Reaction Rates and Temperature; Arrhenius Theory

CHEM 102

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Arrhenius Theory

The Arrhenius Equation

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

k is the rate constant

T is the temperature in K

E_a is the activation energy

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

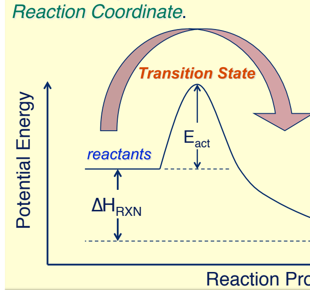
A is known the *frequency or pre–exponential factor*

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.*

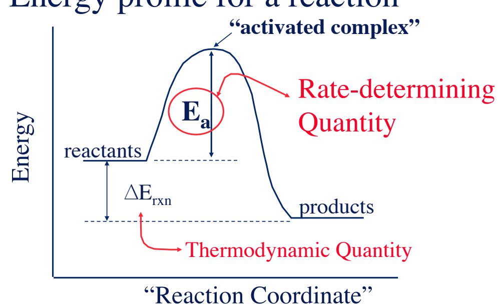
Activation Energy

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

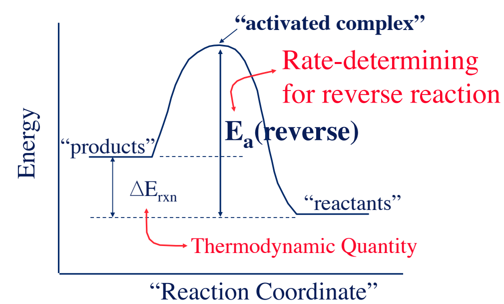


In order for the reaction to proceed, the reactants must posses enough energy to surmount a reaction barrier.

Energy profile for a reaction



The reverse direction...

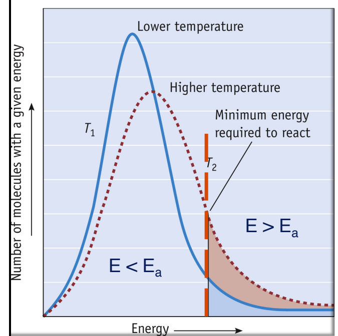


E_a, The Activation Energy

- 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 <u>net</u> 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.

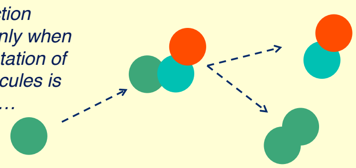
At higher temps, more particles have enough energy to go over the barrier.

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

Orientation Factors (affects 'A')

The orientation of a molecule during collision can have a profound effect on whether or not a reaction occurs.

The reaction occurs only when the orientation of the molecules is just right…

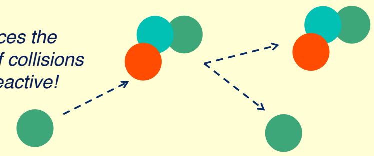


When the green atom collides with the green atom on the molecule, a ***reactive or effective collision*** occurs.

Orientation Factors (affects 'A')

In some cases, the reactants must have proper orientation for the collision to yield products.

This reduces the number of collisions that are reactive!



When the green atom collides with the red atom on the molecule, this leads to a ***non-reactive or ineffective collision*** occurs.

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

Temperature Dependence of the Rate Constant:

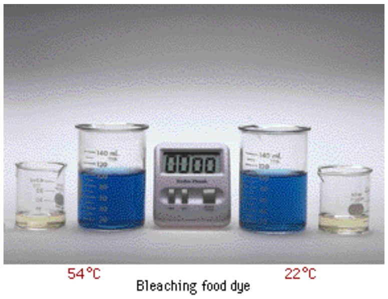
Increasing the temperature of a reaction generally speeds up the process (increases the rate) because the rate constant increases according to the Arrhenius Equation.

$$\text{Rate } (M\ s^{-1}) = k[A]^x[B]^y$$

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

As T increases, the value of the exponential part of the equation becomes less negative thus increasing the value of k.

