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

Physical Chemistry

Lecture 3

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First semester

Temperature and Reaction Rate

By

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Temperature and Reaction Rate

- Purpose
  - To study the effect of temperature on the reaction rate and the reaction rate constant (k) of a chemical reaction and to determine the value of the activation energy (E_a) for the reaction.

- Safety Considerations
  - Wash your hands thoroughly after handling chemical reagents and before leaving the lab.
  - All chemical wastes should be placed in the labeled jar in the hood.

Temperature and Reaction Rate

- Background
  - The chemical reaction being studied in this experiment is:

$$6\,I^- + BrO_3^- + 6\,H^+ \longrightarrow 3\,I_2 + Br^- + 3\,H_2O$$

bromate ion

  - In the previous experiment, you determined the rate law for this reaction to be:

$$\text{Rate} = k\,[I^-]\,[BrO_3^-]\,[H^+]^2$$

  - The value of the rate constant (k) depends on the temperature. The relationship between rate constant and temperature is given by the Arrhenius Equation

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

Temperature and Reaction Rate

- Background

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

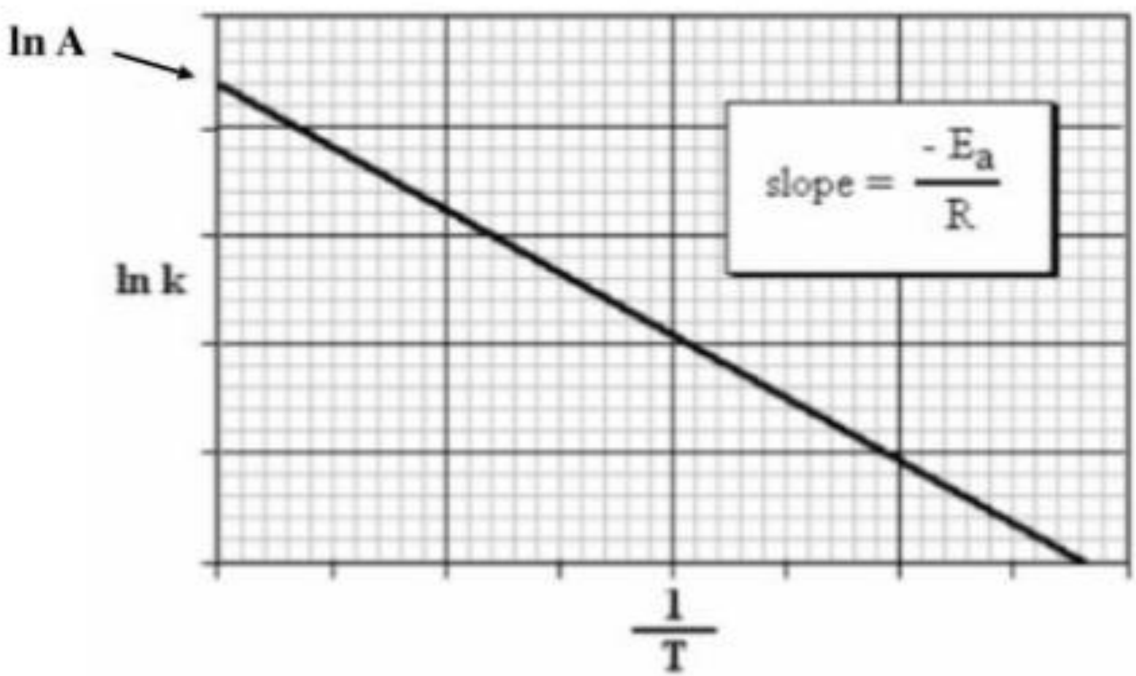
- rate constant → k
- frequency factor → A
- activation energy → Ea
- temperature (K) → T
- Idea Gas constant (8.31 J/K·mol) → R

  - Taking the log of both sides of the Arrhenius Equation transforms it into a linear equation:

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

Temperature and Reaction Rate

- Background
  - The activation energy for a reaction can be found by measuring the value of k at several different temperatures and then plotting ln k vs. 1/T



The Arrhenius Equation

Arhenius discovered that most reaction-rate data obeyed an equation based on three factors:

(1) The number of collisions per unit time.

(2) The fraction of collisions that occur with the correct orientation.

(3) The fraction of the colliding molecules that have an energy greater than or equal to E_a.

From these observations Arrhenius developed the eponymously-named ***Arrhenius equation***.

