Ministry of Higher Education and Scientific Research
AL-Mustaqbal University College of Science
Department of Biochemistry

Physical Chemistry

Lecture 5

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First semester

Temperature and reaction rate

By

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Temperature and reaction rate

A- **Ability to meet:**

(molecules that are well mixed will have a greater chance of colliding)

Concentration of reactants:

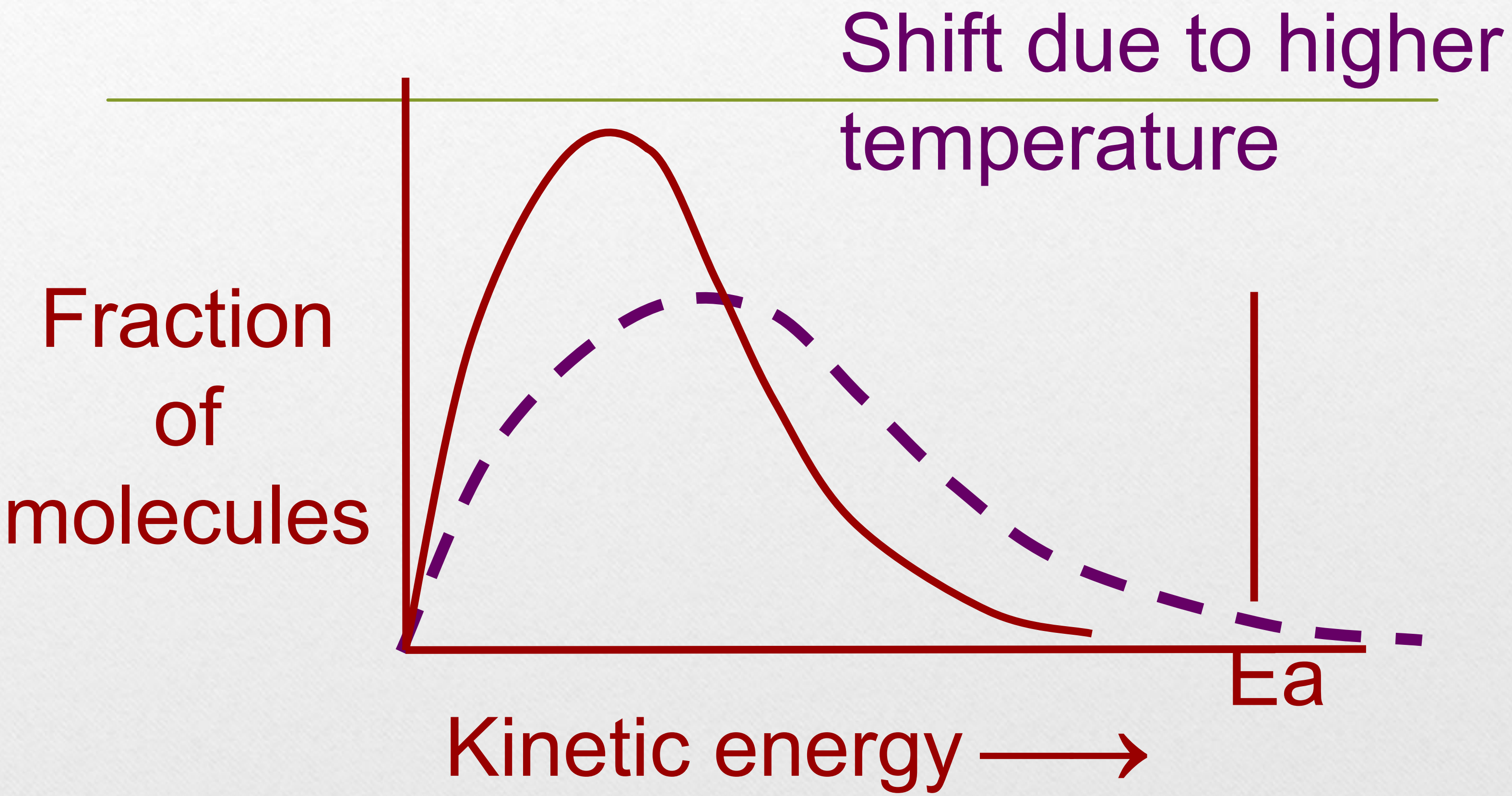
(more molecules means more collisions)

Temperature:

(faster moving molecules means more collisions per unit of time).

