Kinetika Kimia

Studi/kajian tentang laju reaksi

http:// fpmipa.upi.edu/kuliahonline

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

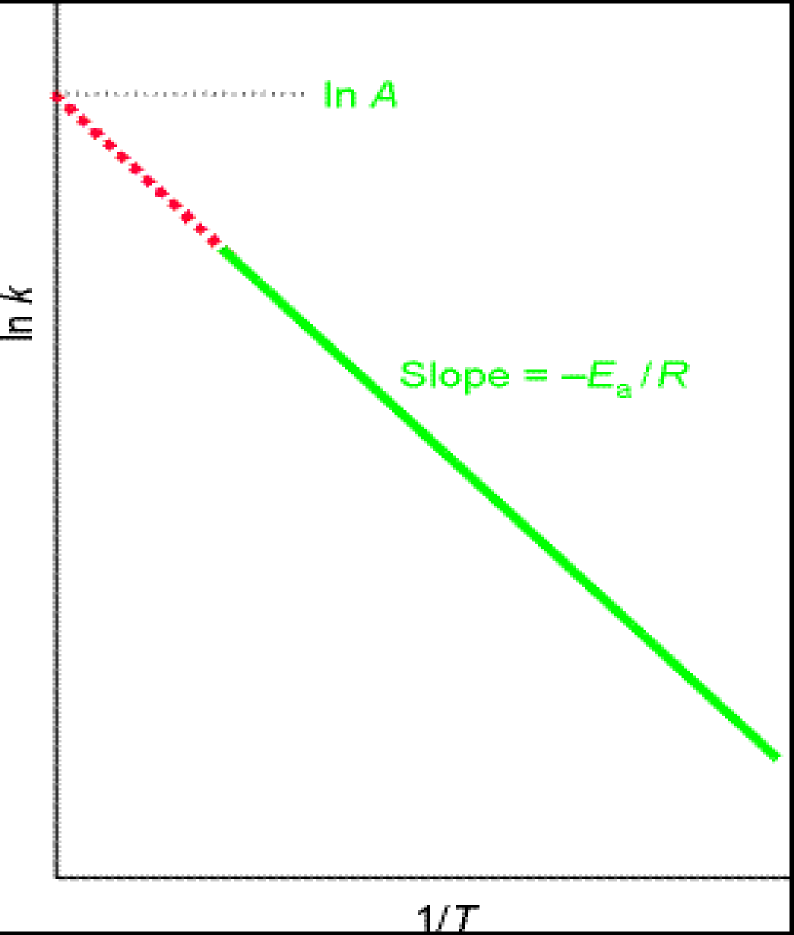
Ujian Tengah Semester

Senin, 31 Maret 2008

Bahan

- Pengertian Laju reaksi
- Pengukuran Laju
- Penentuan Hk. Laju
- Pengaruh Temperatur pada Laju reaksi

Temperatur dan Laju Reaksi; Arhenius



- Arrhenius mengamati bahwa kurva (ln *k)* vs. (1/*T*) menghasilkan garis lurus, pada hampir semua kasus,

- Nilai Gradien adalah charakteristik dari suatu reaksi dan selalu berharga negative.

- Dari pengamatan tersebut dapat diturunkan persamaan

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T}$$

Temperatur dan Laju Reaksi; Arhenius

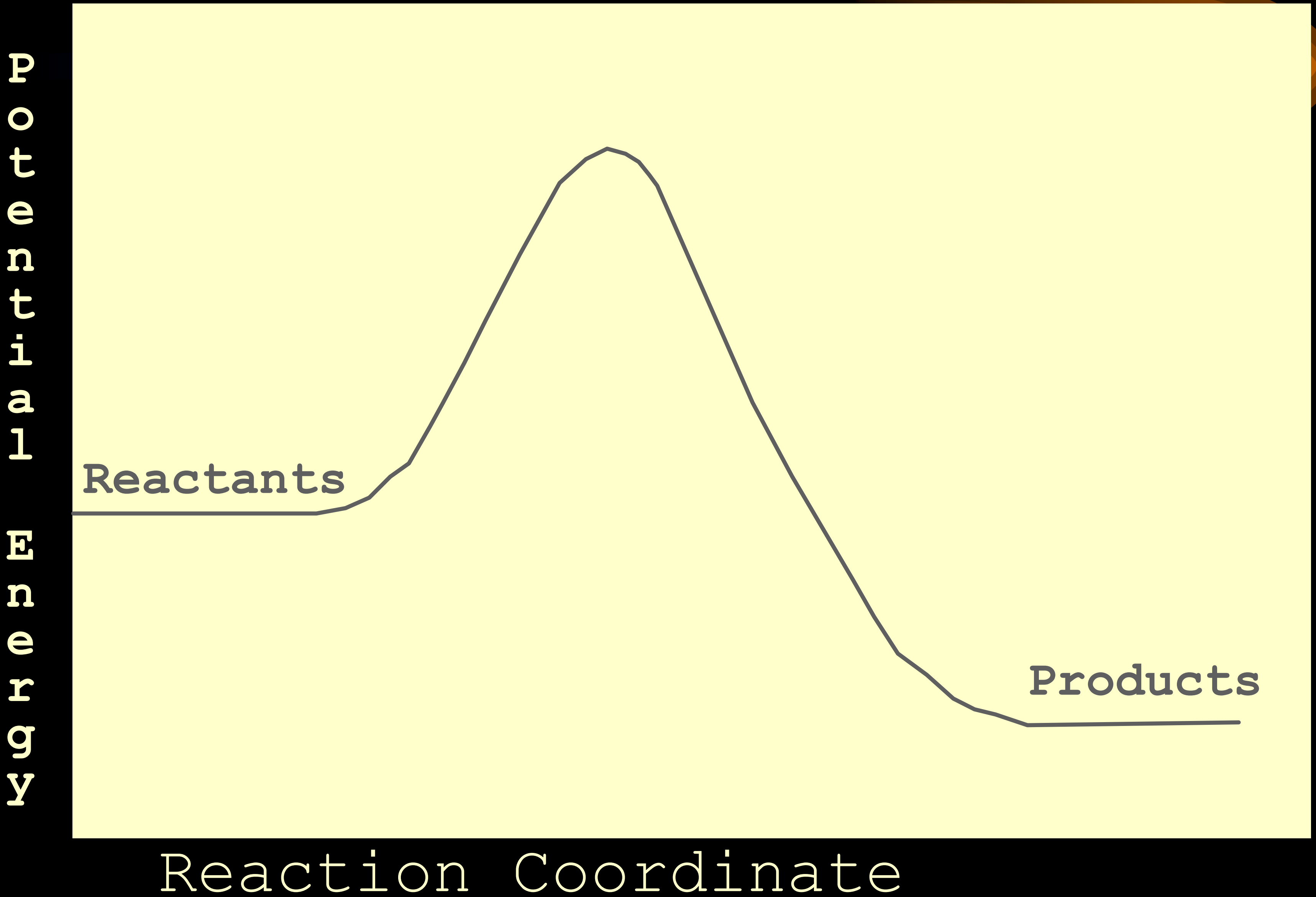
Bentuk lain persamaan di atas adalah:

$$k = Ae^{-\frac{E_a}{RT}}$$

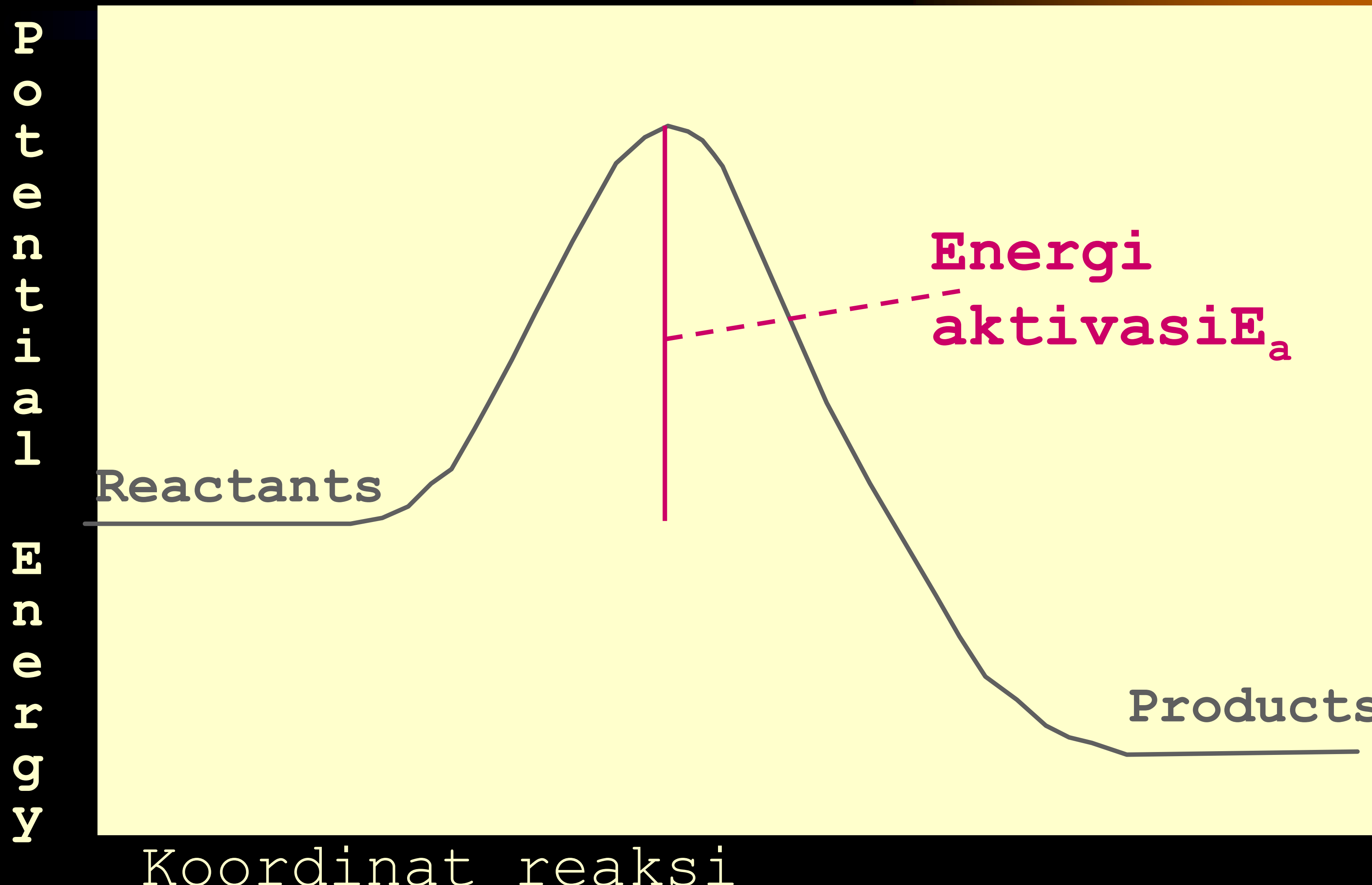
Dinamakana persamaan arhenius

- Ea = Energi aktivasi
- A = faktor preexponensial atau faktor Arhenius

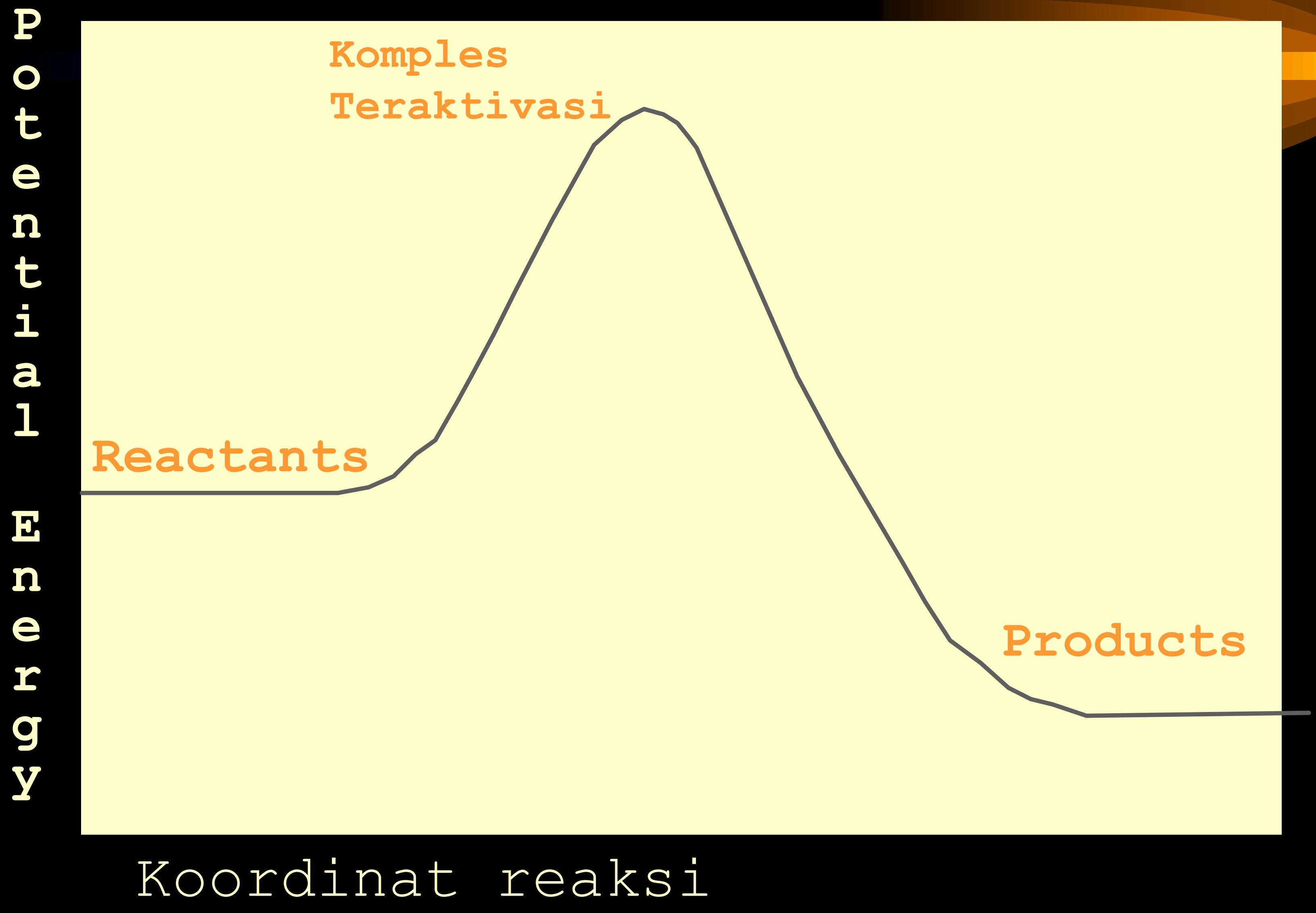
Arhenius; Energi Aktivasi



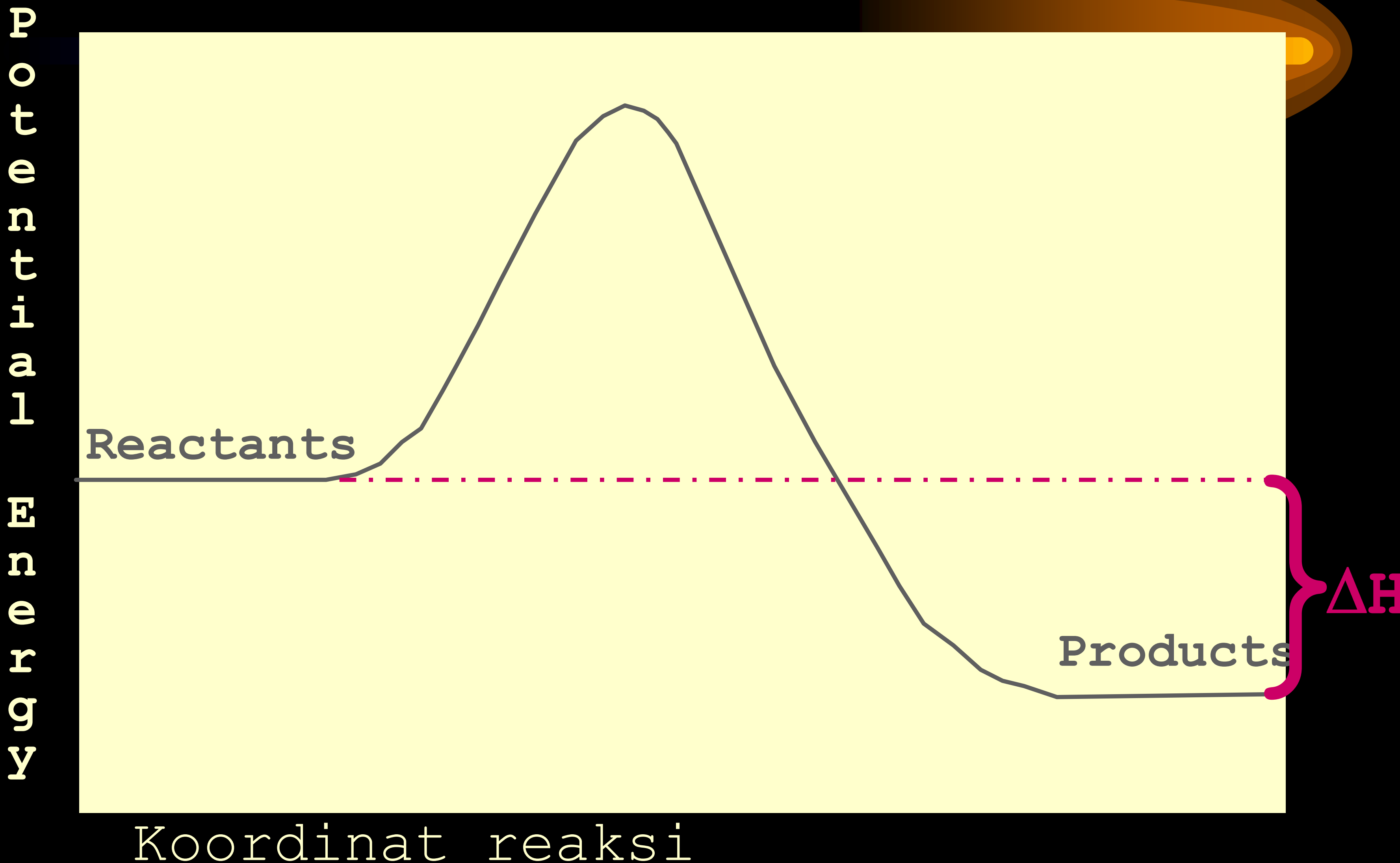
Arrhenius; *Energi Aktivasi*



