Chemical Kinetics

A study on reaction rate and mechanism

Introduction

Measurement of Reaction Rate

Determination of Reaction Rate

Influence of Temperature

Reaction Mechanism

Catalysis

Reaction Mechanisms

- The balanced (overall) chemical equation provides information about the initial reactants and final products, i.e., the beginning and end of a reaction.
- The reaction mechanism gives the path of the reaction.
- Mechanisms provide a very detailed picture of which bonds are broken and formed during the course of a reaction.

Reaction Mechanisms

- A series of (hypothetic) reaction taken place in a chemical process
- The kinetics (rate law) provide a hint on the mechanism

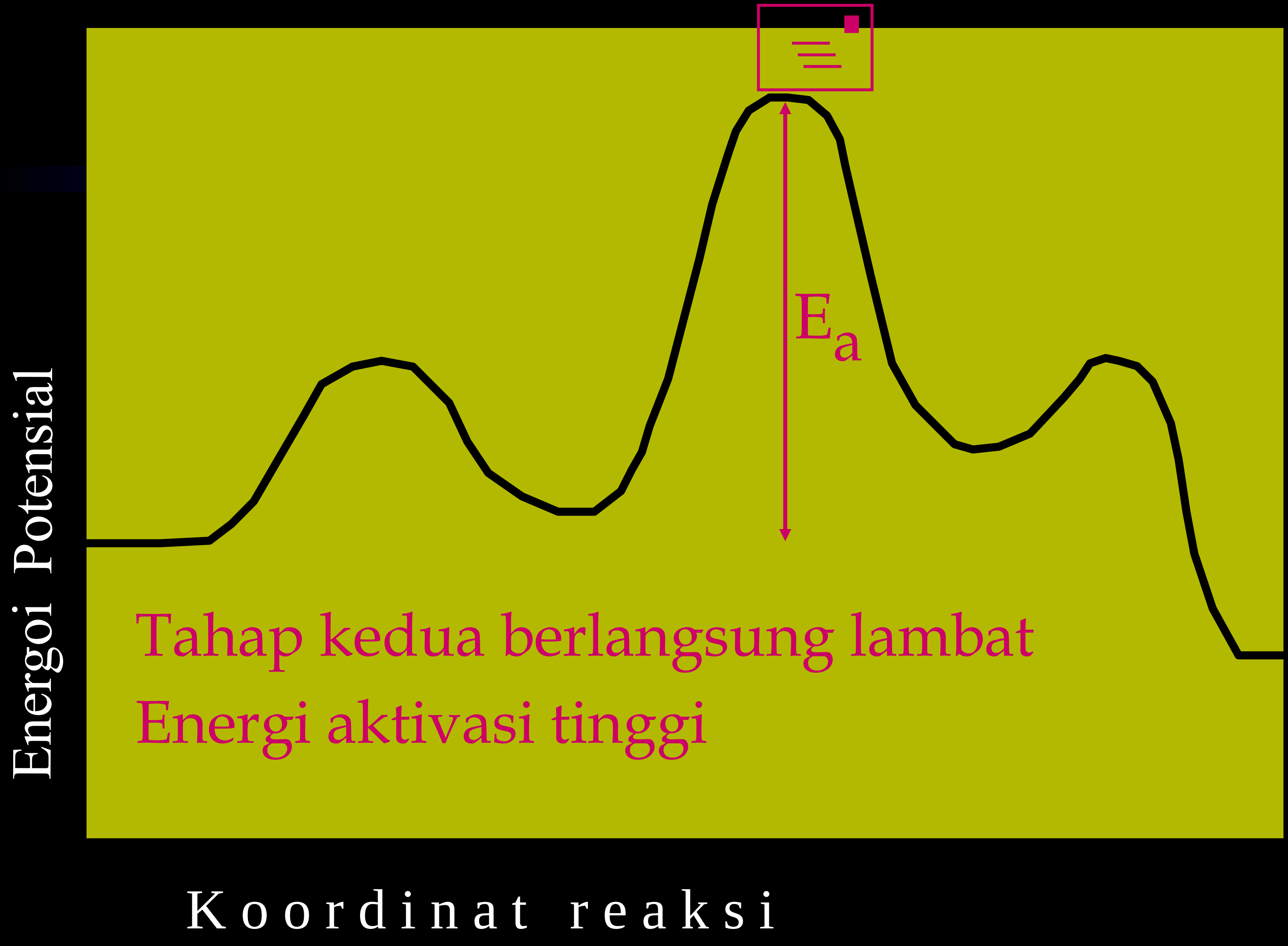
Mechanisms and rates

- Setiap tahap elementer memiliki nilai energi aktivasi
- Energi aktivasi menentukan nilai k.

  $k = Ae^{-(E_a/RT)}$
- k menentukan laju reaksi
- Tahap paling lambat memiliki energi aktivasi terbesar

Reaksi ini berlangsung melalui 3 tahap

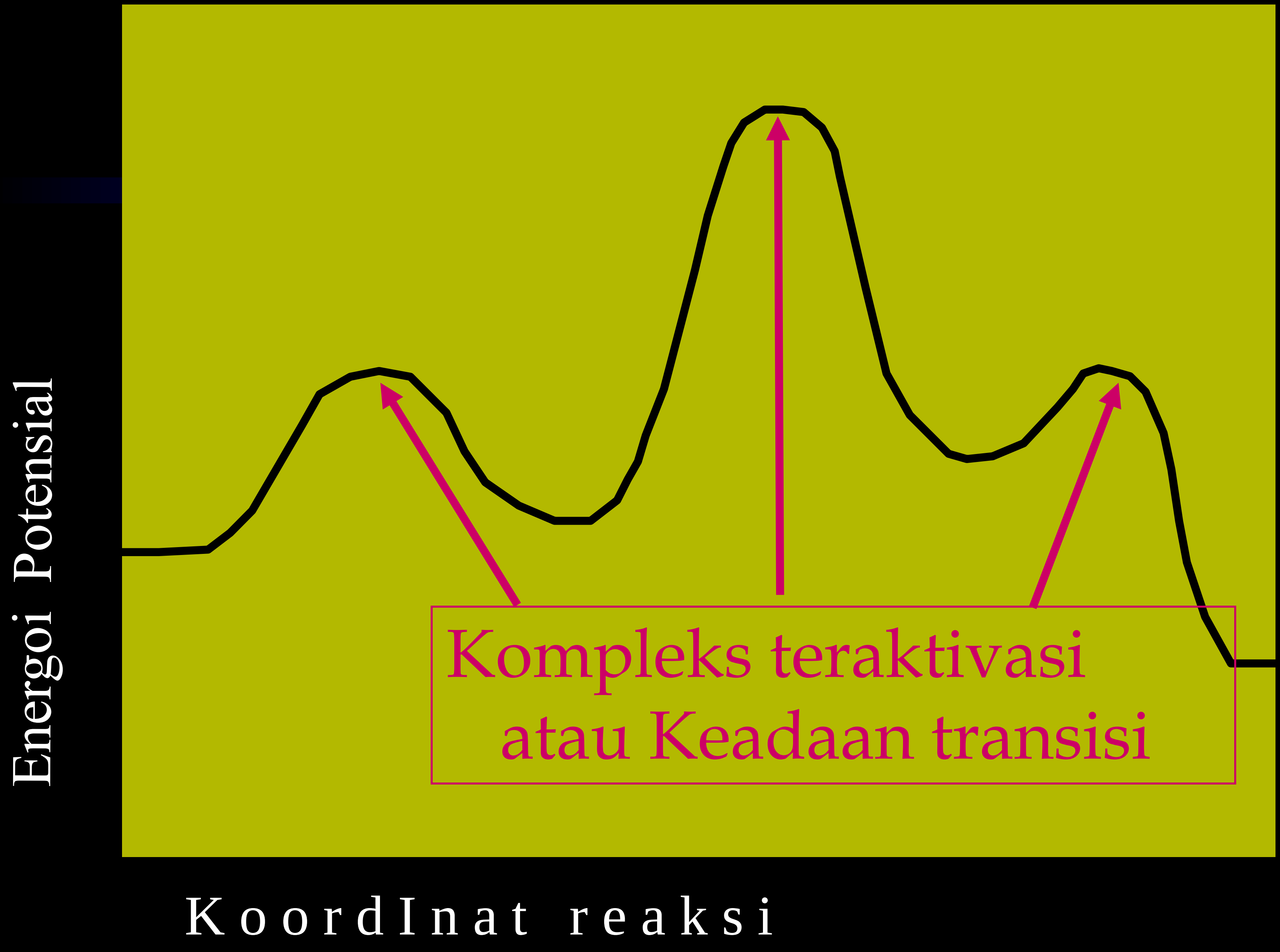
Energoi Potensial
Ea
Tahap pertama berlangsung cepat
Energi aktivasi rendah
Koordinat reaksi