Temperature and reaction rate

- By increasing the temperature, a small number of molecules reach Ea.
- The reaction is exothermic, further increasing temperature and causing more molecules to reach Ea, etc.



Shift due to higher temperature

Fraction of molecules

Ea

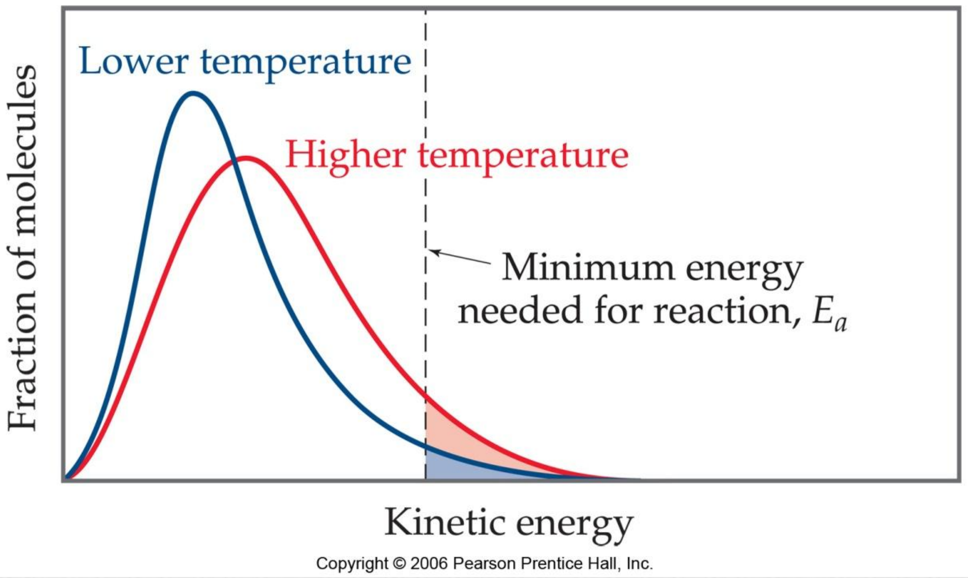
Kinetic energy ⟶

Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

$$f = e^{\frac{-E_a}{RT}}$$

where R is the gas constant and T is the Kelvin temperature.



