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The Reaction Rate Constant

- The quantity ***k*** is referred to as either the **specific reaction rate or the reaction rate constant**.
- The **rate constant *k*** is not truly a constant; it is merely independent of the concentrations of the species involved in the reaction.
- It is almost always strongly **dependent on temperature**.
- It depends on whether or not a **catalyst** is present, and in gas-phase reactions, it may be a function of **total pressure**.
- ln liquid systems it can also be a function of other parameters, such as **ionic strength** and **choice of solvent**.
  - These other variables normally exhibit much less effect on the specific reaction rate than temperature does **with the exception of supercritical solvents**, such as super critical water.

30

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Arrhenius Equation

- k is the specific reaction rate (constant) and is given by the Arrhenius Equation, where:

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

where:

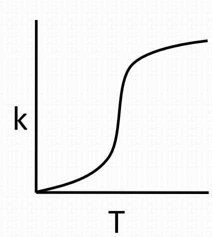
E = Activation energy (cal/mol)

R = Gas constant ($cal/mol \cdot K$)

T = Temperature (K)

A = Frequency factor (same units as rate constant k)

(units of A, and k, depend on overall reaction order)



$T \rightarrow \infty \quad k \rightarrow A$

$T \rightarrow 0 \quad k \rightarrow 0$

$A \approx 10^{13}$

31

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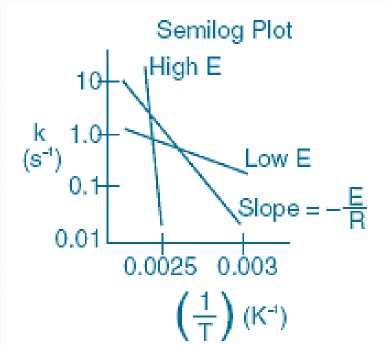
The Arrhenius Plot

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

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



32

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Reaction Coordinates

- The activation energy can be thought of as a barrier to energy transfer (from the kinetic energy to the potential energy) between reacting molecules that must be overcome.
- One way to view the barrier to a reaction is through the **reaction coordinates**.
- These coordinates denote the energy of the system as a function of progress along the reaction path as we go from reactants to an intermediate to products.

Concept 2. Potential Energy Surfaces and Energy Barriers.

33

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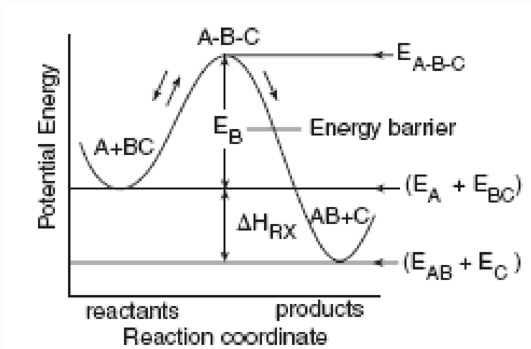
Reaction Coordinates

For the reaction:

$$A + BC \Leftrightarrow A ::: B ::: C \rightarrow AB + C$$

The reaction coordinate is:



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Why is there an Activation Energy?

- For the reaction to occur, the reactants must overcome an energy barrier (**activation energy, E_A**). In order to react,

1. The molecules need energy to disort or stretch their bonds in order to break them and thus form new bonds
2. As the reacting molecules come close together, they must overcome both stearic and electron repulsion forces.

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Why is there an Activation Energy?

- One can also view the activation energy in terms of **collision theory**.
- By increasing the temperature, we increase the kinetic energy of the reactant molecules.
- This kinetic energy can in turn be transferred through molecular collisions to internal energy to increase the stretching and bending of the bonds, causing them to reach an activated state, vulnerable to bond breaking and reaction.

- The energy of the individual molecules falls within a distribution of energies where some molecules have more energy than others.
- $f(E, T)$ = the energy distribution function for the kinetic energies of the reacting molecules.
- $f.dE$ = the fraction of molecules that have an energy between E and $(E + dE)$.

36

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Why is there an Activation Energy?

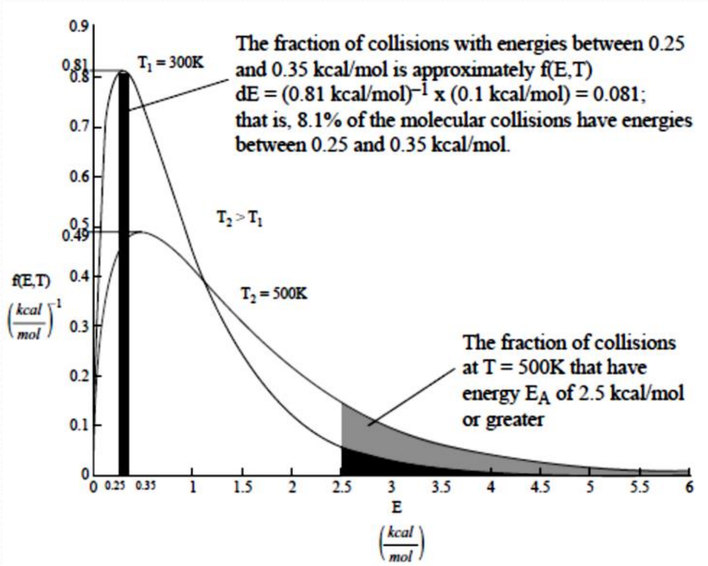

Figure 3-4 Energy distribution of reacting molecules.

37

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Why is there an Activation Energy?

- The activation energy has been equated with a minimum energy that must be possessed by reacting molecules before the reaction will occur.
- The fraction of the reacting molecules that have an energy E_A or greater is shown by the shaded areas.
  - The molecules in the shaded area have sufficient kinetic energy to cause the bond to break and reaction to occur.

38

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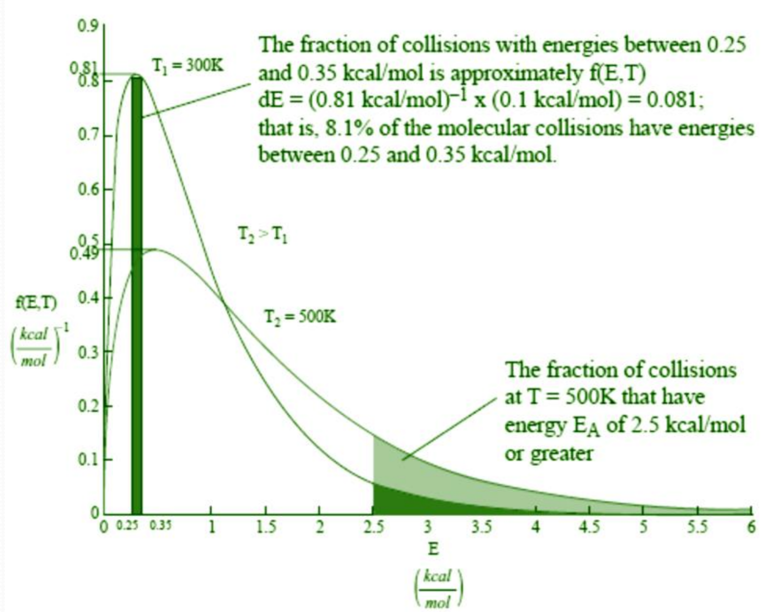
Why is there an Activation Energy?



39