

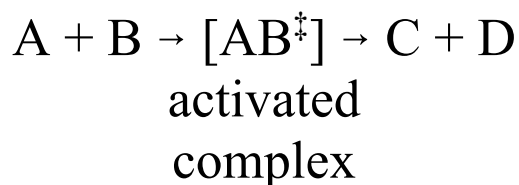
Reaction Rate and Temperature

- ☞ 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

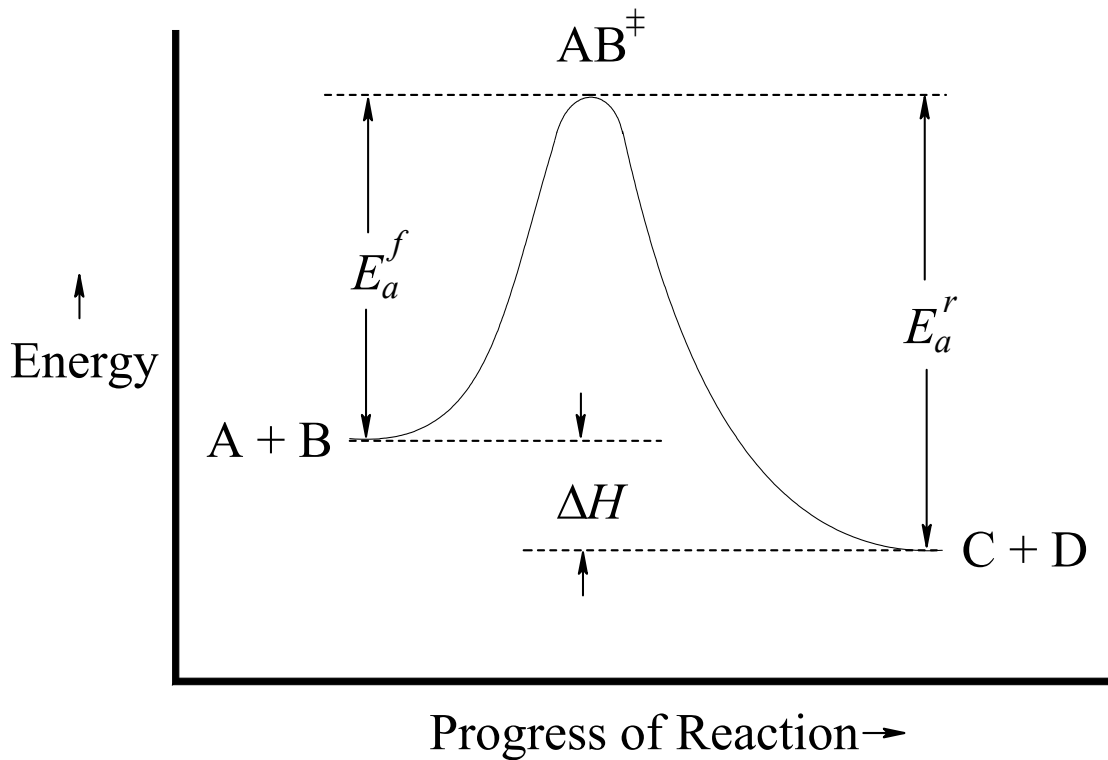
☞ The first successful interpretation of the relationship between k and T was made by Svante Arrhenius in 1887.

- 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.