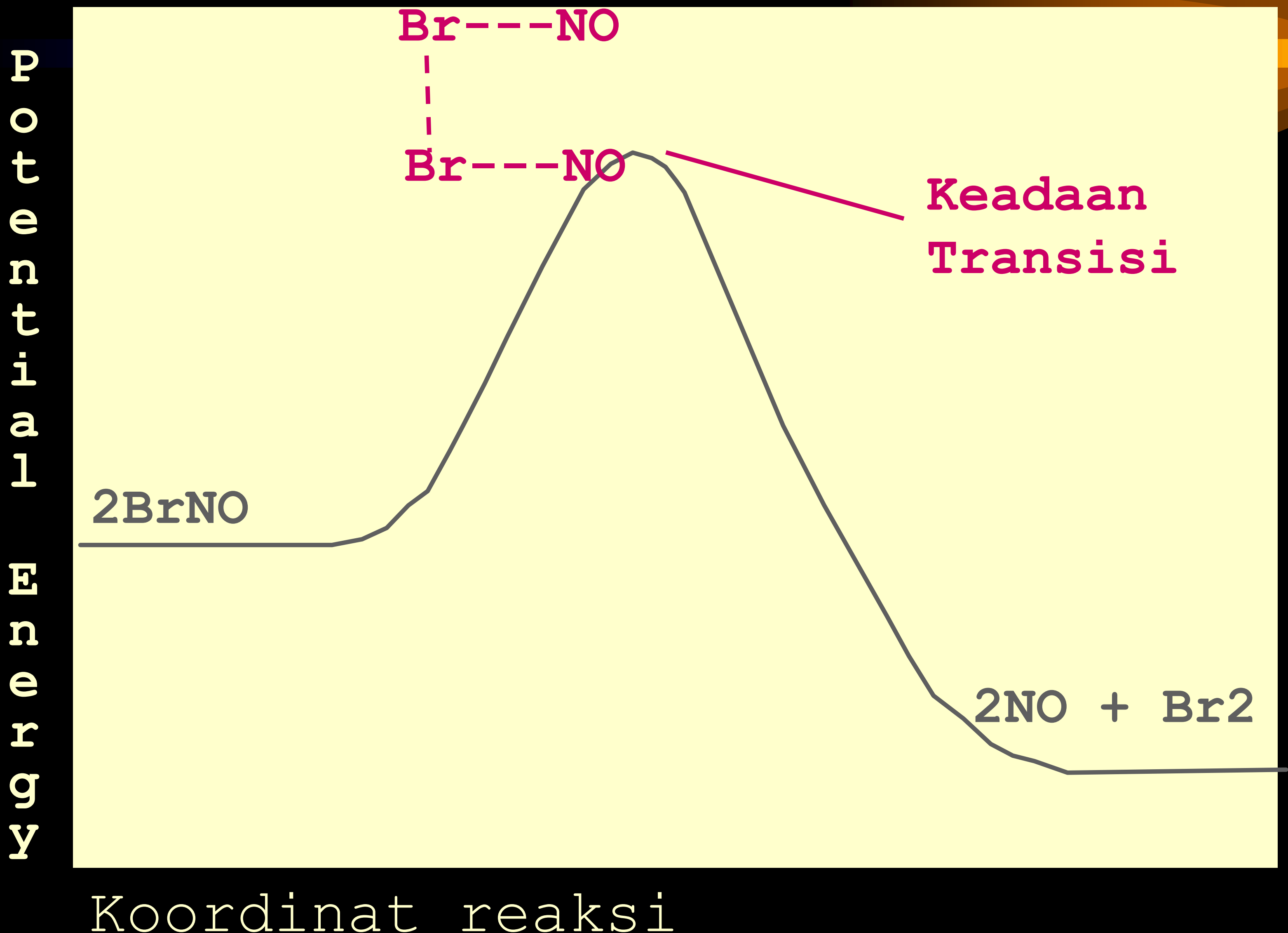
Arhenius; Energi Aktivasi



Arhenius; Energi Aktivasi



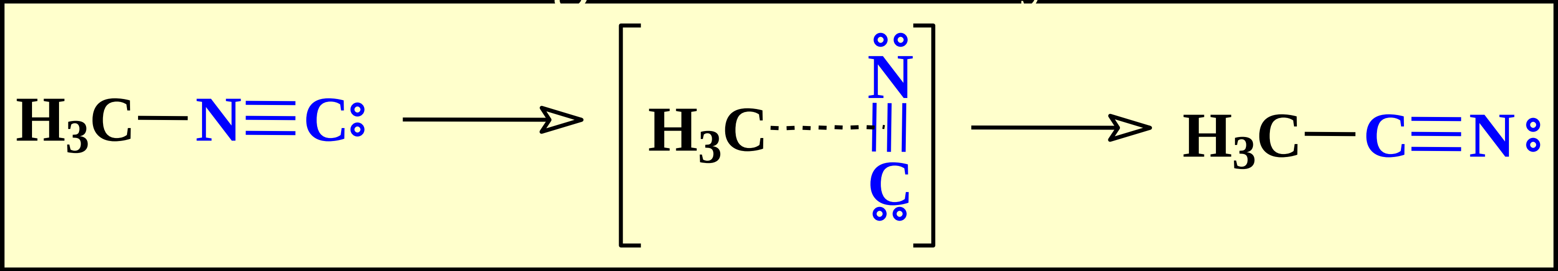
Arrhenius; Energi Aktivasi



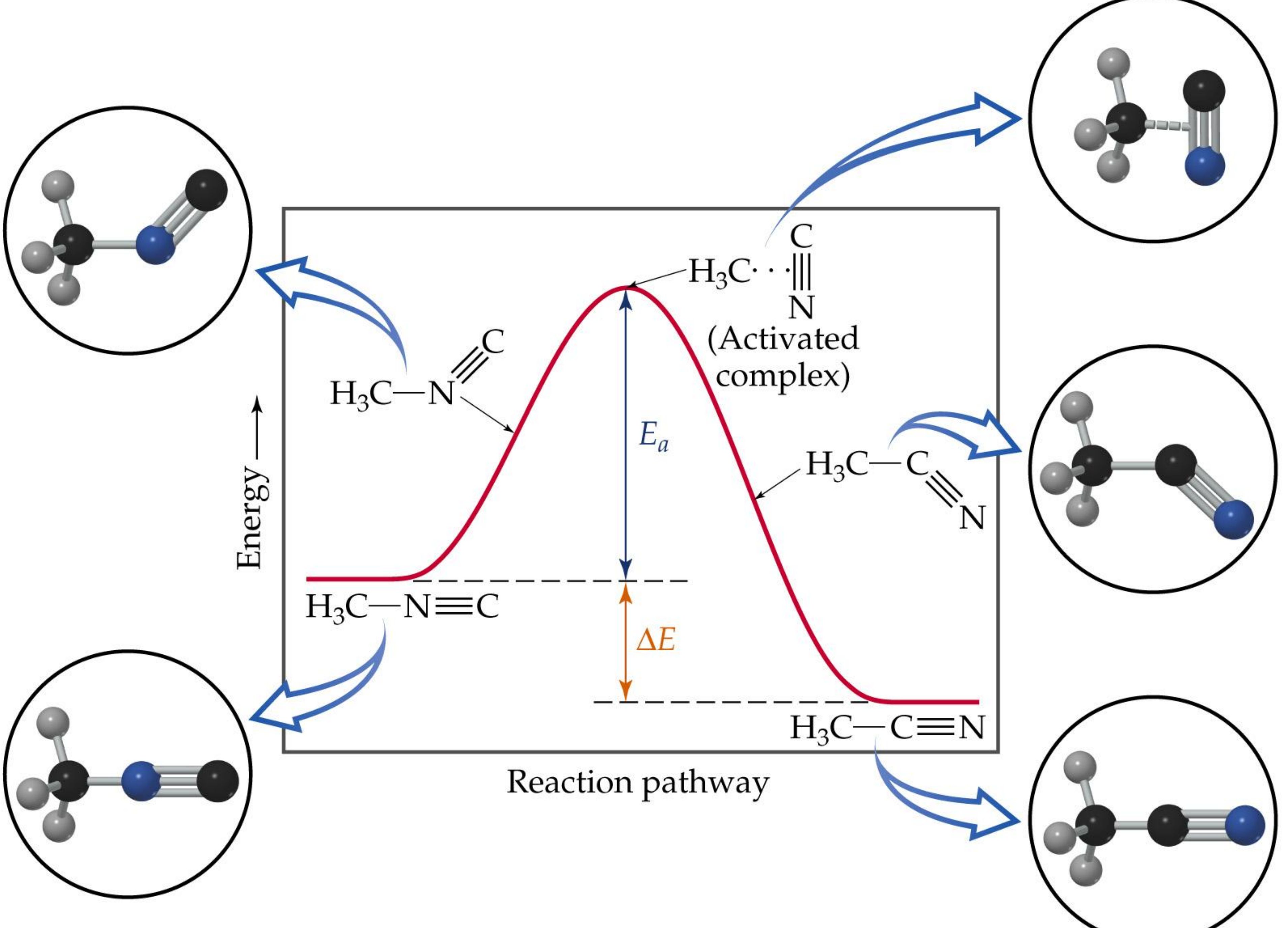
Temperature and Rate

Activation Energy; another example

- Consider the rearrangement of methyl isonitrile:



  - In H_3C-N≡C, the C-N≡C bond bends until the C-N bond breaks and the N≡C portion is perpendicular to the H_3C portion. This structure is called the activated complex or transition state.
  - The energy required for the above twist and break is the activation energy, E_a.
  - Once the C-N bond is broken, the N≡C portion can continue to rotate forming a C-C≡N bond.



Energy
$H_3C—N{\equiv}C$
$H_3C—N{\equiv}C$
$H_3C\cdot\cdot\cdot C{\equiv}N$
(Activated complex)
E_a
ΔE
$H_3C—C{\equiv}N$
$H_3C—C{\equiv}N$
Reaction pathway

Some Points about E_a

- E_a Selalu positif.
- Semakin besar nilai E_a, semakin lambat suatu reaksi
- Semakin besar nilai Ea semakin tajam slope

  (ln *k*) vs. (1/*T*).

  A high activation energy corresponds to a reaction rate that is very sensitive to temperature.
- The value of E_a itself DOES NOT CHANGE with temperature.

Arrhenius; Faktor Frekuensi

Total tumbukan dengan energi yang melampaui Ea:

$$ze^{-Ea/RT}$$

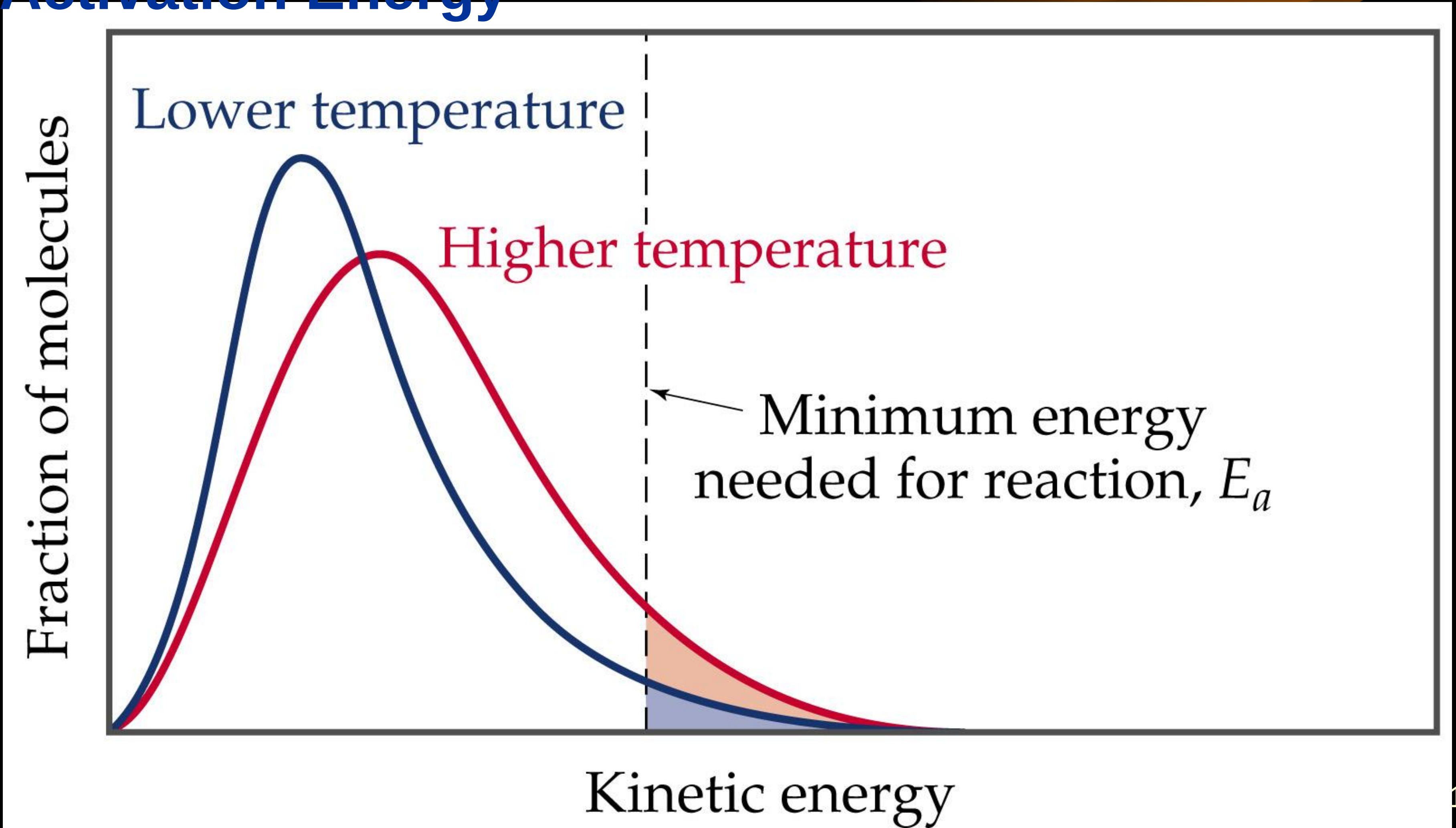
- z = total collisions
- e is Euler's number (opposite of ln = 2,72)
- E_a = activation energy
- R = ideal gas constant
- T is temperature in Kelvin

Jika seluruh tumbukan yang mealmpaui Ea menghasilkan reaksi:

