Class 10.2

Reaction Rates and Temperature; Arrhenius Theory

CHEM 102H

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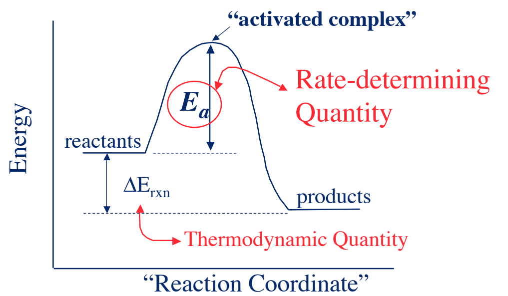
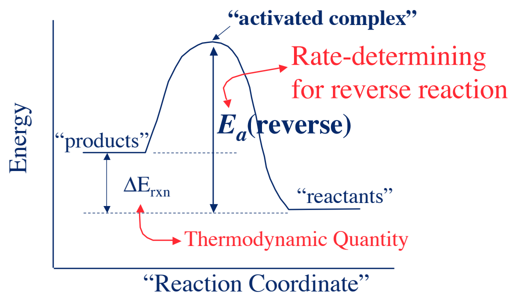
Energy profile for a reaction



The reverse direction...

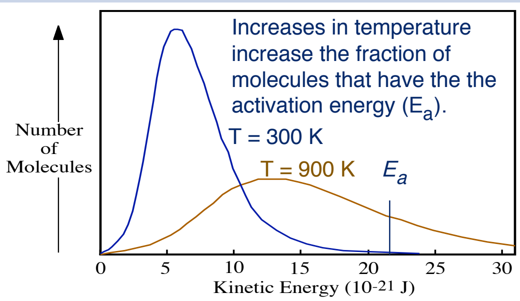


E_a, The Activation Energy

- Energy of activation for forward reaction:

  $E_a = E_{\text{transition state}} - E_{\text{reactants}}$
- The reaction won't proceed unless the reactants collide with enough energy (the activation energy, E_a) break or rearrange bonds.
- ΔE is a thermodynamic quantity for the <u>net</u> reaction. The activation energy, E_a , has to be available in the colliding molecules for the reaction to proceed at a measurable rate.

Temperature, qualitative effect



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:

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

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

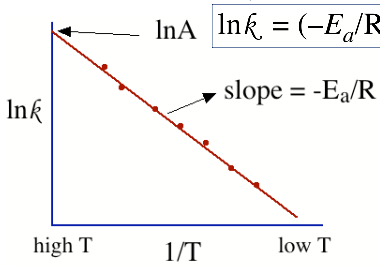
$$\ln k_2 - \ln k_1 = -(E_a/R)[(1/T_2) - (1/T_1)]$$

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

Arrhenius Eqn., Graphical Form

A “best fit” to many data is better!

$$\ln k = (-E_a/R)(1/T) + \ln A$$



Arrhenius Eqn., 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?

$\ln(k_{310}/k_{300}) =$

$-$ (50,000 J/8.314 J/mol K)[(1/310)-(1/300)]

$= 0.647$

$k_{310} = e^{0.647} k_{300}$

$= 1.9 k_{300}$

roughly, rate doubles for every 10 °C.

Catalysts - lowering E_a.
mechanism may change