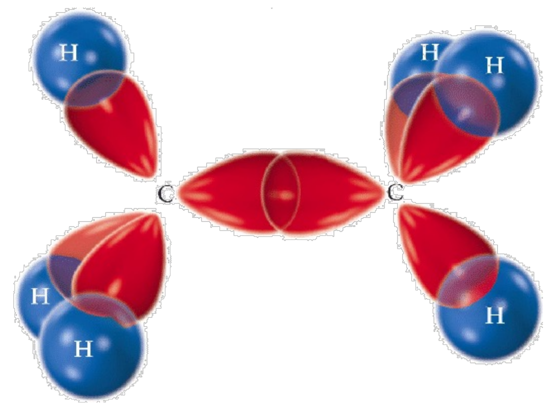
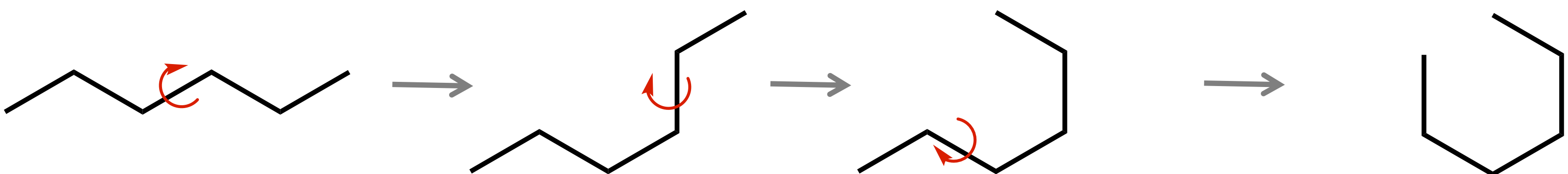
Lecture 3: Conformations of Alkanes

Last time: Orbitals can help us understand the arrangement of atoms in space, within a given molecule.

Considering that C-X bonds can freely rotate, how can we understand **intramolecular** interactions arising from various conformations?



Are these different molecules, or the same?



rotate

Same molecule, different conformations

Conformational Isomers: Molecules that differ in the arrangement of atoms in space, which result from bond rotations within the same molecule.

Constitutional Isomers: Different compounds that have the same molecular formula, but differ in the way atoms are bonded to one another. (In recitation)

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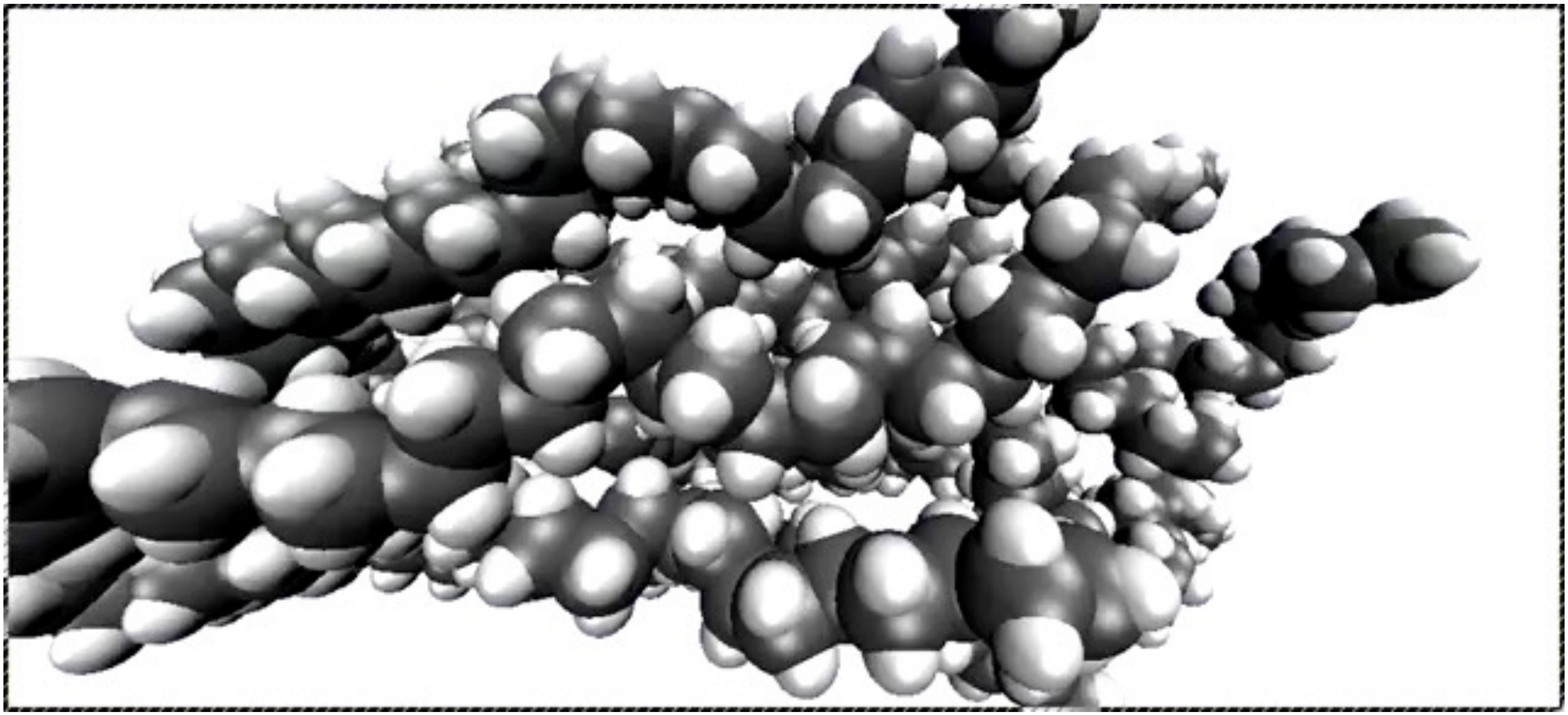
Example 2: The freezing process of hydrocarbons



