REACTION KINETICS AND REACTION MECHANISMS

Different levels of dealing with reaction rates:

I. REACTION KINETICS
macroscopic level – mathematical description
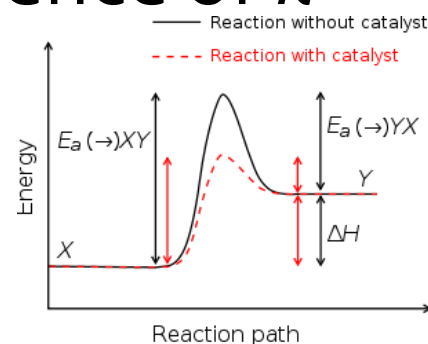
II. REACTION MECHANISMS
molecular level– interpretation

III. THEORIES OF REACTION RATES
Arrhenius equation, collision and activated complex theories

III. THEORIES OF REACTION RATES AND RATE CONSTANTS

- Starting point: temperature dependence of k
- **Arrhenius theory** (Arrhenius, 189X)

$$k = A \cdot e^{-E_a / RT}$$

- **Collision theory** (Arrhenius, McLewis, 1918)

$$k = p \cdot Z \cdot e^{-E_a / RT} = p \cdot \sigma \cdot \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} N_A e^{-E_a / RT}$$

- collisions, steric factor, reactive collisions, harpoon mechanism (mainly **gas phase** reactions)

- **Activated complex theory** (Eyring, Polányi, 193x), general, useful for **solution reactions**.

$$k = k^{\#} \cdot K^{\#} = \kappa \cdot \frac{k_B T}{h} \cdot \overline{K} = \kappa \cdot \frac{k_B T}{h} \cdot e^{\Delta^{\#} S / R} \cdot e^{-\Delta^{\#} H / RT}$$

  - thermodynamic approach (entropy, enthalpy and free energy of activation)

  - quantum mechanical approach (potential surfaces, trajectories)

  - statistical mechanical approach

- **The three different approaches complement each other!**

Temperature dependence of rate constants

- **General** (but not infallible) **guideline**: an increase in T causes an increase in v (both for exothermic and endothermic reactions).
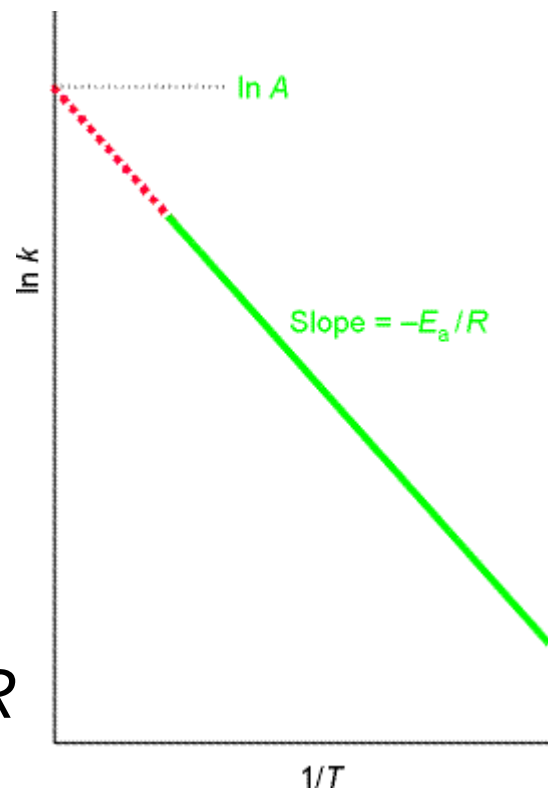 - Thermostatting is important!
- **Semiquantitative**:
  a factor of 2-3× for each 10°C
- **Fully quantitative**:
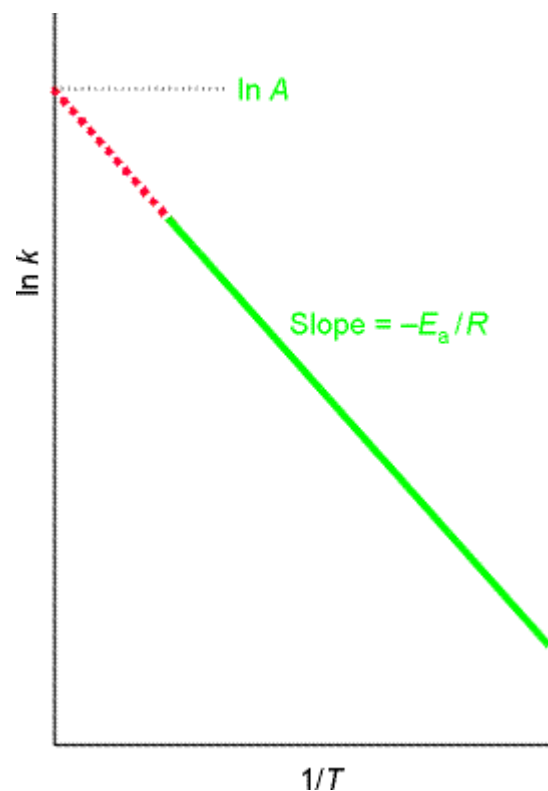 the T dependence of k:
  - $k = A \exp(-E_a/RT)$.
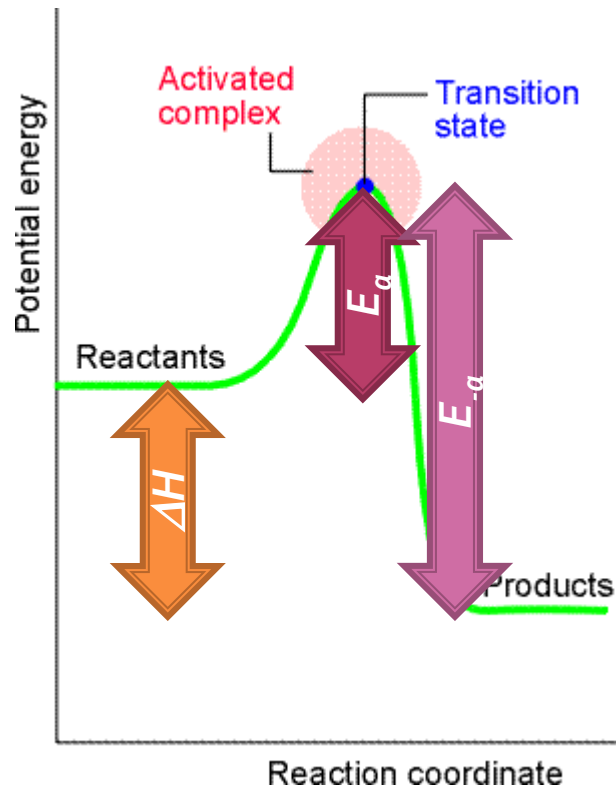 - Logarithmic form: $\ln k = \ln A - E_a/R$

