followed manometrically. An example of this experimental results is shown a follows:

t (s)	[NOBr](mol/L):
0	0.01
2	0.0071
4	0.005
6	0.0045
8	0.0038
10	0.0033

- Use graphical methods to estimate the rate at 3 s and 7 s!
- Determine the reaction order

Rate law

- **Rate Law (Rate Equation);**
a mathematical expression that relates reaction rate as a function of reactant concentration

$$r = k[A]^m[B]^n$$

- Reaction rate is normally proportional with concentration and has simple **power number**
- This power number is called **reaction order**
- For the rate law = $k[A]^m[B]^n$,
the reaction has m order with respect to A, n order with respect to B
the overall reaction has m+n order

Rate Law; Integration form

- Describe reactant concentration (ex. [A]) as a function of time (t);
- The differential definition for the rate is equated to the rate law,

For zero order reaction:

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

Rate Law; Integration form

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

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

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

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

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

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

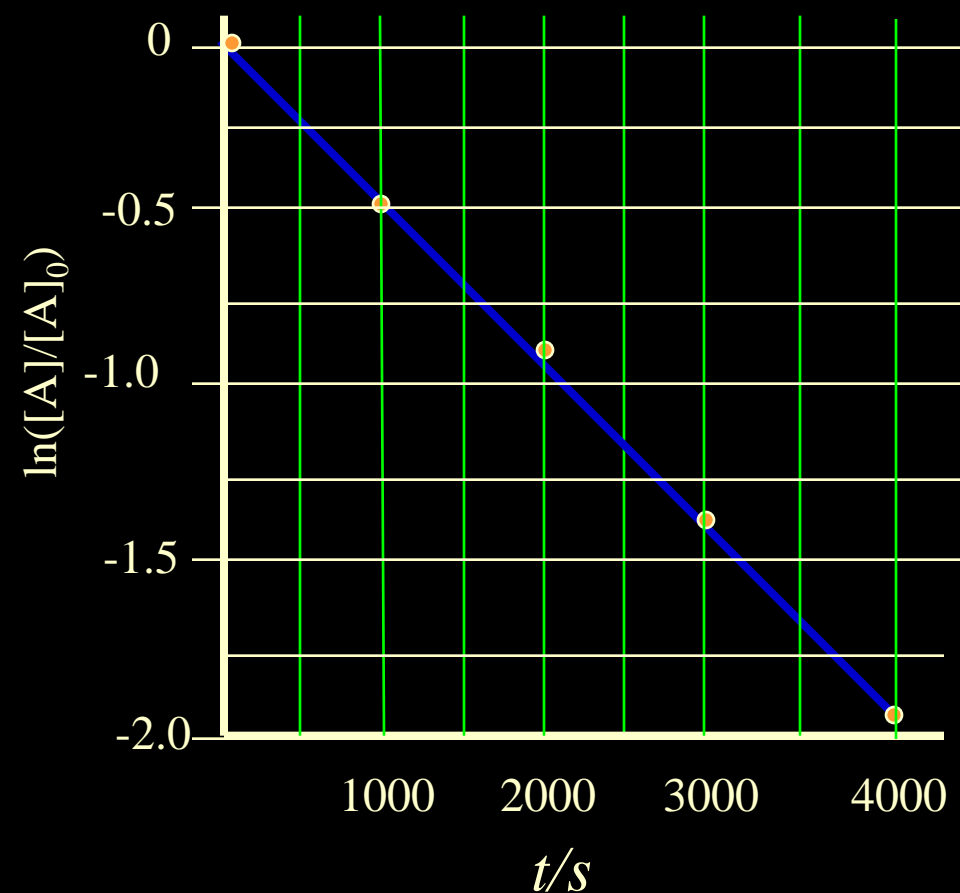