Ea
Tahap kedua berlangsung lambat
Energi aktivasi tinggi
Energoi Potensial
K o o r d i n a t r e a k s i

Energoi Potensial
Ea
Tahap ketiga cepat
Energi aktivasi rendah
Koordinat reaksi


Energoi Potensial
Tahap kedua merupakan tahap penentu laju
Koordinat reaksi

Energoi Potensial
Keadaan yang menggambarkan adanya intermediate
K o o r d i n a t r e a k s i


Energoi Potensial
Kompleks teraktivasi
atau Keadaan transisi
KoordInat reaksi

Reaction Mechanisms

Elementary Steps

- An elementary step is any reaction that occurs as a result of a single molecular collision.
- Molecularity: the number of molecules involved in an elementary step.
  - Unimolecular: one molecule in the elementary step,
  - Bimolecular: two molecules in the elementary step, and
  - Termolecular: three molecules in the elementary step.
- It is not common to see termolecular processes (statistically improbable).

Reaction Mechanisms

Multistep Mechanisms

- Some reactions proceed through more than one step:

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

- Notice that if we add the above steps, we get the overall reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

- This reaction is said to take place via a <u>two-step</u> mechanism.

Reaction Mechanisms

Multistep Mechanisms

- If a reaction proceeds via several elementary steps, then the elementary steps must add to give the balanced chemical equation.

Reaction Mechanisms

Multistep Mechanisms

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

sum to give the overall reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Notice that the reactive intermediate is formed in the first step and is consumed in the second step.