$$k = ze^{-Ea/RT}$$

Temperature and Rate

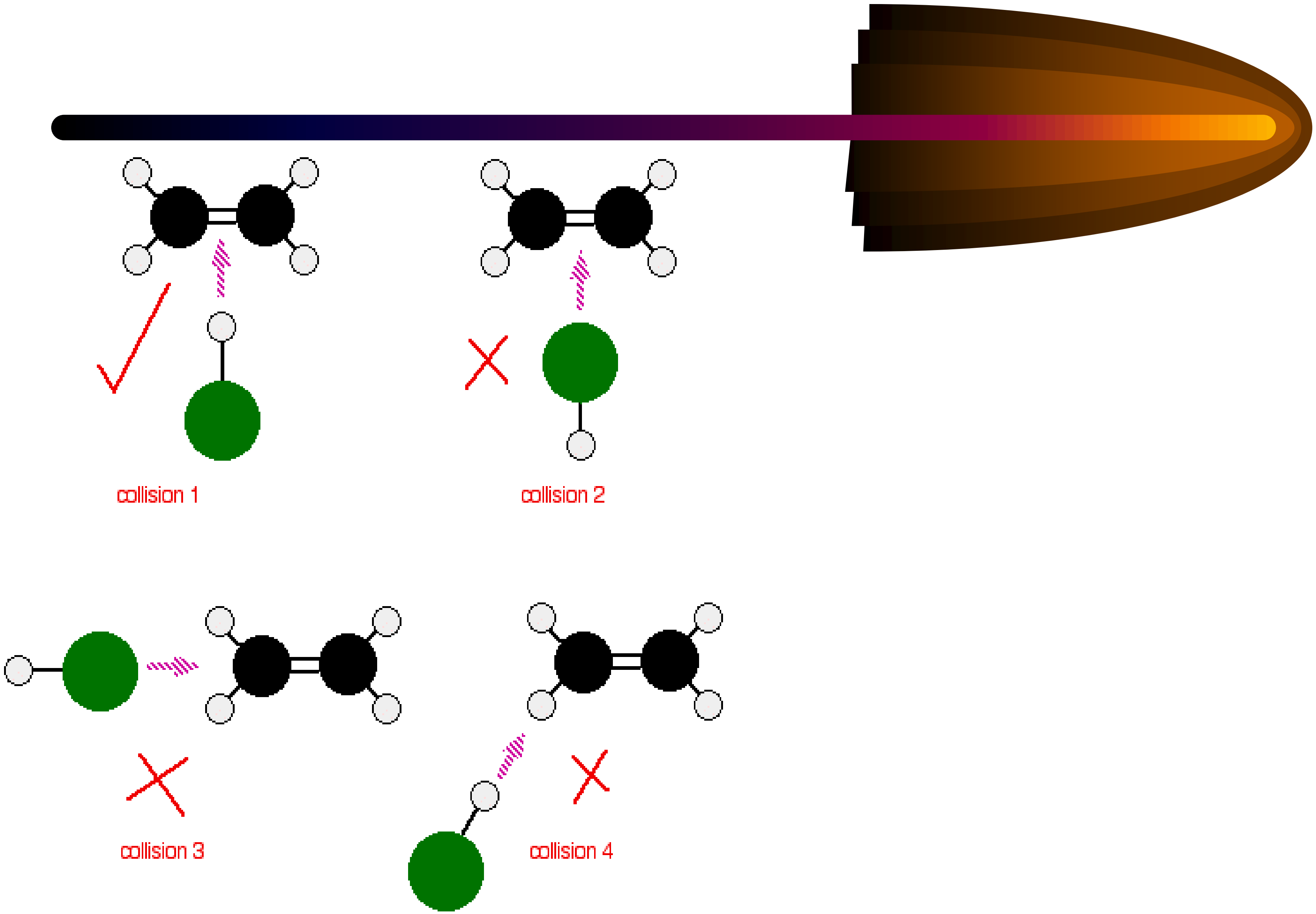
Activation Energy



Arrhenius; Faktor Frekuensi

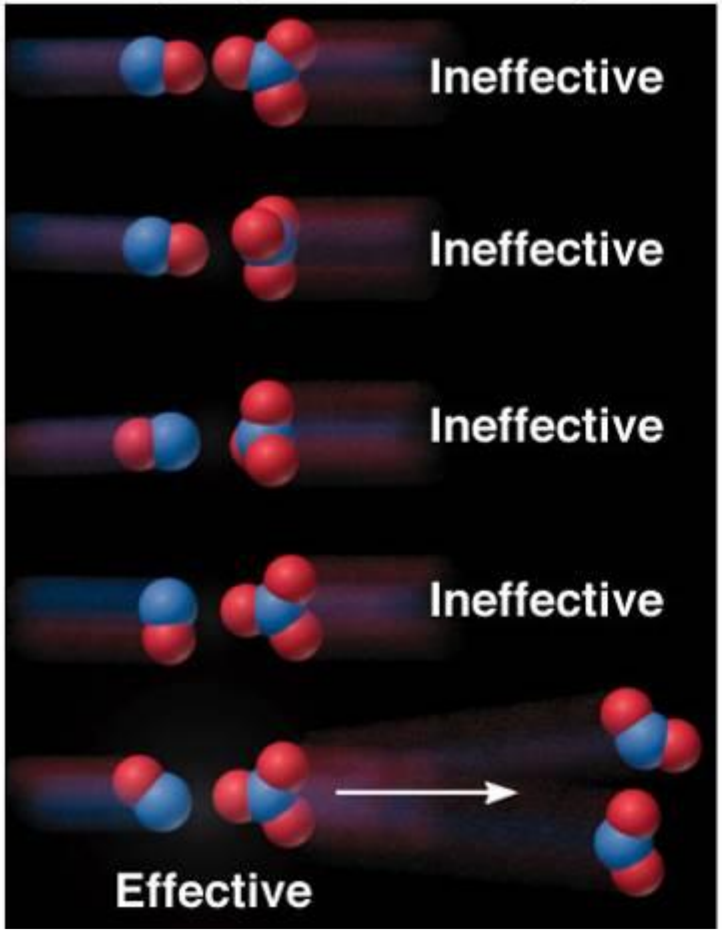
- Laju reaksi yang diamati selalu lebih rendah dari jumlah tumbukan
- Hanya tumbukan efektif yang menghasilkan reaksi
- Tumbukan yang effective terkait dengan orientasi molekul (faktor sterik)
- Dalam persamaan Arhenius factor sterik ditulis sebagai p
- Sehingga:

$$k = pze^{-Ea/RT}$$

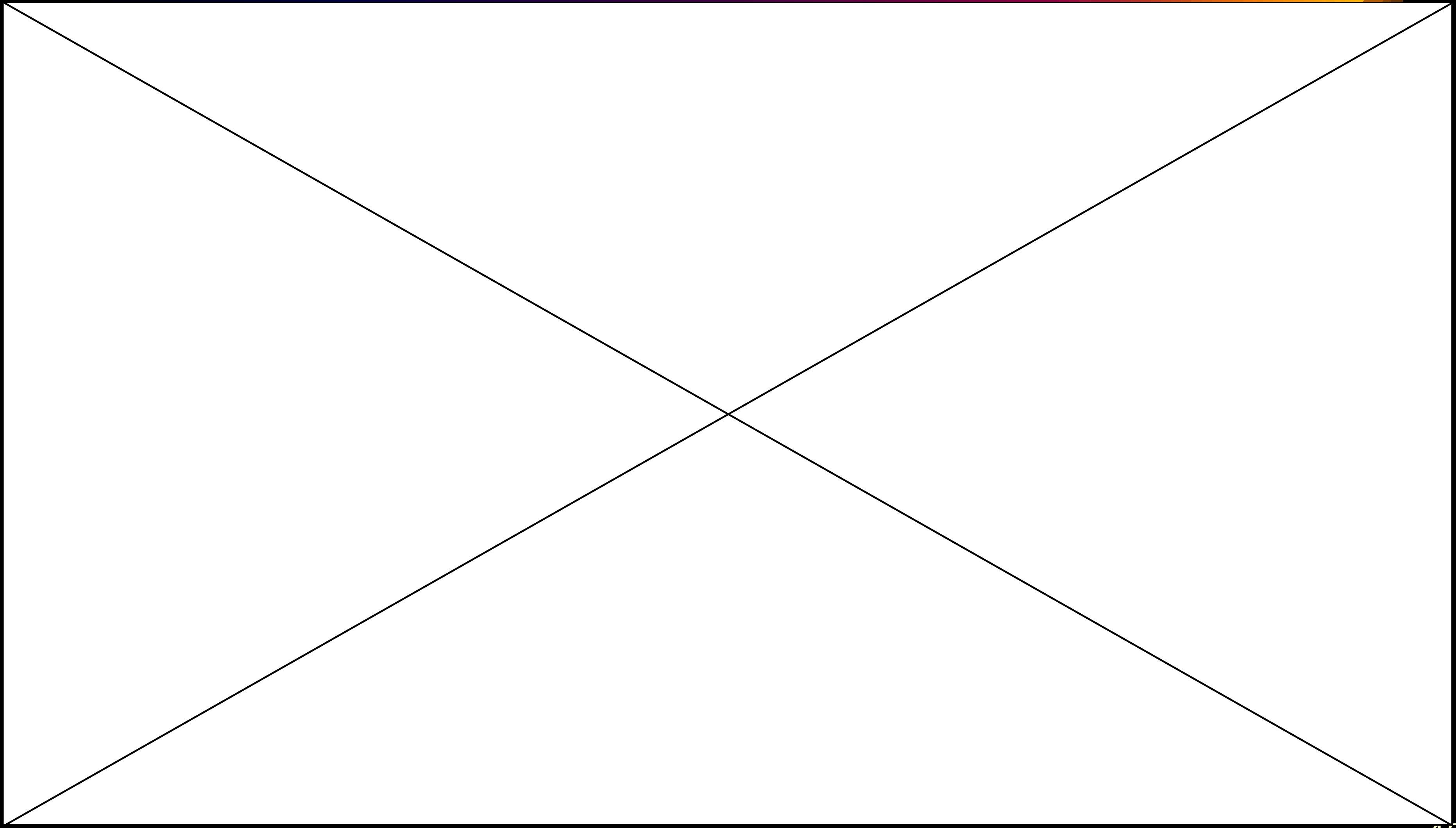

collision 1
collision 2
collision 3
collision 4

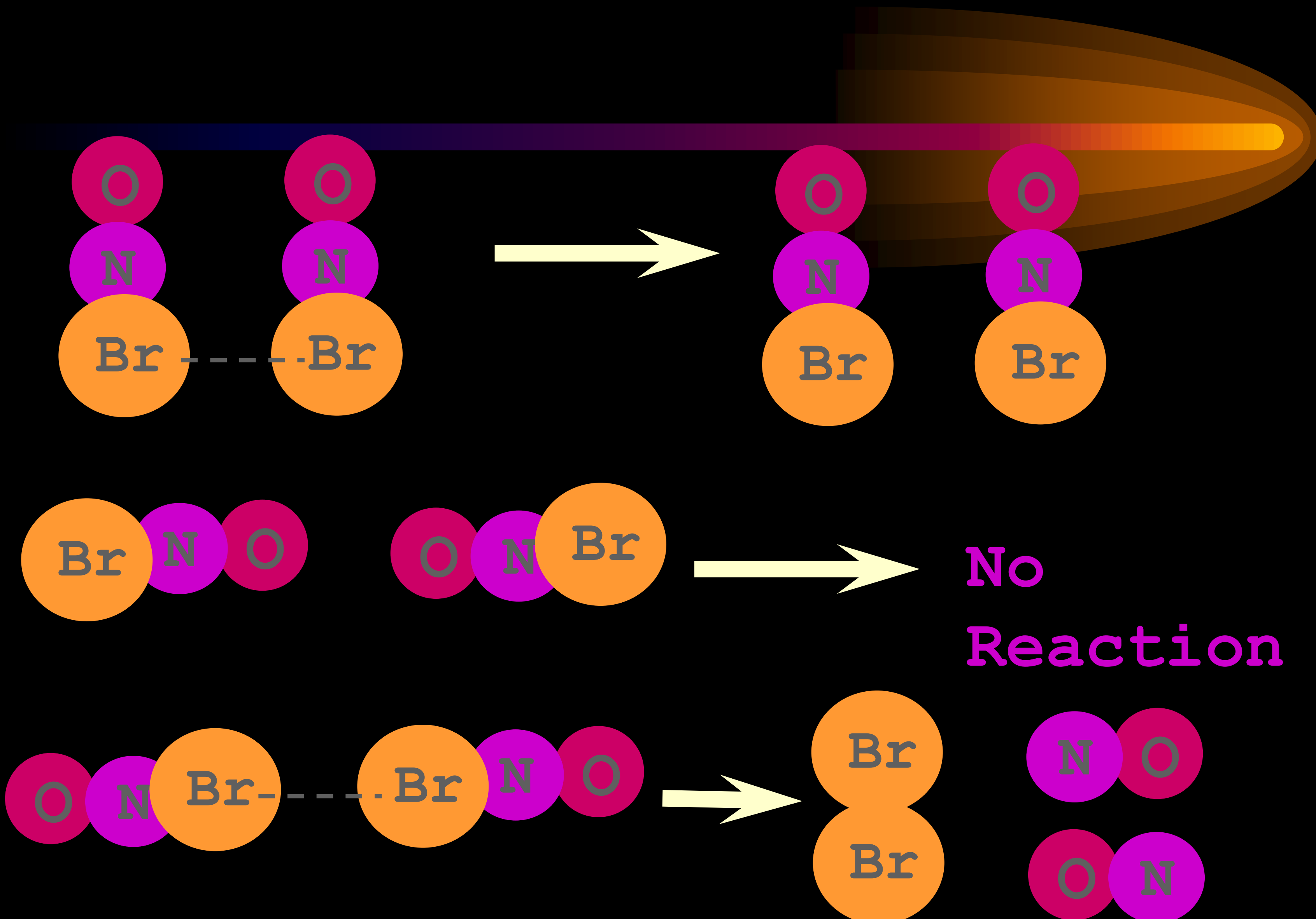
Not all collisions leads to a reaction

For effective collisions proper orientation of the molecules must be possible



Molecular Orientation and Effective Collisions





O
N
Br
O
N
Br
O
N
Br
O
N
Br
Br
N
O
O
N
Br
No
Reaction
O
N
Br
Br
N
O
Br
Br
N
O
O
N

Temperature and Rate

The Orientation Factor

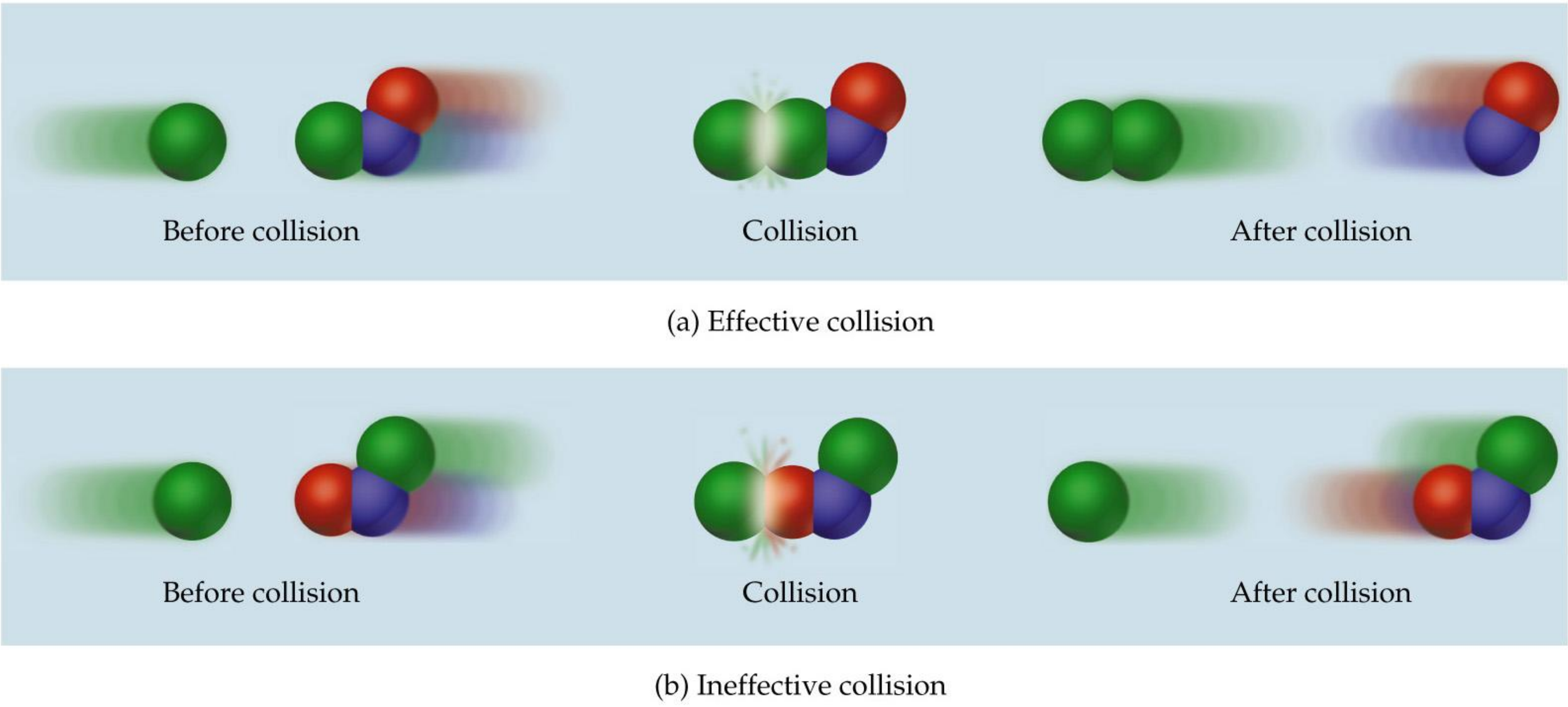
- Consider the reaction between an atom of chlorine and a molecule of nitrosyl chloride:

$$Cl + NOCl \rightarrow NO + Cl_2$$

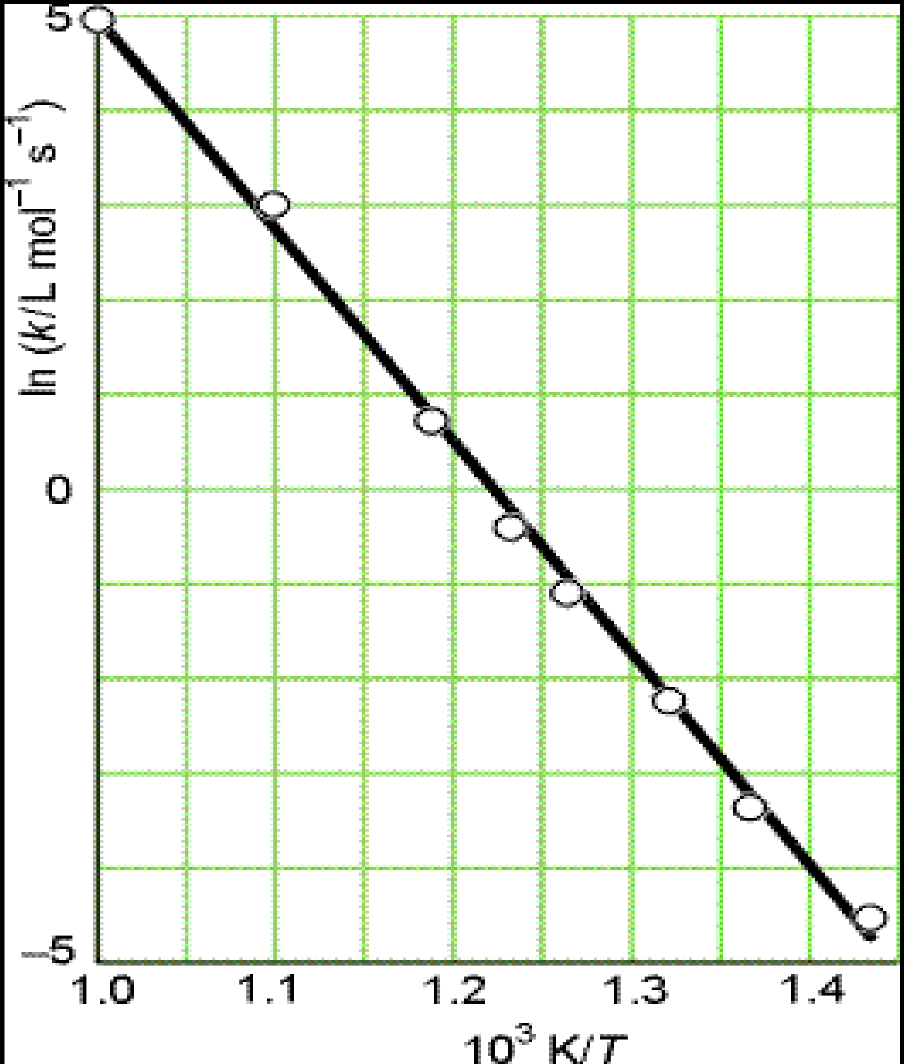
- There are two possible ways that Cl atoms and NOCl molecules can collide; one is effective and one is not.