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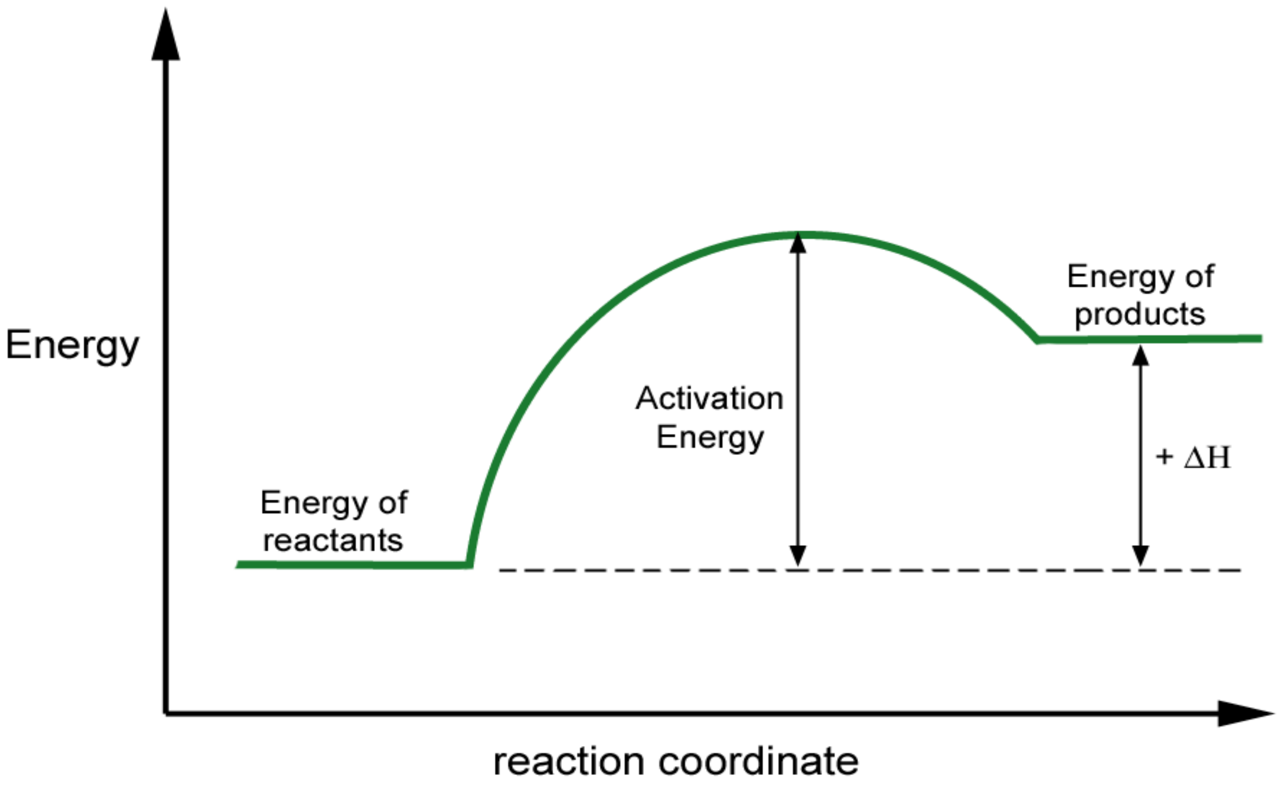