The answer lies in understanding **kinetics**: The Arrhenius Equation

-this will tell us how fast ethane moves from one *energy minimum* to the next

For the process: Staggered $\xrightarrow{k}$ Eclipsed

k = rate constant

$$k = Ae^{\left(-E_a/RT\right)}$$

E_a **= Activation energy** (3 kcal/mol for Ethane)

A = Pre-exponential constant:

$10^{12}\ s^{-1}$ for a unimolecular process

$10^{8}\ M^{-1}\ s^{-1}$ for a bimolecular process

R = Ideal gas constant

T = Temperature (in this case, room temp)

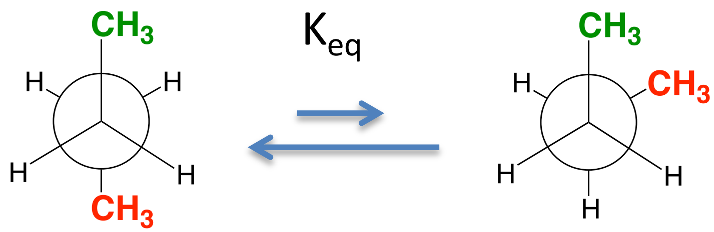
Plugging in all values into the equation:

k = $10^{10}\ s^{-1}$

SUPER FAST!!!!

it's always rotating at room temp

Anti [A]



Gauche [G]

Thermodynamics: We can calculate the **[A]** and [G] at equilibrium

-Consider the rotation from 180° to 60° (through 120°)

-Calculate % Anti and % Gauche

where ΔG = 0.9 kcal/mol

$$K_{eq} = \frac{[G]}{[A]}$$

$$\Delta G = -R\,T \ln K_{eq}$$

$$K_{eq} = e^{-\Delta G / R\,T}$$

$$K_{eq} = e^{-(0.9 kcal/mol) / [(1.98\ cal\ mol^{-1}\ K^{-1})(298\ K)]}$$

$$K_{eq} = 0.22 = \frac{[G]}{[A]} = \frac{0.22}{1} = \frac{1}{4.5}$$

At room temp, **ANTI** is preferred!

Therefore: 4.5 [G] + [G] = 100%

[G] = 18%

so, **[A] = 82%**

Kinetics: Information on the rates of transformations
(in this case, rotations)

Thermodynamics: Information on relative concentrations at equilibrium