The Arrhenius Equation

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

k is the rate constant

E_a is the activation energy

T is the temperature in K

R is the ideal-gas constant (8.314 J/K⊠mol)

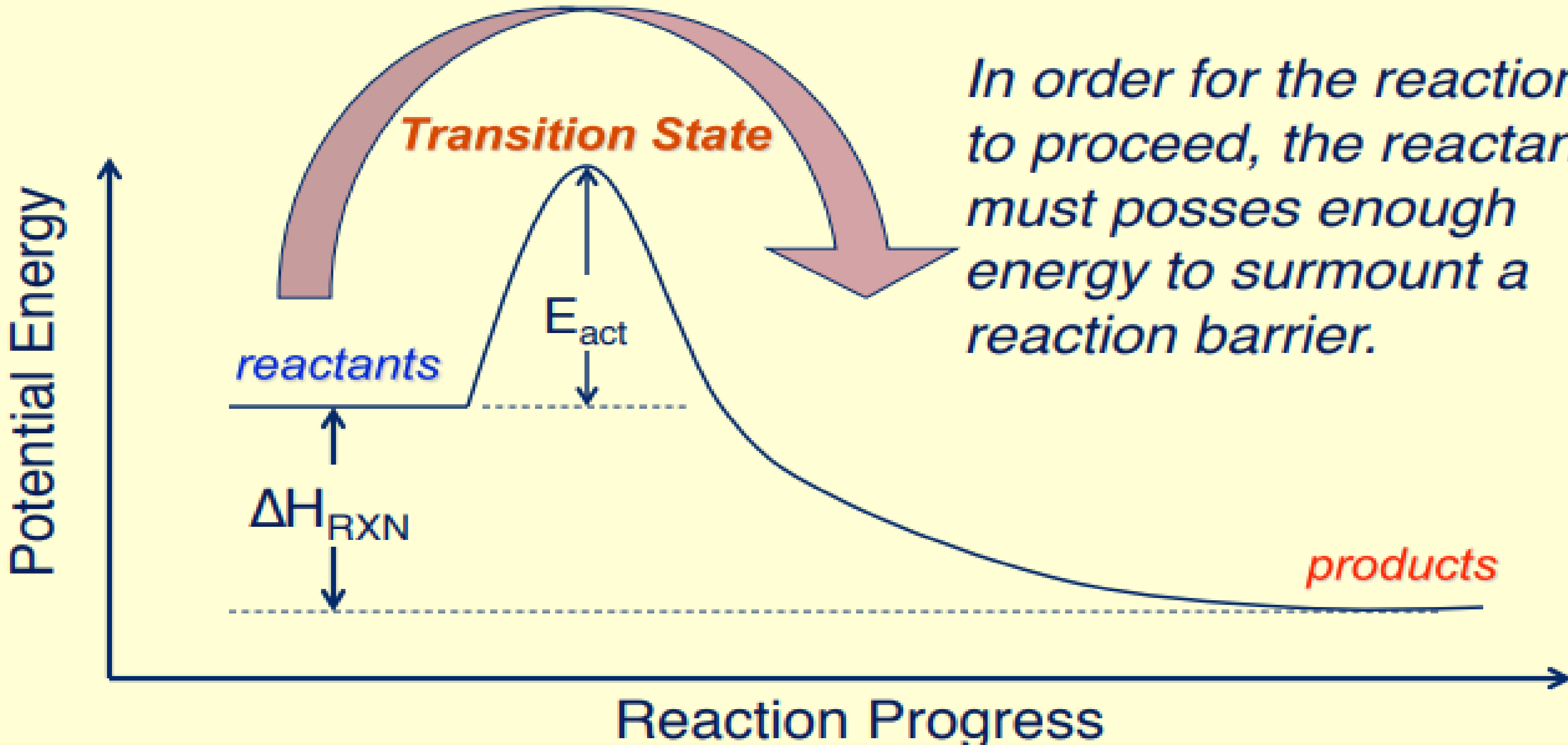
A is known the *frequency or pre–exponential factor*

In addition to carrying the units of the rate constant, "**A**" relates to the frequency of collisions and the orientation of a favorable collision probability