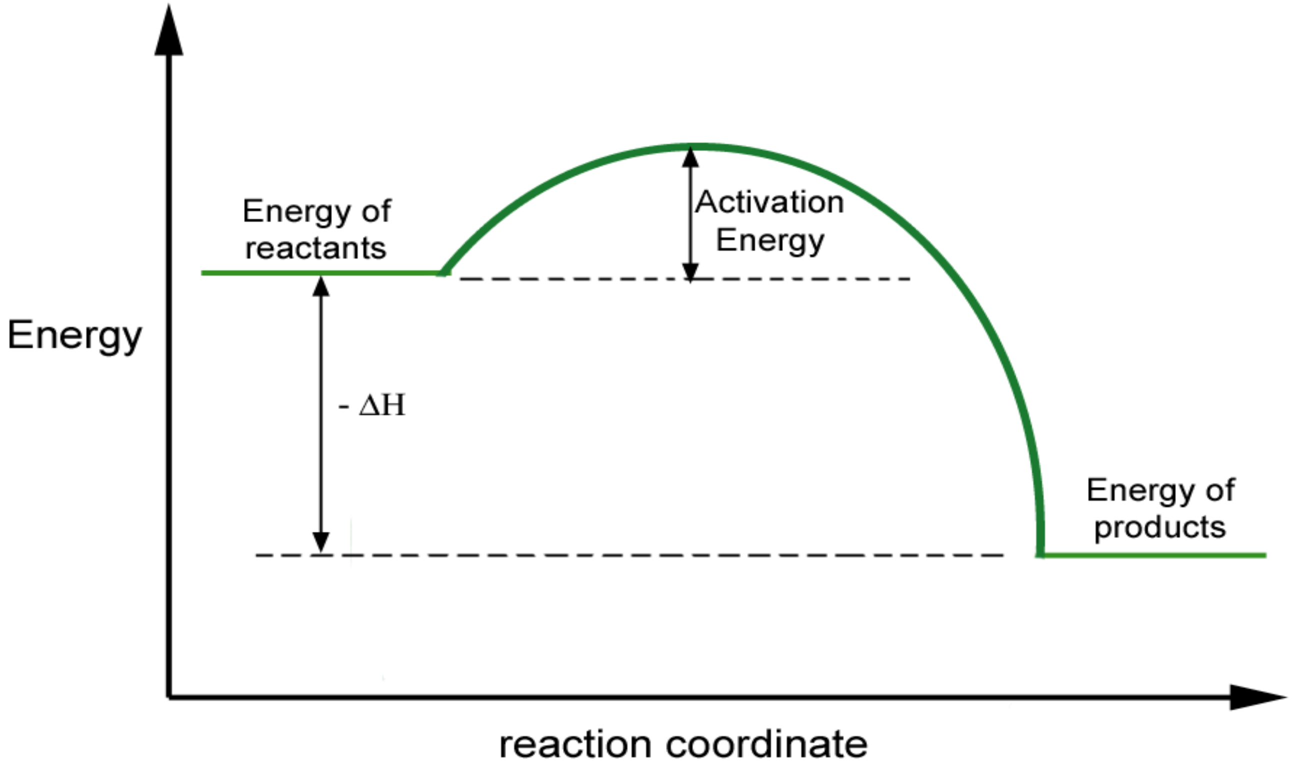
Endothermic Reactions



