Reaction Rate and Temperature

☞ Rates of chemical reactions increase with increasing temperature.

  - This means *k*, the rate constant in the differential rate law for any reaction, increases with *T*, the temperature.

✔ Typical chemical reactions show roughly a doubling of rate for every 10° C temperature increase.

Arrhenius Theory

☞ The first successful interpretation of the relationship between k and T was made by Svante Arrhenius in 1887.

- Arrhenius reasoned that any reaction process must proceed through a ***transition state***, involving formation of a high-energy species, called the ***activated complex***, which then breaks apart to form products.

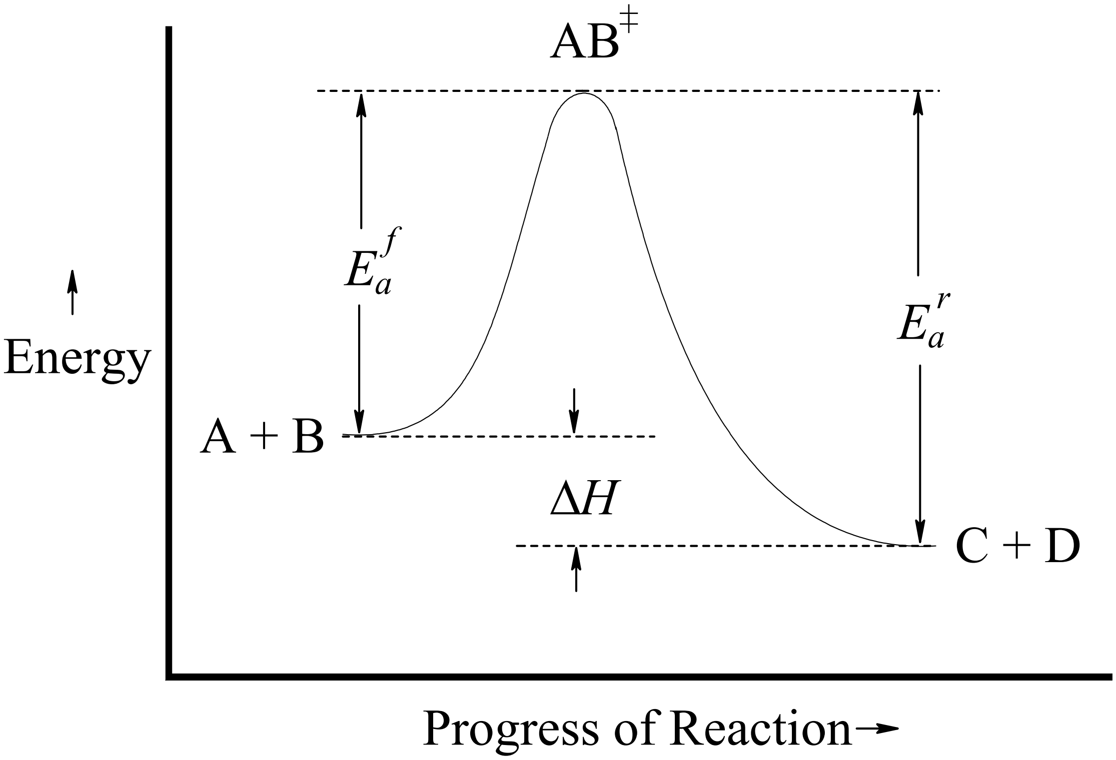
$$\mathrm{A + B \rightarrow \underset{\substack{\text{activated}\\ \text{complex}}}{[AB^{\ddagger}]} \rightarrow C + D}$$

- The difference in potential energy between the activated complex, $AB^{\ddagger}$, and the reactants, A + B, is the ***activation energy of the forward reaction,*** E_a^f.

- The difference in potential energy between the activated complex, $AB^{\ddagger,}$ and the products, C + D, is the ***activation energy of the reverse reaction,*** E_a^r.

Potential Energy Curve (Arrhenius Plot) for a One-Step Exothermic Reaction

$A + B \rightarrow C + D$



☞ If $E_a^f < E_a^r$, then $\Delta H_{\text{rxn}} < 0$ (exothermic)