Temperature and Rate

The Orientation Factor



Determining Arrhenius Parameters



- Baik *A* atau E_a dapat ditentukan dari grapik (ln *k*) vs. (1/*T*).
- Gradien yang bernilai negatif dapat dikalikan dg. -*R* to give E_a (positive).
- The y-intercept = ln *A*

Example E7.8

- Tentukan A dan E_a dari data berikut

T/K	300	350	400	450	500
k/$M^{-1}s^{-1}$	7.9E6	3.0E7	7.9E7	1.7E8	3.2E8

-

Example E7.8

ln *k*	15.88	17.22	18.18	18.95	19.58
$1/T$ (x 10^3)	3.33	2.86	2.50	2.22	2.00

- Putting these values into a linear regression program gives intercept = 25.11 = ln *A*, so $A = 8.0 \times 10^{10}\ M^{-1}s^{-1}$
- Slope = - 2.8 x 10^3, so E_a = - slope x *R* = 23 kJ/mol

Example E7.9

- The activation energy of one of the reactions in the Krebs citric acid cycle is 87 kJ/mol. What is the change in the rate constant when the temperature falls from 37^{o}C to 15^{o}C?

Exercise E7.10

- What is the fraction of collisions that have sufficient energy for reaction if the activation energy is 50 kJ/mol and the temperature is (a) 25^{o}C, (b) 500^{o}C?

Exercise E7.10

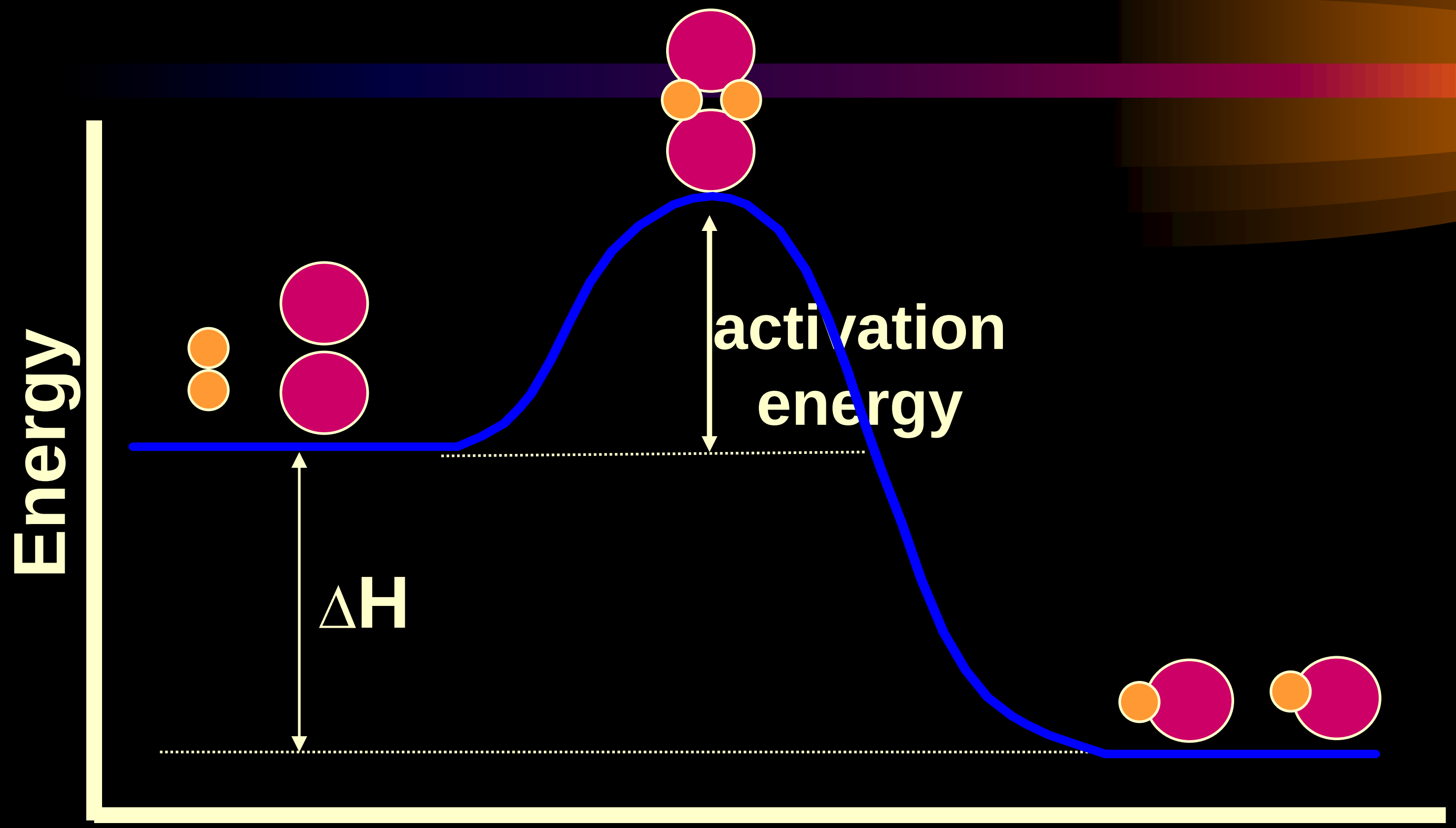
- $f = e^{-Ea/RT}$
- (a) *f* = exp [✐50 x 10^3 J/mol/(8.314 J/K/mol x 298 K)] = exp [✐20.18] = <u>1.7 x 10^{-9}</u>
- (b) *f* = exp [✐50 x 10^3 J/mol/(8.314 J/K/mol x 773 K)] = exp [✐7.78] = <u>4.2 x 10^{-4}</u>

Activated Complex Theory

energy rising and reaching a maximum.

- At this maximum the activated complex is formed.
- This concept applies to reactions in solution as well as to gas-phase reactions.
  - The solvent molecules may be involved in the activated complex.

Energy Diagrams



At the energy maximum the activated complex, which has a definite composition and a loose structure, is formed.

However, the complex is not stable and cannot be isolated.

Temperature and Rate

The Collision Model

- Goal: to explain why rates of reactions increase as concentration and temperature increase.
- Basic assumption of the collision model: in order for molecules to react they must collide.
- The greater the rate of collisions the faster the rate of reaction.
- The greater the concentration of molecules present, the greater the probability of collision and the faster the rate of reaction.

Temperature and Rate

The Collision Model

- The higher the temperature, the faster the molecules will move on average, thereby increasing both the rate of collisions and the rate of reaction.
- Complication: known that not all molecular collisions lead to products. In fact, only a small fraction of collisions lead to product. Why? Two reasons.
- In order for reaction to occur the reactant molecules must collide in the correct orientation and with enough energy to form products.

Temperature and Rate

Activation Energy

- The change in energy for the reaction is the difference in energy between CH_3NC and CH_3CN.
- The activation energy is the difference in energy between reactants, CH_3NC and transition state.
- The rate of reaction depends on E_a.
- Notice that if a forward reaction is exothermic ($CH_3NC \rightarrow CH_3CN$), then the reverse reaction is endothermic ($CH_3CN \rightarrow CH_3NC$).

Temperature and Rate

Activation Energy

- How does a methyl isonitrile molecule gain enough energy to overcome the activation energy barrier?
- From kinetic molecular theory, we know that as temperature increases, the total kinetic energy increases.
- We can show the fraction of molecules, *f*, with energy equal to or greater than E_a is

$$f = e^{-E_a/RT}$$

where *R* is the gas constant (8.314 J/mol·K).

Temperature and Rate

The Arrhenius Equation

- Arrhenius discovered that most reaction-rate data obeyed the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

  - k is the rate constant, E_a is the activation energy, R is the gas constant (8.314 J/K-mol) and T is the temperature in K.
  - A is called the frequency factor.
  - A is a measure of the probability of a favorable collision.
  - Both A and E_a are specific to a given reaction.