Both *A* and E_a are *specific to a given reaction.*

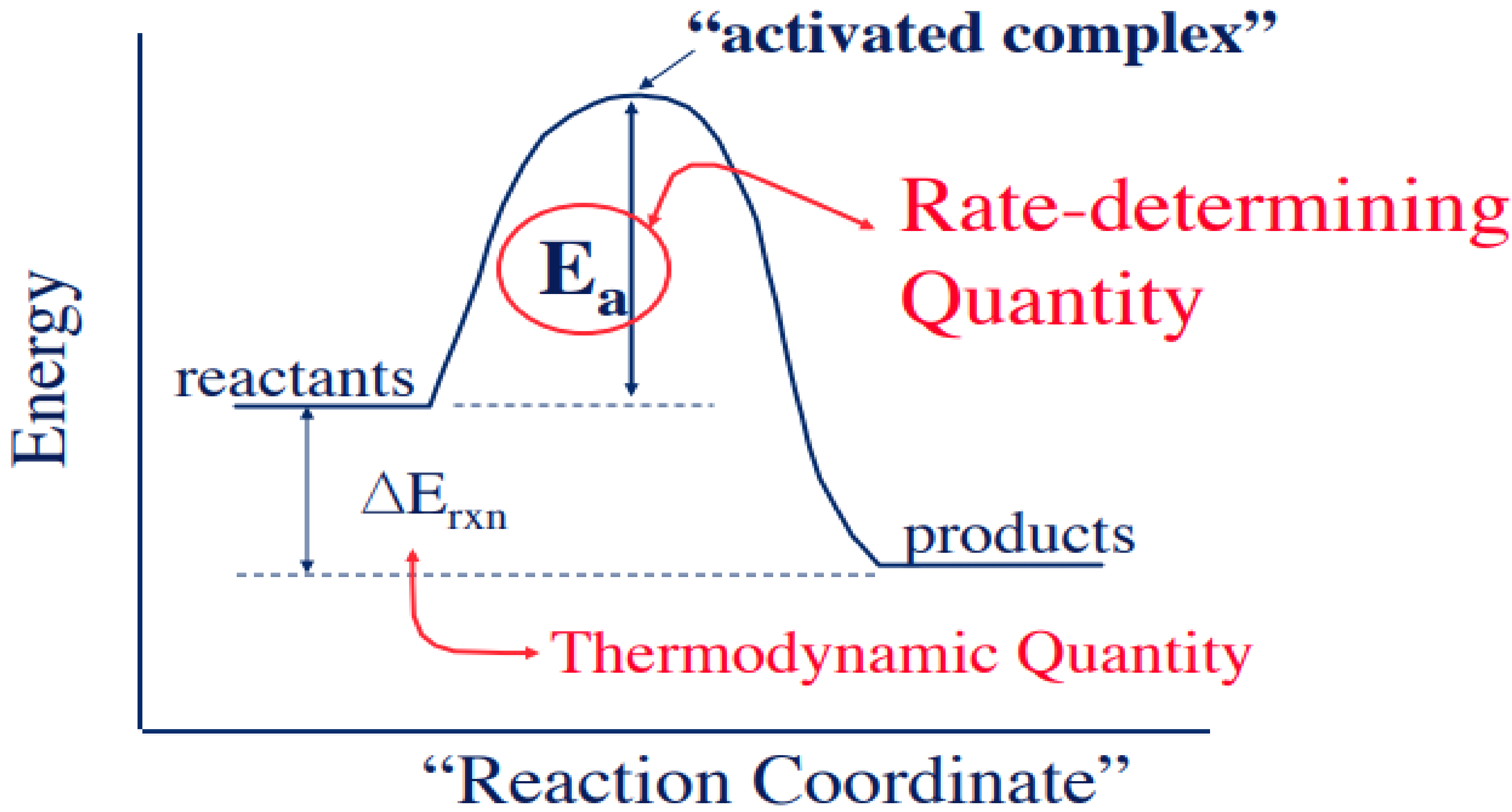
Activation Energy

The progress of a chemical reaction as the *reactants* transform to *products* can be described graphically by a *Reaction Coordinate*.



In order for the reaction to proceed, the reactants must posses enough energy to surmount a reaction barrier.