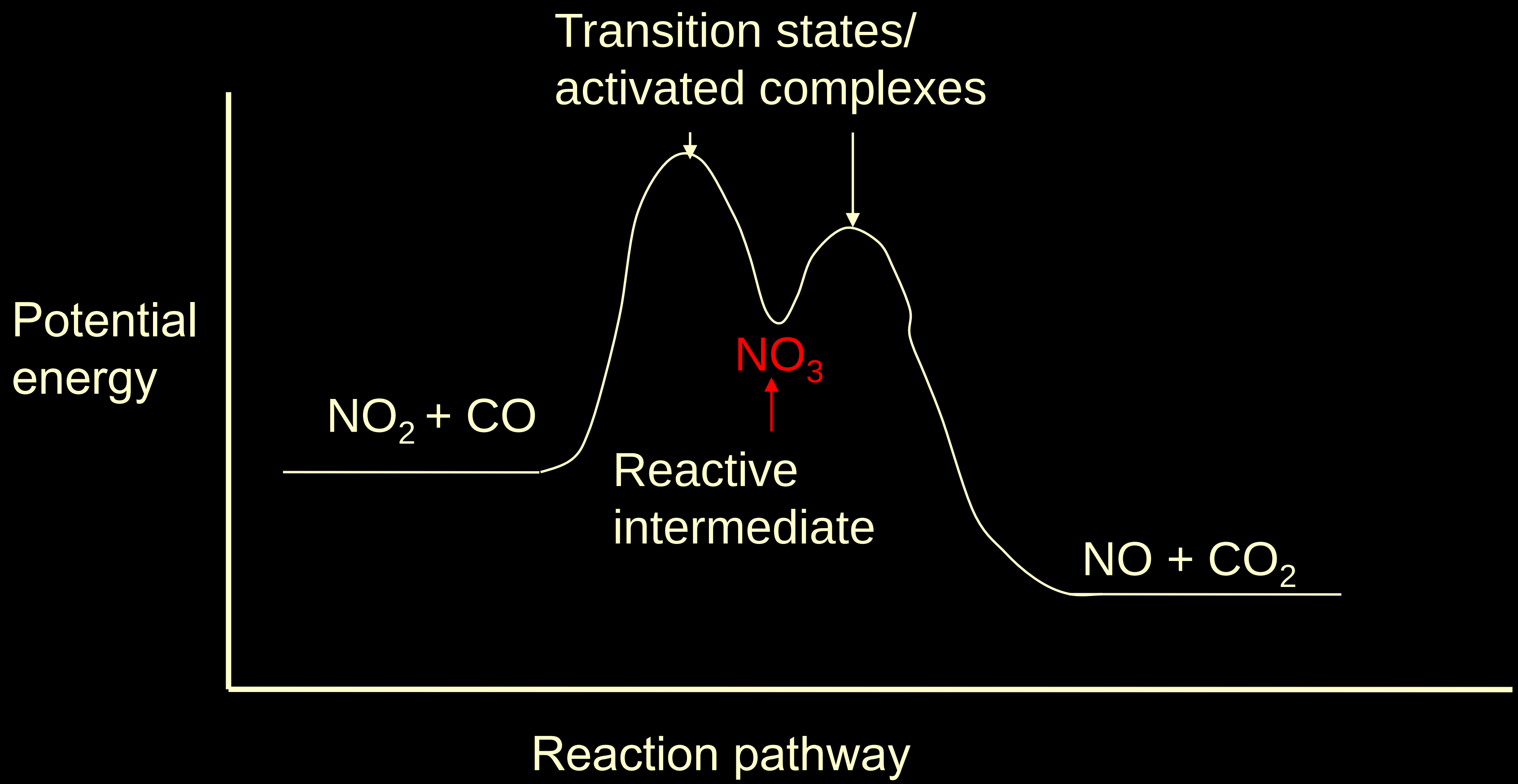
Reaction Mechanisms

Reactive intermediates

- Reactive intermediate: a species which appears in an elementary step but which is not a reactant or product in the overall reaction.
- Example: NO_3 in the previous example
- Usually a rather unfamiliar and unstable species

Reaction Mechanisms

PE diagram for a reaction with a two-step mechanism



Reaction Mechanisms

Rate Laws for Elementary Steps

- The rate law for an elementary step is determined by its molecularity:
  - Unimolecular elementary reactions have a first order rate law,
  - Bimolecular elementary reactions have a second order rate law, and
  - Termolecular elementary reactions have a third order rate law.

Reaction Mechanisms

Rate Laws for Elementary Steps

TABLE 14.3 Elementary Steps and Their Rate Laws

Molecularity	Elementary Step	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

Reaction Mechanisms

- $2NO_2 + F_2 \rightarrow 2NO_2F$

  $r = k[NO_2][F_2]$ (Empiric)

- Proposed mechanism:

  $NO_2 + F_2 \rightarrow NO_2F + F$ Lambat

  $F + NO_2 \rightarrow NO_2F$ Cepat

- F dinamakan intermediet. It is formed then consumed in the reaction

Rate-determining step

The various elementary steps in the mechanism of a reaction proceed at different rates

- The slowest step in the reaction mechanism is called the rate-determining step or the rate-limiting step in the reaction mechanism.
- Ex. It has been established experimentally that the rate law for the reaction

$$NO_2(g) + CO(g) = NO(g) + CO_2(g)$$

is $r = k[NO_2]^2$. Propose 2-step mechanism for this reaction !!!