Exothermic Reactions



The Arrhenius Equation

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

- k = rate constant at temperature T
- A = frequency factor
- E_a = activation energy
- R = Gas constant, 8.31451 J/K·mol

The Arrhenius Equation, Rearranged

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln(A)$$

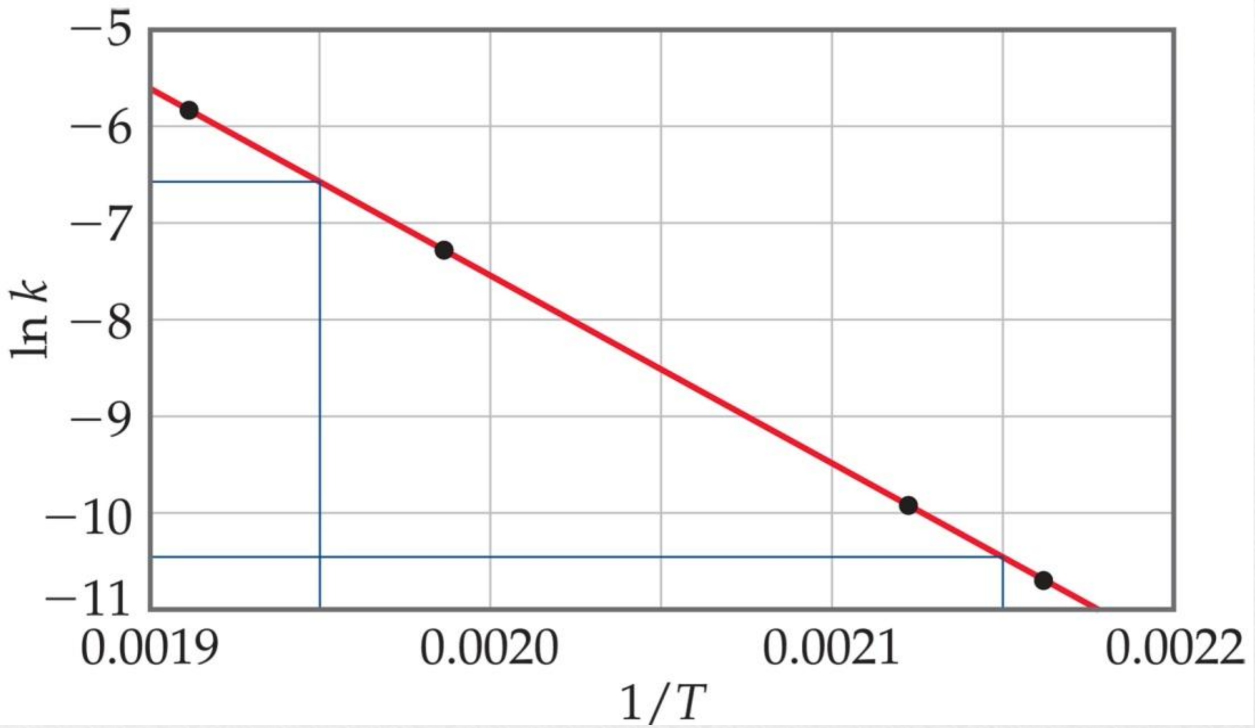
- Simplifies solving for E_a
- $-E_a / R$ is the slope when $\ln(k)$ is plotted against $(1/T)$
- $\ln(A)$ is the y-intercept
- Linear regression analysis of a table of $\ln(k)$ vs. $(1/T)$ can quickly yield a slope
- ***$E_a = -R(slope)$***