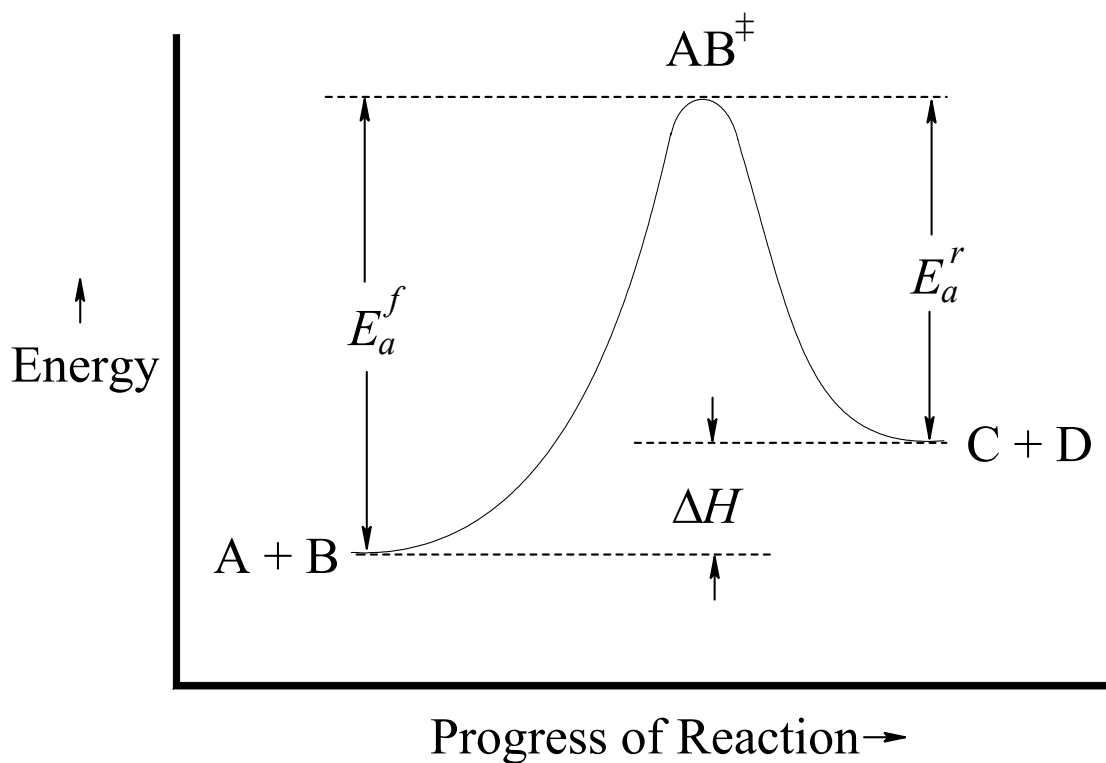
- The difference in potential energy between the activated complex, AB^\ddagger , and the reactants, $\text{A} + \text{B}$, is the *activation energy of the forward reaction*, E_a^f .
- The difference in potential energy between the activated complex, AB^\ddagger , and the products, $\text{C} + \text{D}$,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

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

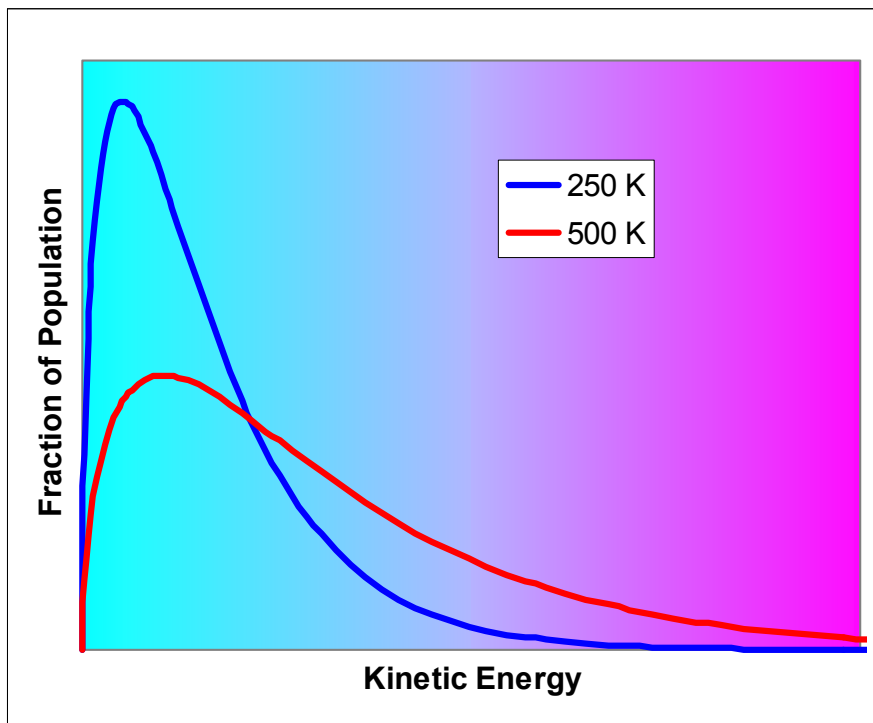
- We can make this an equation by introducing the proportionality constant, A, called the *Arrhenius constant*.