Rate-determining step

Step 1 $NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)$ (slow)

Step 2 $NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$ (fast)

- Step 1 is much slower than step 2 → $k_1 << k_2$, i.e., then step 1 will be the rate-determining step.
- $r_1 = k_1 [NO_2]^2$.
- Since step 1 is the rate-determining step, we can say that, for the overall reaction
- $r = k_1 [NO_2]^2$.

Formulating a Mechanism

- The overall reaction 2 NO + O_2 → 2 NO_2 has been found empirically to be 2nd-order in NO and 1st order in O_2. What could be the mechanism?

$$\frac{dNO_2}{dt} = k[NO]^2[O_2]$$

Mekanisme yang mungkin:

$$NO + NO \underset{k_2}{\overset{k_1}{\rightleftarrows}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{k_3} 2NO_2$$

Formulating a Mechanism

Dari mekanisme reaksi:

$$r = 2k_3[N_2O_2][O_2]$$

Not acceptable !!!!!!

Hukum laju ini masih mengandung intermediate:

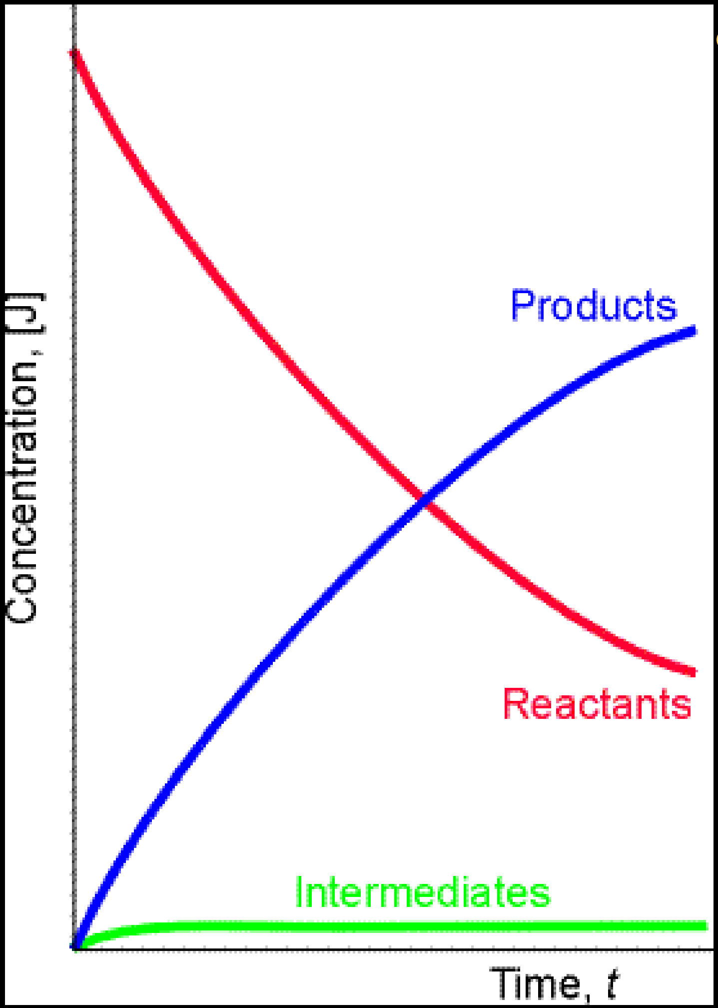
An acceptable rate law for an overall reaction is expressed solely in terms of the species that appear in the overall reaction

- Untuk menghilangkan [N_2O_2] dari ungkapan hk laju digunakan pendekatan steady-state.

Menurut pendekatan ini

$$\frac{d[N_2O_2]}{dt} = 0$$

Solution Using S-S Approx..



- The concentration of intermediate is assumed to remain small and hardly change during much of the reaction.

