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CHEM 3410: Physical Chemistry I — Fall 2008

November 14, 2008

Lecture 31: Reaction mechanisms

References

1. Levine, *Physical Chemistry*, Sections 16.1–6

Key Concepts

- One of the complications in determining rate laws comes from the temperature dependence of the rate constant: $k = f(T)$. The functional form of this relationship is given as:

$$k(T) = Ae^{\frac{-E_a}{RT}}$$

  where E_a is the activation energy, or the energy needed to get over the activation barrier. The exponential form of this expression is common for so-called activated processes.

- To connect theory to experiments, we need to come up with reaction mechanisms. These mechanisms are set of elementary steps or reactions that describe how the reaction proceeds.
- Elementary reactions proceed as written on the molecular level. This allows you to write the rate expression for a particular elementary reaction by inspection.
- The plan in trying to determine mechanisms is to: (1) propose a mechanism, (2) predict the rate expression based on your mechanism, (3) compare with experiments. If it doesn't fit the experimental data, you need a new mechanism. If it fits, your proposed mechanism might be correct.
- We can connect a proposed mechanism with our understanding of chemistry in order to determine reasonableness. (Example S_N1 vs. S_N2 reaction mechanism)
- There are some "simple" mechanisms where the solutions are solvable analytically or numerically.
- In competing or parallel reactions, a reactant, A, can produce two products, either B or C.
  - The rate constants for the two parallel reactions are different.
  - The concentration of A will decay exponentially. This result is attainable through the mechanics we applied to first order kinetics.

$$[A] = [A]_o e^{-(k_1+k_2)t}$$

  - To find the concentration of B as a function of time we had to solve a differential equation:

$$\frac{d[B]}{dt} = k_1[A] = k_1[A]_o e^{-(k_1+k_2)t}$$

  - We could solve a similar relationship for [C](t). The ratio of the two concentrations was fixed by the ratio of the two rate constants, the so-called branching ratio.

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

  - This analysis can be applied to the S_N1 vs. S_N2 example discussed previously, where the case for either mechanism can be made. The actual reaction may be a competition between both mechanisms.