Temperature and Rate

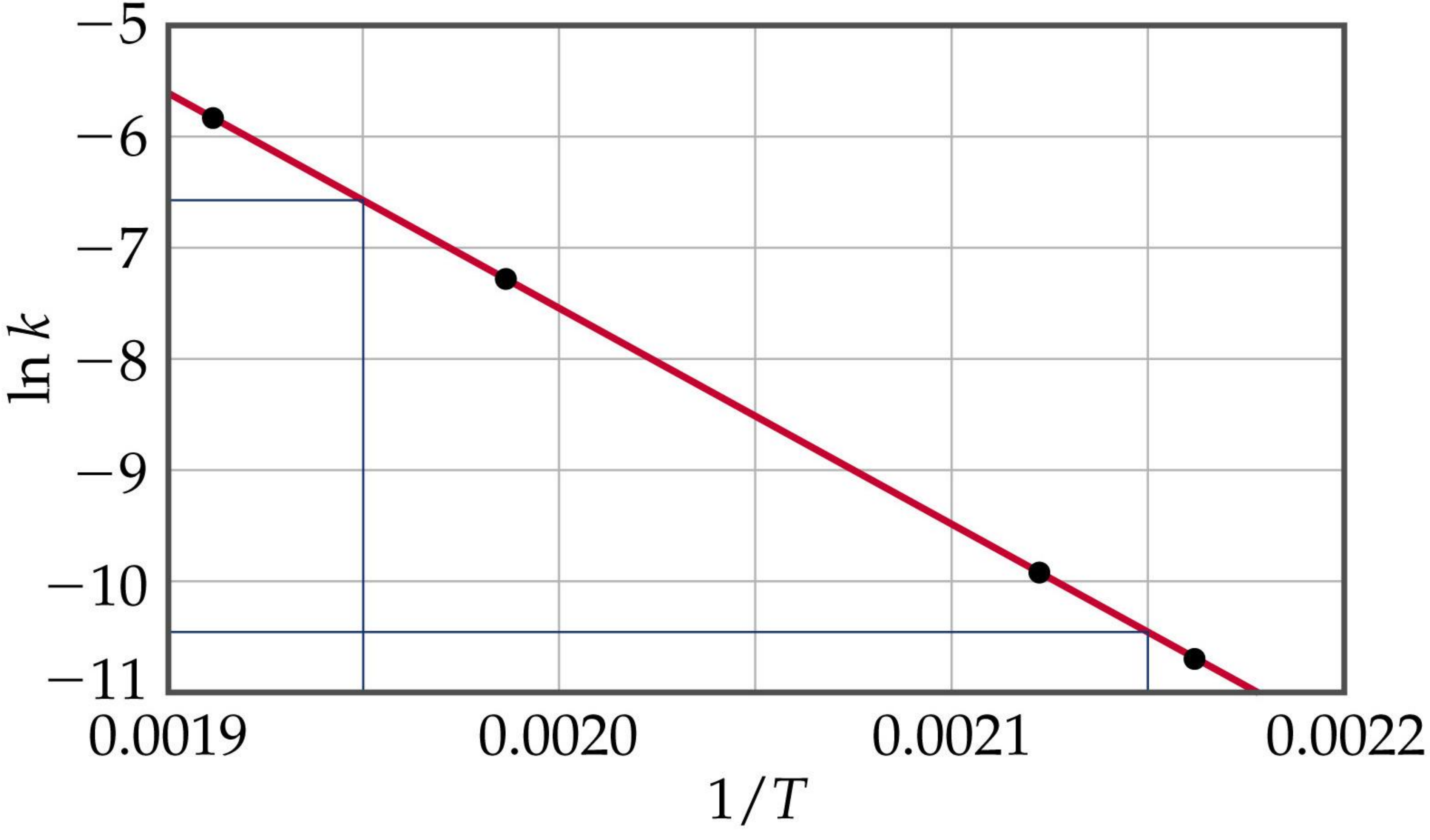
Determining the Activation Energy

- If we have a lot of data, we can determine E_a and A graphically by rearranging the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

- From the above equation, a plot of ln k versus $1/T$ should be a straight line with a slope of $-E_a/R$ and an intercept of ln A.

Temperature and Rate



Temperature and Rate

Determining the Activation Energy

- If we do have only two values of the rate constant, k_1 and k_2 say, determined at temperatures T_1 and T_2 respectively, then we apply the Arrhenius equation to both sets of conditions:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

$$\ln k_1 - \ln k_2 = \left(-\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Dependence of reaction rate on concentration and temperature

We shall now use a mathematical model, into which the rate law expression and the Arrhenius equation have been built, in order to gain a feel for the roles played by concentration, temperature and activation energy in determining the rate of a simple reaction:

$$A(aq) = B(aq)$$

Suppose that the reactant A is coloured blue in solution, while the product B is colourless.

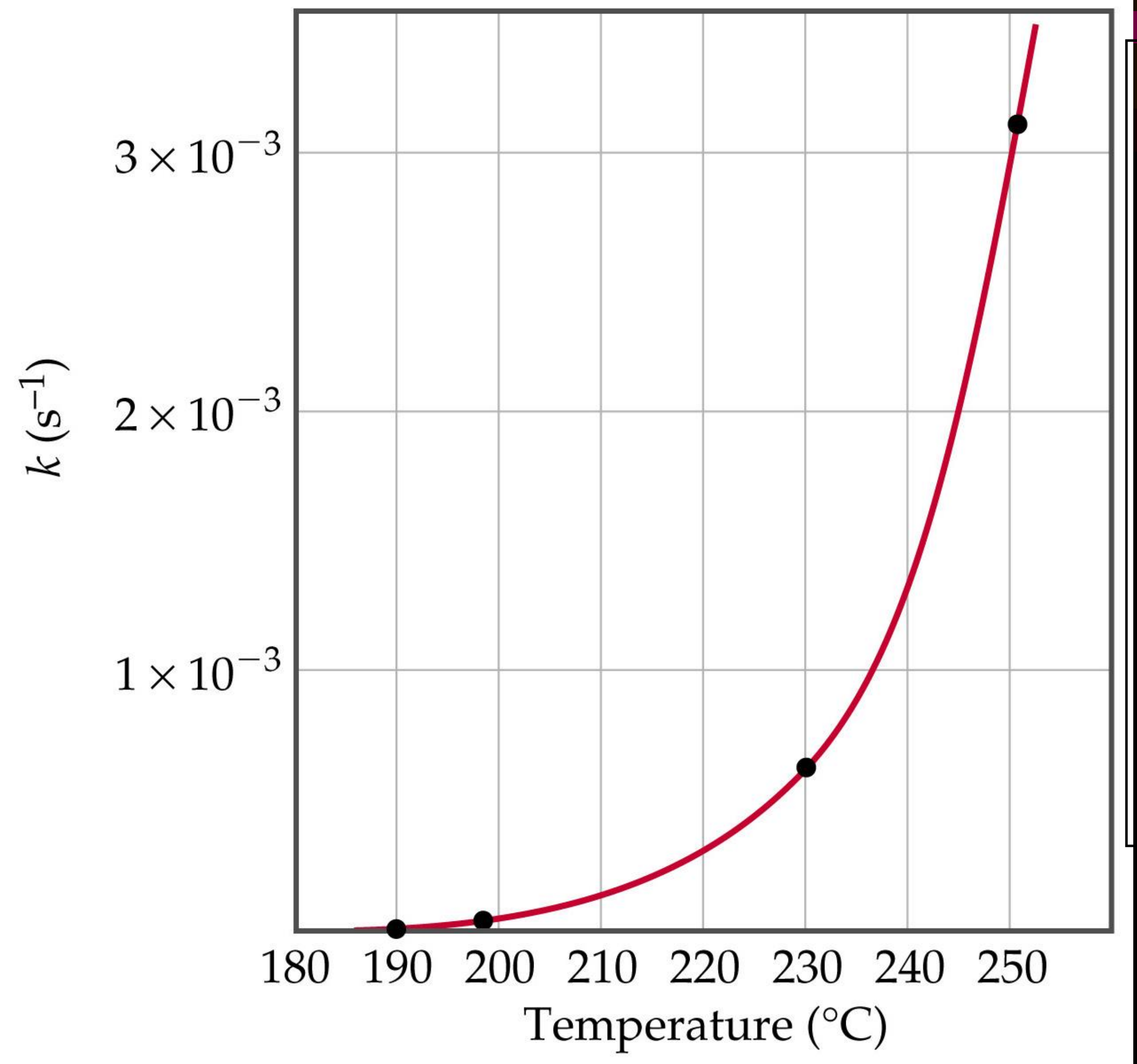
Outcome of molecular collisions

We shall now see how the temperature of the reaction and the orientation of the molecules can affect the likely outcome of a molecular collision.

Temperature and Rate

- Most reactions speed up as temperature increases. (E.g. food spoils when not refrigerated.)
- It is commonly observed that the rates of chemical reactions are very sensitive to temperature
- As a rough rule of thumb, the rates of many chemical reactions approximately double for every 10 $^{\circ}C$ rise in temperature.

Temperature and Rate



- As temperature increases, the rate constant for the reaction increases quite dramatically.