Energy profile for a reaction



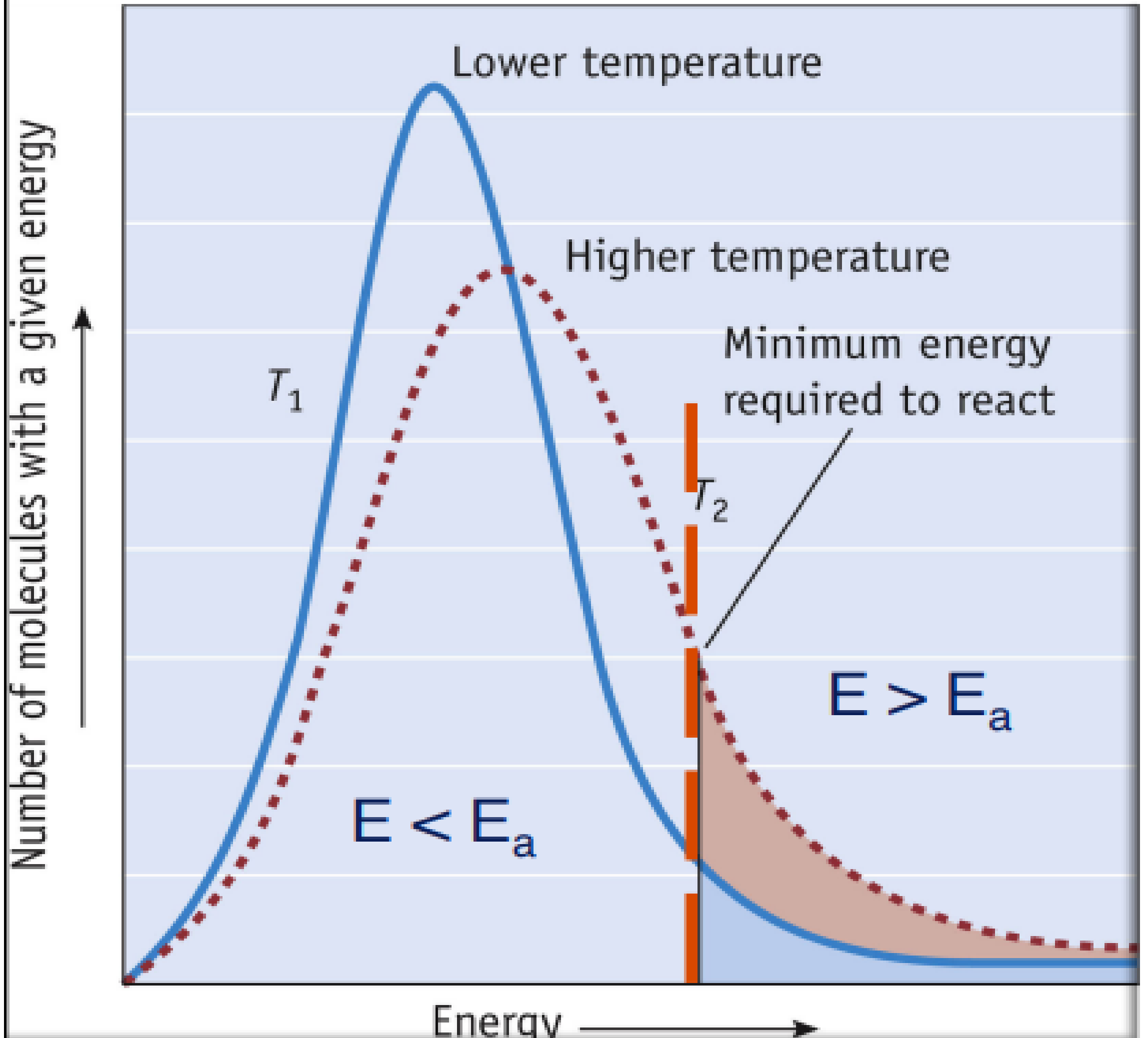
E_a, The Activation Energy

- Energy of activation for forward reaction:

  $$E_a = E_{transition\ state} - E_{reactants}$$

- A reaction can't proceed unless reactants possess enough energy to give E_a.
- ΔE, the thermodynamic quantity, tells us about the net reaction. The activation energy, E_a , must be available in the surroundings for the reaction to proceed at a measurable rate.

Activation Energy



The temperature for a system of particles is described by a distribution of energies.

At higher temps, more particles have enough energy to go over the barrier.

Since the probability of a molecule reacting increases, the rate increases.

$Ln\ K = Ae^{-Ea/RT}$

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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) $\frac{1}{T_2} = 3.24 \times 10^{-3}\,\text{K}^{-1}$ → **$T_2 = 308$ 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

$$\mathrm{Log}\ \frac{K2}{K1} = \frac{Ea}{2.303R} * \frac{T2-T1}{T1-T2}$$

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

Ea = 24.800 cal


Thank you