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

- 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

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

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

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

- Therefore,

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

which is called the *Arrhenius equation*.

Logarithm Form of the Arrhenius Equation

- Taking natural logarithms of both sides:

$$\ln k = \ln A - E_a/RT$$

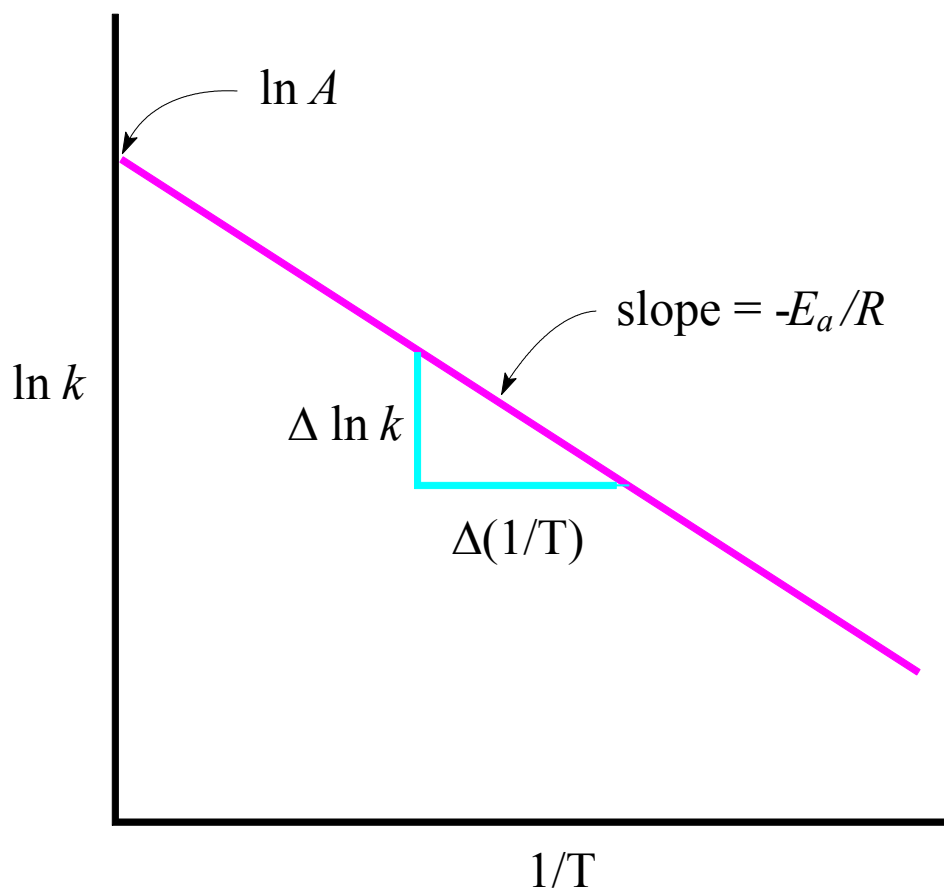
- Rearranging:

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

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

Linear Plot of the Arrhenius Equation

Arrhenius Plot



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:

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