Formulating a Mechanism

$$\frac{dN_2O_2}{dt} = 0 = k_1[NO]^2 - k_2[N_2O_2] - k_3[N_2O_2][O_2]$$

$$N_2O_2 = \frac{k_1[NO]^2}{k_2 + k_3[O_2]}$$

$$r = 2k_3[N_2O_2][O_2]$$

$$r = 2k_3 \frac{k_1[NO]^2}{k_2 + k_3[O_2]}[O_2]$$

$$r = \frac{2k_3k_1[NO]^2}{k_2 + k_3[O_2]}[O_2]$$

Formulating a Mechanism

$$r = \frac{2k_3k_1[NO]^2[O_2]}{k_2 + k_3[O_2]}$$

Jika $k_2 >>> k_3$

$$r = \frac{2k_3k_1[NO]^2[O_2]}{k_2}$$

$$\frac{dNO_2}{dt} = k[NO]^2[O_2]$$

Hukum laju empirik terpenuhi jika $k_2 >>> k_3$

Another Rate-Determining Step

- Untuk reaksi dan mechanisme yang sama, dan O_2 jumlahnya sedikit::

$$NO + NO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{k_3} 2NO_2$$

- Reaksi 3 sekarang menjadi tahap penentu laju. Karena O_2 jumlahnya terbatas, maka N_2O_2 yang terbentuk menjadi sukar untuk bereaksi dengan O_2. Karena itu hukum laju harus diturunkan dari reaksi 3:

$$r = 2k_3[N_2O_2][O_2]$$

Another Rate-Determining Step

- Tetapi N_2O_2 harus dieliminasi dari persamaan Hk. Laju.
- Jika reaksi 1 dan 2 mencapai keadaan setimbang:
- maka $k_a[NO]^2 = k_a'[N_2O_2]$

$$K = \frac{[N_2O_2]}{[NO]^2} = \frac{k_1}{k_2}$$

$$r = 2k_3[N_2O_2][O_2]$$

$$[N_2O_2] = K[NO]^2$$

$$r = 2k_3K[NO]^2[O_2]$$

Atau k = 2k3K

Rate-Determining Step

- Consider again the oxidation of NO by the first proposed mechanism.

$$NO + NO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{k_3} 2NO_2$$

- Jika O_2 dalam keadaan berlebih dan reaksi 3 berlangsung cepat, so that $k_3[O_2] \gg k_2$
- N_2O_2 bereaksi sangat cepat sehingga sesaat setelah terbentuk langsung bereaksi dg O_2.

Rate-Determining Step

- The overall rate of the reaction is therefore determined by the rate of forming N_2O_2.
- Formation of N_2O_2 is the **rate-determining step**/tahap penentu laju
- Laju reaksinya menjadi: $r = 2\, k_1[NO]^2$

Exercise E7.12

- An alternative mechanism that may apply when the concentration of O_2 is high and that of NO is low is one in which:

$$NO + O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO-O_2$$

Diikuti oleh:

$$NO-O_2 + NO \xrightarrow{k_3} 2NO_2$$

Turunkan bahwa hukum lajunya sesuai dengan pengamatan empiris

$$\frac{dNO_2}{dt} = k[NO]^2[O_2]$$

Exercise E7.12

- Dekomposisi ozon menjadi oksigen berlangsung melalui mekanisme sbg berikut:
  - Turunkan ungkapan hukum laju untuk –d[O3]/dt
  - Pada kondisi apakah reaksi ini merupakan orde 1 terhadap O3?, tunjukan bagaimana hukum laju pada jawaban a dapat direduksi untuk hal tersebut.

$$O_3 \xrightarrow{k_1} O_2 + O$$

$$O + O_2 \xrightarrow{k_{-1}} O_3$$

$$O_3 + O \xrightarrow{k_2} 2O_2$$

Minggu Depan

- Pelajari kinetika (Ungkapan hukum lajunya)

- Reaksi berantai
- Reaksi bercabang