Temp. and Rate Acceleration



Arrhenius Equation

- Arrhenius noted that reaction rates could be understood to depend on E_a and T with the exponential form:

$$k = A\exp(-E_a/RT)$$

- Or, in logarithmic form:

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

using base 10 logs: [$\log k = \log A - (E_a/2.303RT)$]

Arrhenius Eqn., Alternative Form

- Taking two measured values of the rate (at two different temperatures) one can write:

$$\ln k_1 = \ln A - (E_a/RT_1)$$

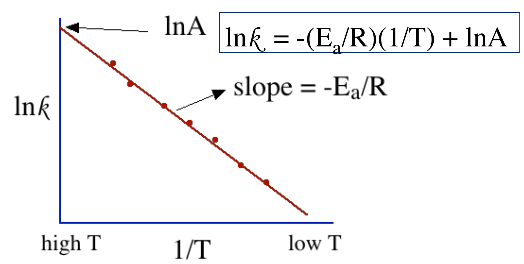
$$\ln k_2 = \ln A - (E_a/RT_2)$$

$$\ln k_2 - \ln k_1 = -(E_a/R)[(1/T_2) - (1/T_1)]$$

$$\ln(k_2/k_1) = -(E_a/R)[(1/T_2) - (1/T_1)]$$

Arrhenius Eqn., Graphical Form

A "best fit" to many data is better!



Arrhenius Equation, Example

- If a reaction has an activation energy of 50 kJ/mol, then how much should the rate of the reaction accelerate if the temperature is raised from 300 K to 310 K?

Arrhenius Equation, Example

- If a reaction has an activation energy of 50 kJ/mol, then how much should the rate of the reaction accelerate if the temperature is raised from 300 K to 310 K?

$\ln(k_{310}/k_{300}) = -(E_a/R)[(1/T_2) - (1/T_1)]$

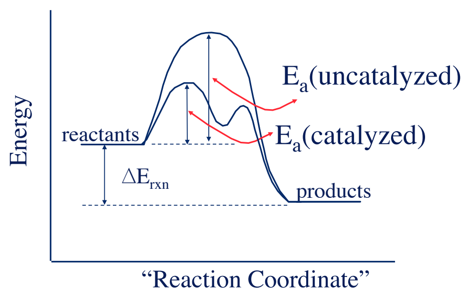
$-(50{,}000\ \text{J/mol})/(8.314\ \text{J/mol K})\bullet$

$[(1/310\text{K}) - (1/300\text{K})] = 0.647$

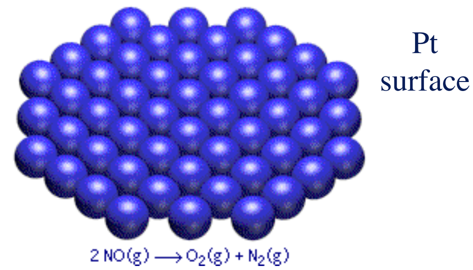
$k_{310} = e^{0.647}k_{300}$ roughly, rate doubles

$= 1.9k_{300}$ for every 10 ˚C.

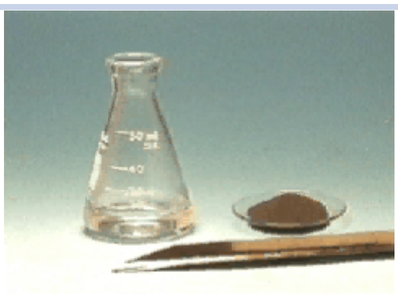
Catalysts - lowering E_a. Mechanism may change.



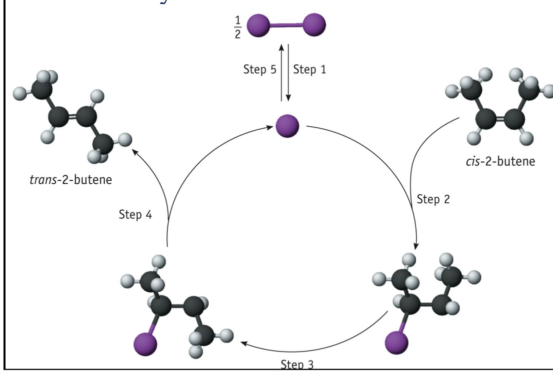
Catalytic Converters, $2NO \xrightarrow{Pt} O_2 + N_2$



$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$



Iodine-Catalyzed Isomerization of *cis*-2-Butene



Iodine-Catalyzed Isomerization of *cis*-2-Butene