$$\mathbf{y = mx + c}$$

Integrated form of the
1st order rate expression



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

A Straight-Line Plot for a First-Order Reaction



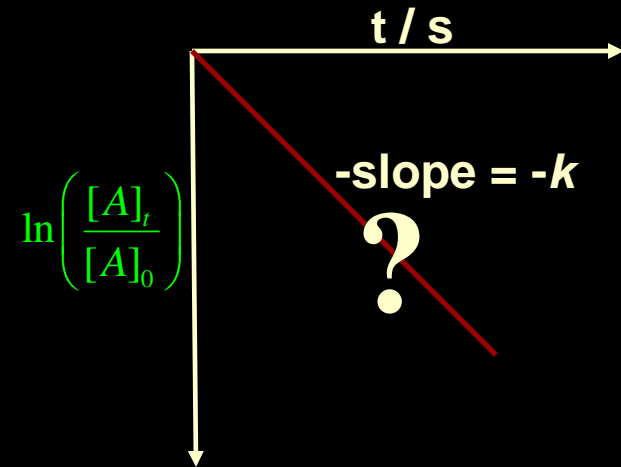
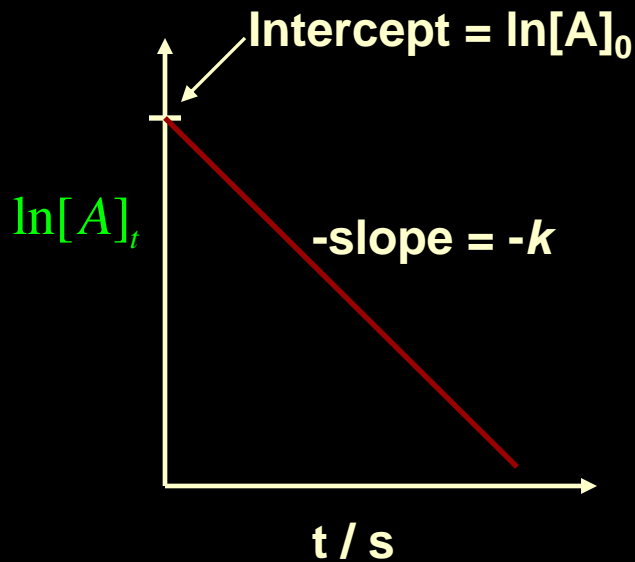
- For first order reaction, $\ln([A]/[A]_0) = -kt$
- Plott $\ln [A]$ vs t result in a straight line
- So does $\ln ([A]/[A]_0)$ vs. t
- So does plotting the log of pressure of a reactant.

Such a plot can be used to determine k and to evaluate the order

Bentuk Kurva reaksi orde 1

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

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$



Other useful forms

Exercise E7.5

- The concentration of N_2O_5 in liquid bromine varied with time as follows:

t/s	0	200	400	600	1000
$[\text{N}_2\text{O}_5]/\text{M}$	0.110	0.073	0.048	0.032	0.014

- Show that the reaction is first order in respect to N_2O_5 and determine the rate constant.



What can we conclude about RATE LAWS versus INTEGRATED RATE EXPRESSIONS??

- a rate law can tell us the rate of a reaction, once the composition of the reaction mixture is known
- An integrated rate expression can give us the concentration of a species as a function of time. It can also give us the rate constant and order of the reaction by plotting the appropriate graph