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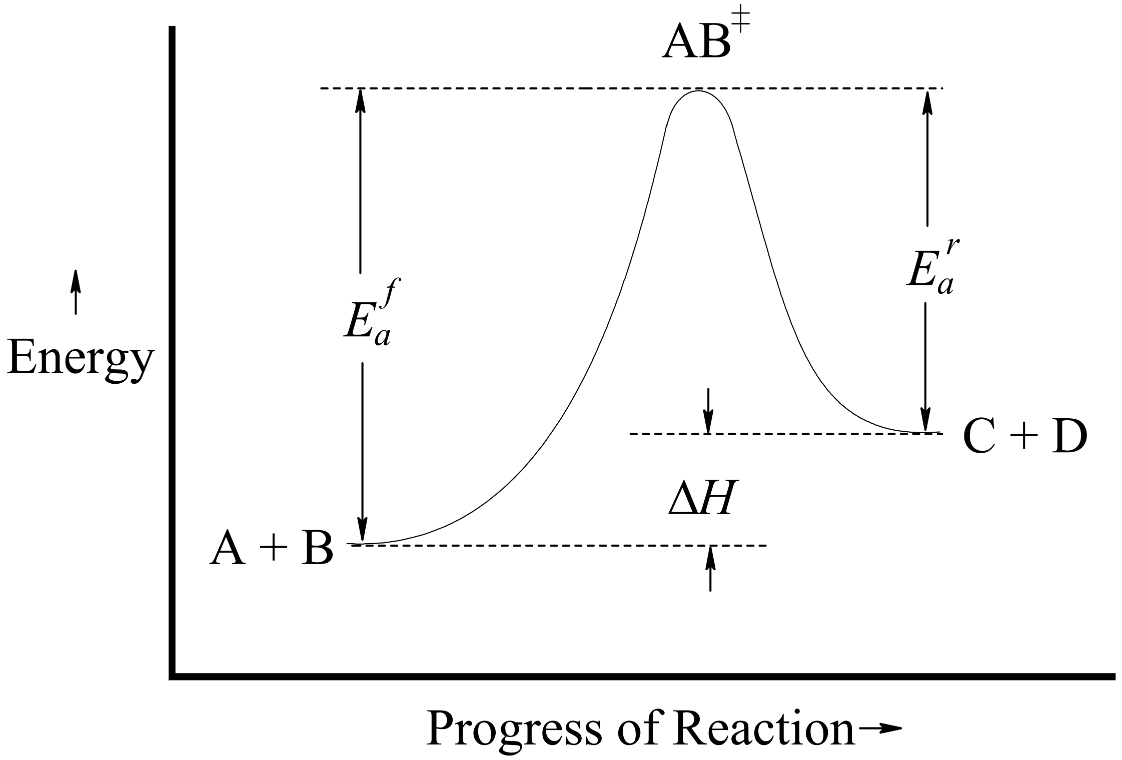

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Arrhenius Theory and
The Empirical Differential Rate Law

- The differential rate law for a reaction has the general form

$$Rate \propto [\text{reactants}]^n$$

- By Arrhenius Theory, the rate of a reaction must be proportional to the concentration of activated complex:

$$Rate \propto [\text{reactants}]^n\ (\text{fraction activated})$$

- We can make this an equation by introducing the proportionality constant, A, called the ***Arrhenius constant***.

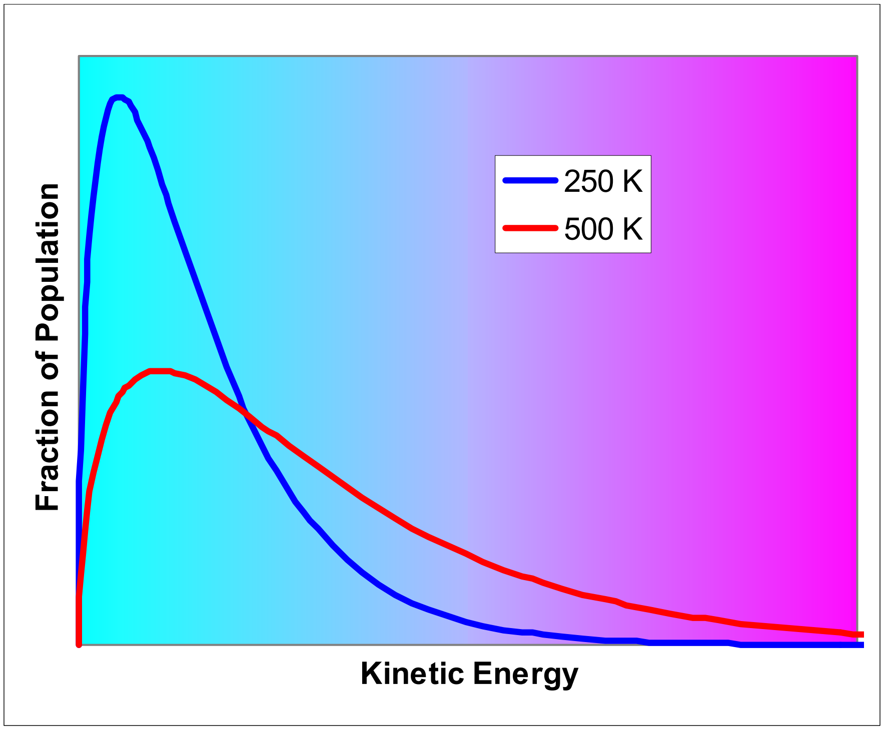
$$Rate = \text{A}[\text{reactants}]^n\ (\text{fraction activated})$$

    - The Arrhenius constant is specific to the reaction and includes effects of molecular shape and orientation on the effectiveness of converting reactants into products.