Arrhenius Equation

Taking the natural logarithm of both sides, the equation becomes.

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y \quad = \quad m \quad x \quad + \quad b$$



Therefore, if k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of $\ln k$ vs. $\frac{1}{T}$.

Catalysis

- Catalyst:
- A substance that speeds up a reaction without being consumed

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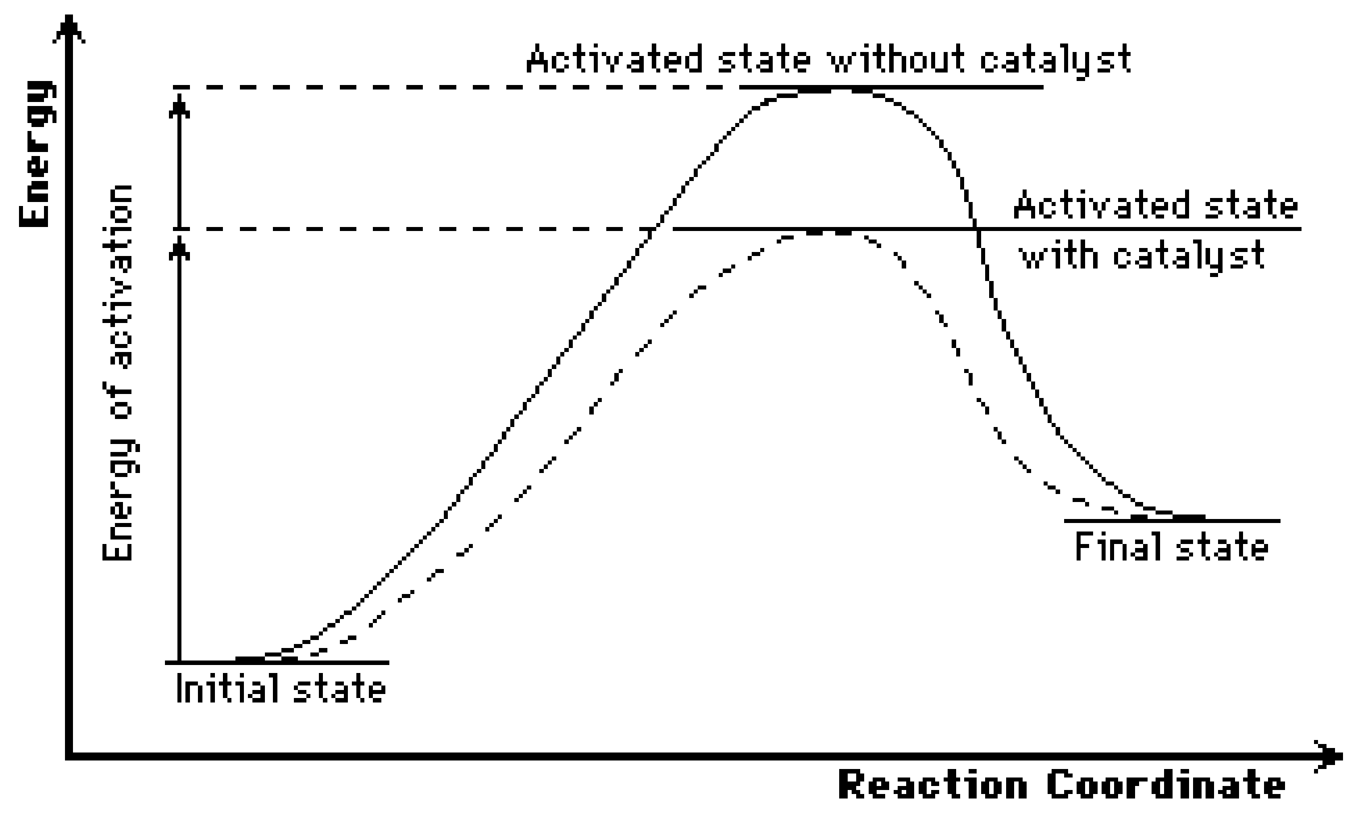
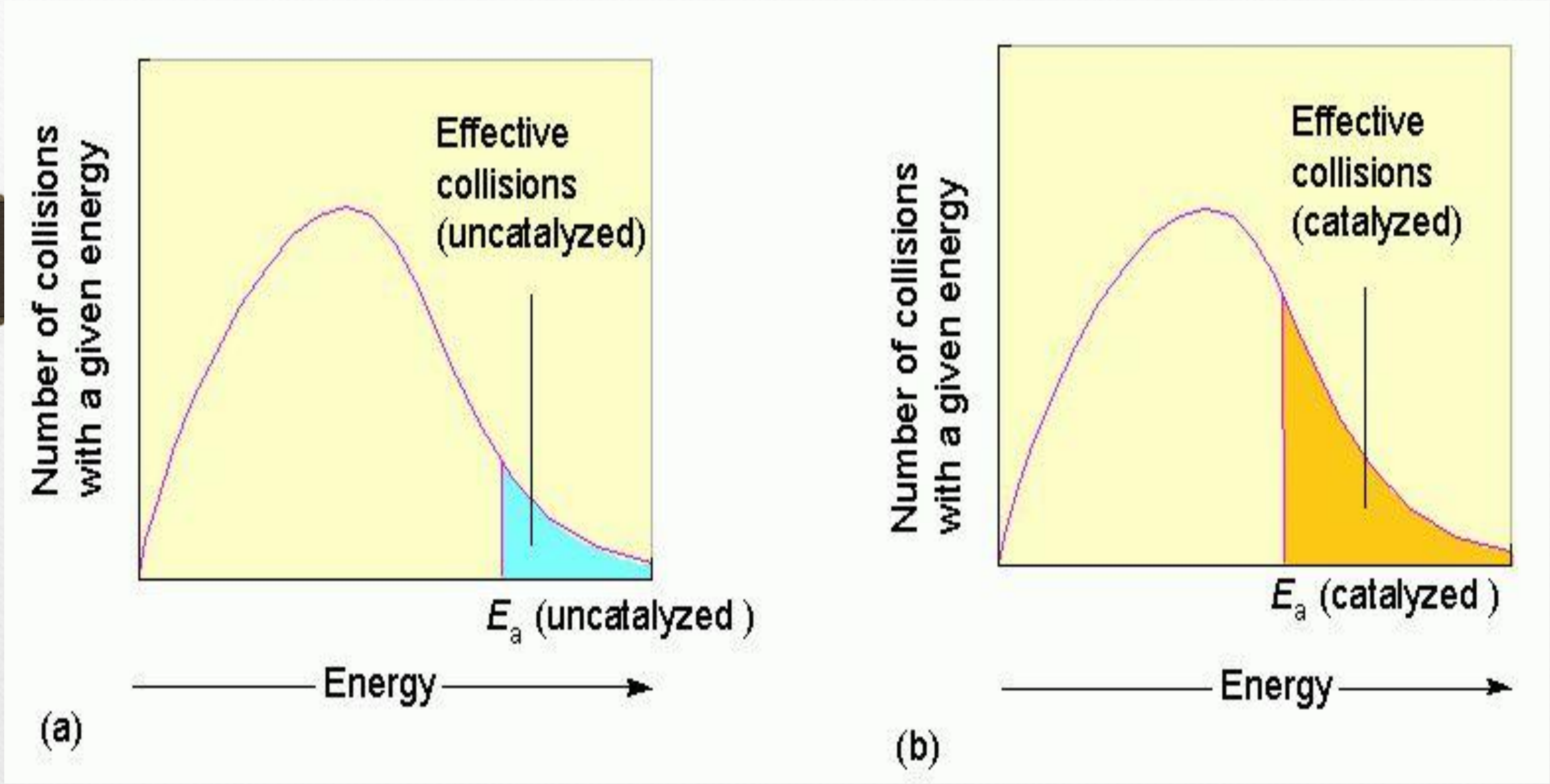
- Enzyme:
- A large molecule (usually a protein) that catalyzes biological reactions.
- Homogeneous catalyst:
- Present in the same phase as the reacting molecules.
- Heterogeneous catalyst:
- Present in a different phase than the reacting molecules.