Kinetika Orde dua; bentuk integrasi

Kinetika Orde 2

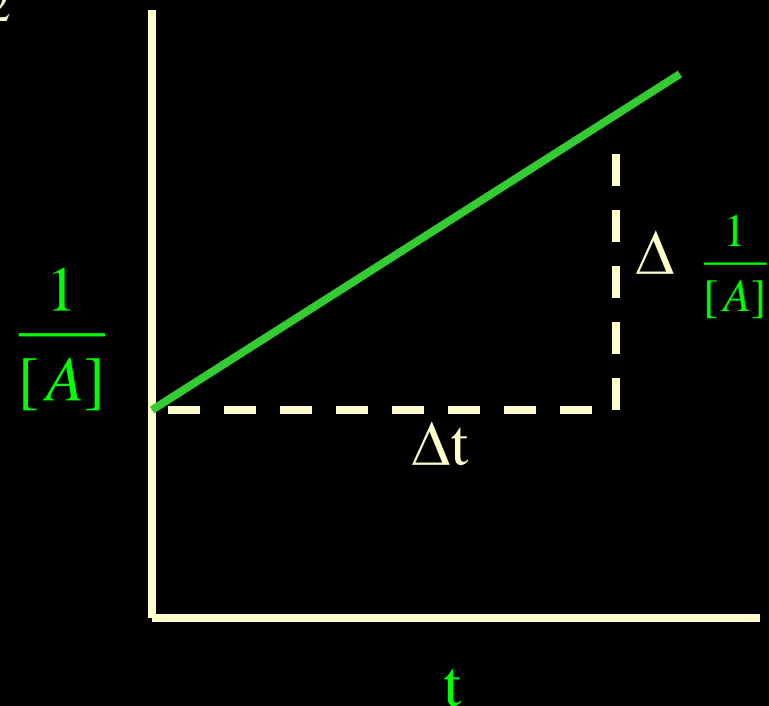
$2A \rightarrow$ produk

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

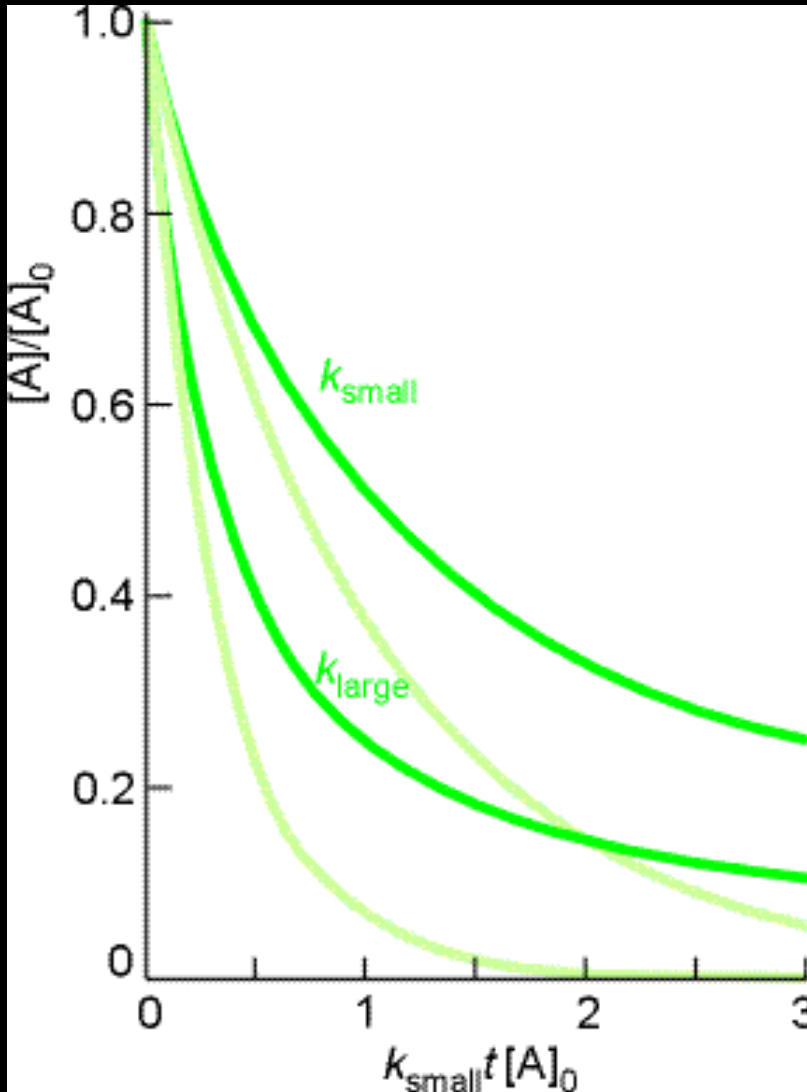
$$\int_{A_0}^A \frac{d[A]}{[A]^2} = - \int_0^t k dt$$