Collision Theory

- ☞ The fraction of reactant molecules that will be capable of forming product is the portion of the population that has the minimum necessary energy to form the reactive activated complex.

- ☞ We can estimate this on the basis of an extension of the kinetic molecular theory, called ***collision theory***.



The Arrhenius Equation and Collision Theory

- The fraction with the necessary energy to react, as given by the Boltzmann distribution, is

$$\text{fraction activated} = \frac{[\text{activated complex}]}{[\text{reactants}]} = e^{-E_a/RT}$$

where e = base of the natural logarithm
R = ideal gas constant = 8.3143 J/K·mol
T = temperature in Kelvin

- Substituting this into our expression for *Rate* we get

$$Rate = \mathrm{A}e^{-E_a/RT}[\text{reactants}]^n$$

- We have seen that experimentally our rate law expressions have the form

$$Rate = k[\text{reactants}]^n$$

- Therefore,

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

which is called the ***Arrhenius equation***.

Logarithm Form of the Arrhenius Equation

- Taking natural logarithms of both sides:

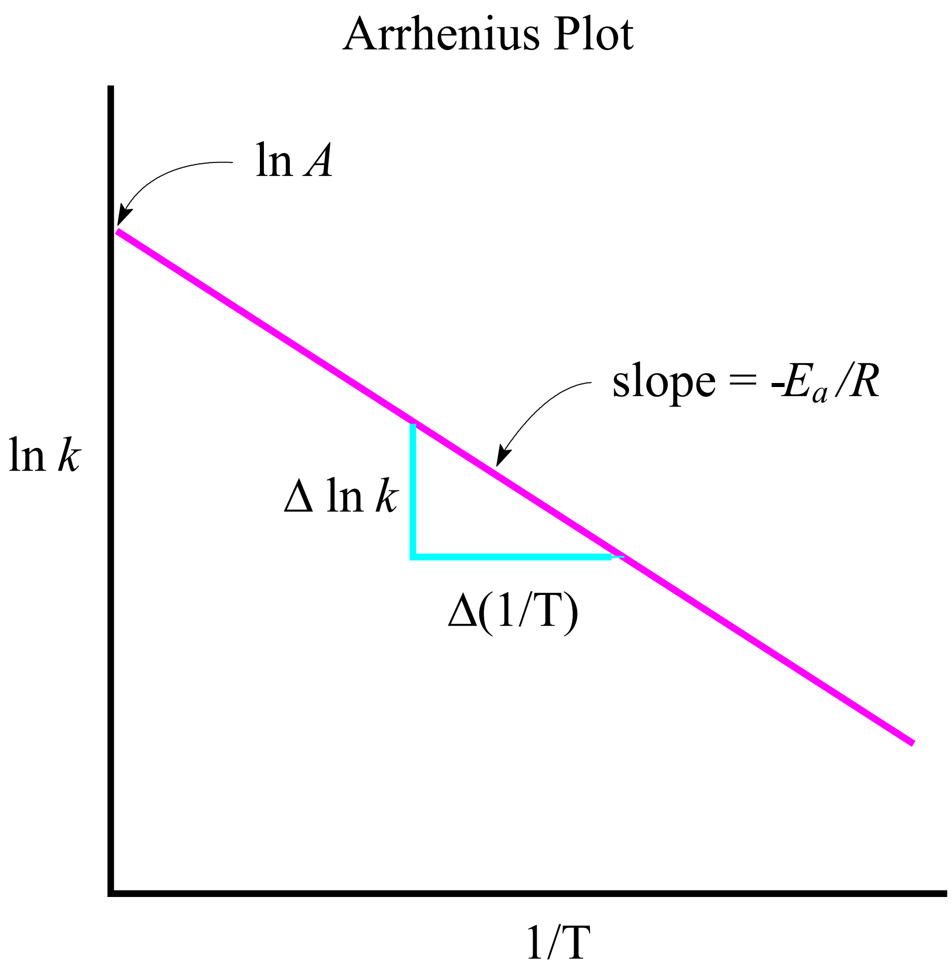
$$\ln k = \ln \mathrm{A} - E_a/RT$$

- Rearranging:

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

☞ This is a linear equation of the form $y = mx + b$.

Linear Plot of the Arrhenius Equation



Two-Temperature Form of the Arrhenius Equation

☞ Only two points are needed to define a straight line, so only two pairs of ln *k* and 1/T data are needed to define the slope.

- At two different temperatures, T_1 and T_2, we can write the expressions for the rate constants, k_1 and $k_{2:}$

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

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

- Subtracting the second equation from the first:

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