Lowering of Activation Energy by a Catalyst



Catalysts Increase the Number of Effective Collisions



Determining the Activation Energy

One can determine the activation energy of a reaction by measuring the rate constant at two temperatures:

Writing the Arrhenius equation for each temperature:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \qquad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

If one takes the natural log of the ratio of k_2 over k_1 we find that:

$$\ln\left(\frac{k_2}{k_1}\right) = \ln k_2 - \ln k_1$$

Substituting in the values for E_a into the equation:

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

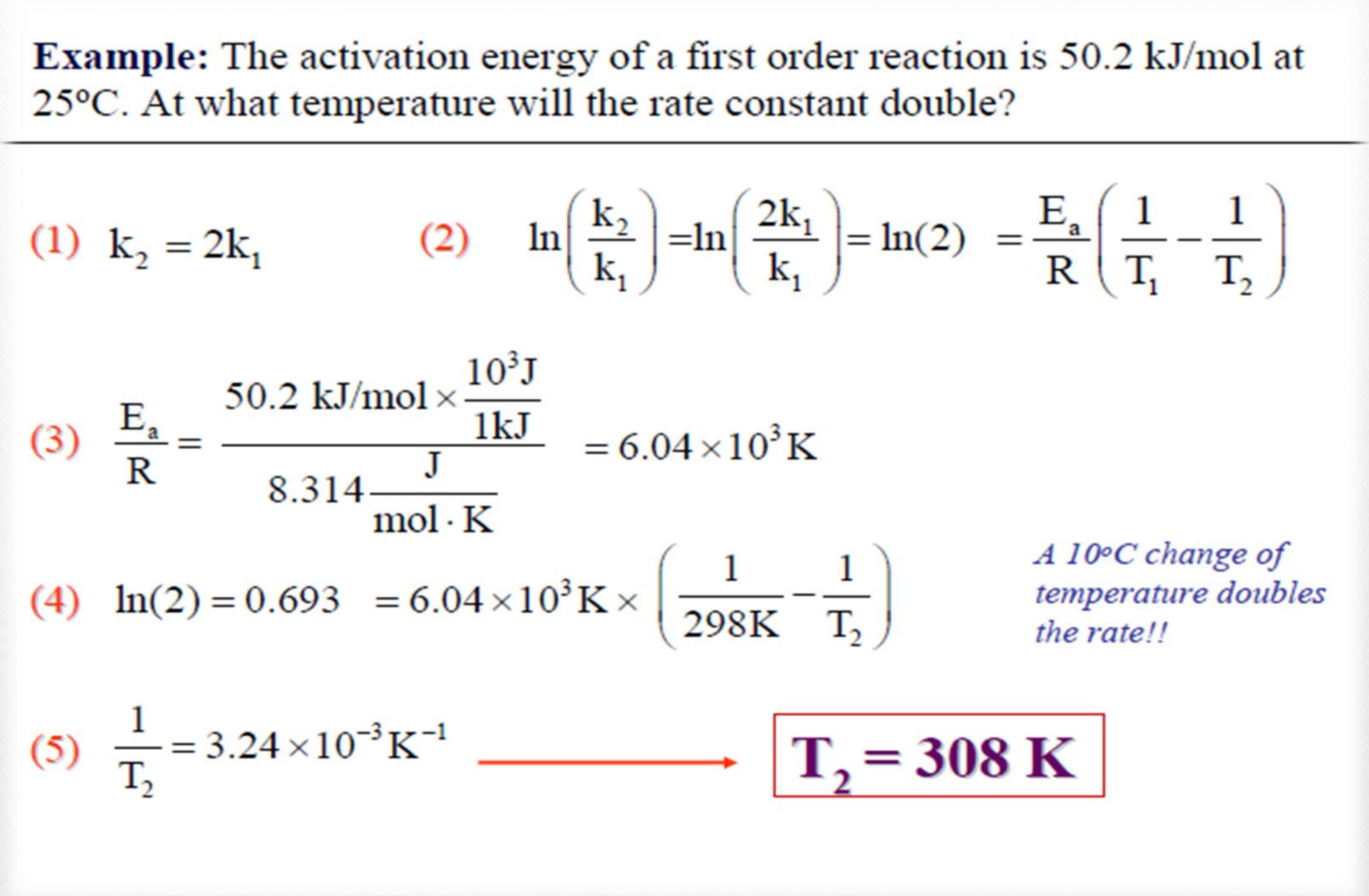
Lookie what happens…

Knowing the rate at two temps yields the rate constant.

or

Knowing the E_a and the rate constant at one temp allows one to find $k(T_2)$

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



Example: The activation energy of a first order reaction is 50.2 kJ/mol at 25°C. At what temperature will the rate constant double?

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(1) $k_2 = 2k_1$

(2) $$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{2k_1}{k_1}\right) = \ln(2) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(3) $$\frac{E_a}{R} = \frac{50.2\ \text{kJ/mol} \times \frac{10^3\,\text{J}}{1\,\text{kJ}}}{8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}} = 6.04 \times 10^3\,\text{K}$$

(4) $$\ln(2) = 0.693 = 6.04 \times 10^3\,\text{K} \times \left(\frac{1}{298\text{K}} - \frac{1}{T_2}\right)$$

A 10°C change of temperature doubles the rate!!

(5) $$\frac{1}{T_2} = 3.24 \times 10^{-3}\,\text{K}^{-1} \longrightarrow \boxed{T_2 = 308\ \text{K}}$$

Example/ Using the data for 25C° and 65C° in table, calculate Ea, the energy of activation for the decomposition of Nitrogen pentoxide N_2O_5.

25+273 = 298 k
65+273 = 338 k
K1 = 3.46*10-5
K2 = 4.87*10-3

$$\mathrm{Log}\ \frac{K_2}{K_1} = \frac{Ea}{2.303R} * \frac{T_2-T_1}{T_1-T_2}$$

$$\mathrm{Log}\ \frac{4.87*10\text{-}3}{3.46*10\text{-}5} = \frac{Ea}{2.303R}\ \frac{338-298}{338-298}$$

Ea = 24.800 cal


Thank
you