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

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



Kinetika Orde dua; bentuk integrasi



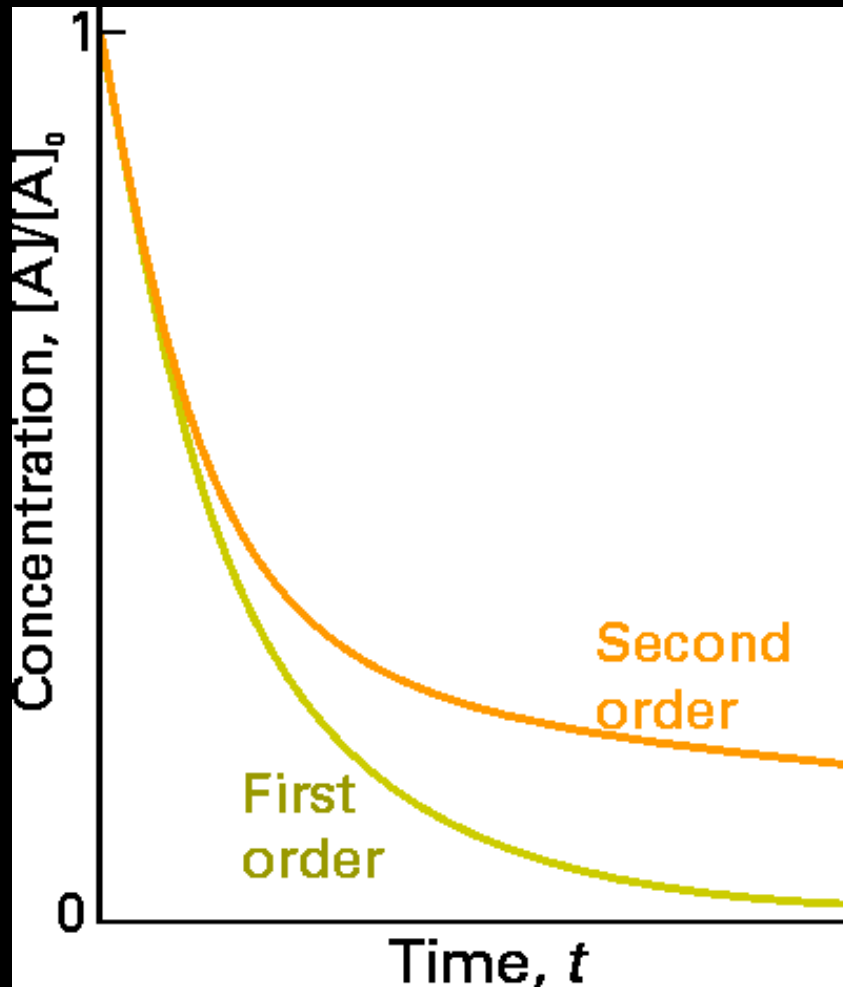
Kinetika Orde 2
 $2A \rightarrow \text{produk}$

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

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

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

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

Exercise

- 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!



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 $\frac{1}{2}[A]_0$

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

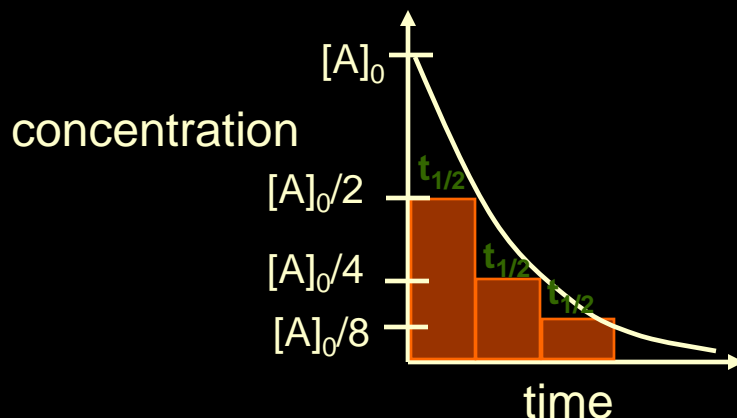
$$t_{1/2} = \frac{\ln 2}{k}$$

Hence,

or

What is/are the main point(s) to note from this expression??