Temperature dependence of rate constants

- The **Arrhenius plot** gives a straight line:
    - **slope**: $-E_a/R$

    - **intercept** (extrapolation to $1/T =$ 0): $\ln A$
        - A: pre-exponential factor
        - (Later terminology: collision constant)
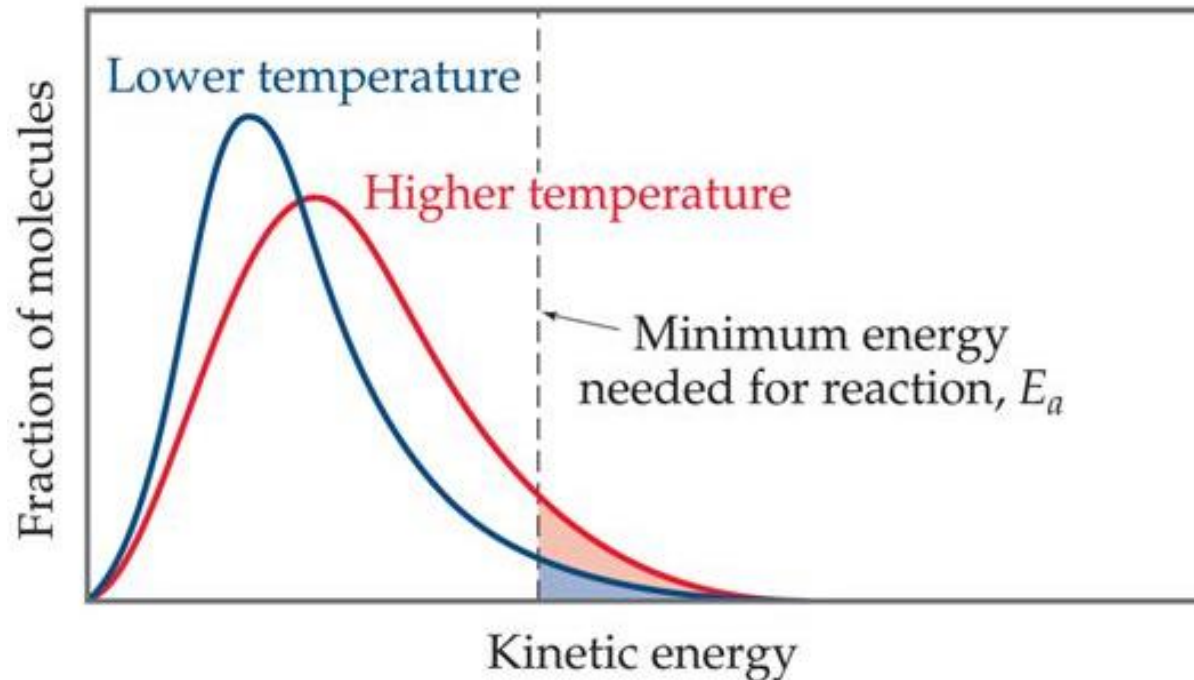
Arrhenius equation:

- E_a activation energy: the excess energy needed for a reactive collision vs. an average collision.

- E_a is visualized on a reaction profile as shown in the figure.

Arrhenius equation:

- Interpretation: **Maxwell–Boltzmann distribution**:

- At a higher temperature T_2, more particles have a kinetic energy greater than the E_a energy of activation.

Arrhenius equation:

- **Theoretical objectives**: to derive the experimentally observed equation form the model and find a way to obtain the parameters from more fundamental properties.

  - Activation energy E_a was a characteristic reaction parameter that could not be calculated in any theoretical way. ➡ **Activated complex theory**

  - *A* was not interpreted by Arrhenius originally.

    ➡ **Collision theory**

- **Importance**: Svante Arrhenius started the development of reaction rate theories.
- The core idea is still considered to be valid.

Non-thermal activation:

- **Electrochemistry** (dynamic electrochemistry)
- **Photochemistry** (*e.g. HCl formation, also many biological examples*)
- **Radiation chemistry**
- **Microwave chemistry**
- **Magnetochemistry**
- **Sonochemistry** (*e.g. ripening of wine*)
- **Mechanochemistry, tribochemistry** (*e.g. cement solidifies faster, metal tool surfaces are more resistant*)