- For a 1st order reaction, the **half-life is independent of reactant concentration** but **dependent on k** .
- The **half-life is constant** for a 1st order reaction



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

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 $t = t_{1/2}$

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

Kinetika Orde dua; bentuk integrasi

- Bentuk lain dari reaksi orde 2 adalah

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

More difficult to integrate !!!

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

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

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

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

Kinetika Orde dua; bentuk integrasi

perbandingan $[A]$ dan $[B]$ yang bereaksi : $r = \frac{1}{a} \frac{d[A]}{dt} = -k[A][B]$

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

atau

$$\frac{b}{a} = \frac{([B_0] - [B])}{([A_0] - [A])}$$

atau

$$[B] = [B_0] - \frac{b}{a}[A_0] + \frac{b}{a}[A]$$

Integrasi persamaan hk laju :

$$\frac{1}{a} \frac{d[A]}{dt} = -k[A] \left([B_0] - \frac{b}{a}[A_0] + \frac{b}{a}[A] \right)$$

Kinetika Orde dua; bentuk integrasi

Integrasi persamaan hk laju :

$$\frac{1}{a} \int_{[A]_0}^{[A]} \frac{1}{[A] \left([B_0] - \frac{b}{a}[A_0] + \frac{b}{a}[A] \right)} d[A] = - \int_0^t k dt$$

Integrasi persamaan hk laju menghasilkan :

$$\frac{1}{a[B_0] - b[A_0]} \ln \frac{\left(\frac{[B]}{[B]_0} \right)}{\left(\frac{[A]}{[A]_0} \right)} = kt$$

Exercise

- The initial rate of a reaction depended on the concentration of a substance J as follows.

$[J]_0/(10^{-3} \text{ M})$	5.0	8.2	17	30
$r_0/(10^{-7} \text{ M s}^{-1})$	3.6	9.6	41	130

- Find the order of the reaction with respect to J and the rate constant.

$r_0 = k[J]_0^n$, so $\log r_0 = n \log [J]_0 + \log k$

>	$\log [J]_0$	0.70	0.91	1.23	1.48
>	$\log r_0$	0.56	0.98	1.61	2.11

$\log r_0$ goes up twice as fast as $\log [J]_0$, so $n = 2$ and $\log k = 0.56 - 2(0.70) = -0.84$; $k = 0.15 \text{ M}^{-1}\text{s}^{-1}$

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 $[B_0] = 0,4 \text{ mmol/dm}$ menghasilkan data

t/s	0	120	240	360	~
[C]/mmol.L ⁻¹	0	0.2	0.3	0.35	0.4
[A]/mmol.L ⁻¹					
[B] /mmol.L ⁻¹					

Pada $[A_0] = 0,4 \text{ mmol/L}$, dan $[B_0] = 400 \text{ mmol/dm}$ menghasilkan data

t/s	0	69	206	485	~
[C]x10/mmole.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?

- Untuk reaksi: $2A + B \rightarrow C + D + 2E$, data untuk reaksi yang berlangsung pada $[A]_0 = 800 \text{ mmol dm}^{-3}$, dan $[B]_0 = 2 \text{ mmol dm}^{-3}$ adalah:

t/1000s	8	14	20	30	50	90
[B]/[B] ₀	0,836	0,745	0,680	0,582	0,452	0,318

Sedangkan data untuk reaksi yang berlangsung pada $[B]_0 = 600 \text{ mmol dm}^{-3}$, dan $[A]_0 = 2 \text{ mmol dm}^{-3}$ adalah:

- | | | | | |
|----------------------|-------|-------|-------|-------|
| t/1000s | 8 | 20 | 50 | 90 |
| [A]/[A] ₀ | 0.901 | 0,787 | 0,593 | 0,453 |

Tentukan orde reaksi dan konstanta laju reaksi tersebut!

Your Teacher

