The Richard Stockton College of New Jersey
Chemistry Program, School of Natural Sciences and Mathematics
PO Box 195, Pomoma, NJ

CHEM 3410: Physical Chemistry I — Fall 2008

November 10, 2008

Lecture 29: Introduction to chemical kinetics

References

1. Levine, *Physical Chemistry*, Sections 16.1–4

Key Concepts

- In studying kinetics we will attempt to answer two broad questions regarding how reactions get to equilibrium (if they can):
  1. Experimental: how can we determine the rate of a reaction? — how fast, what does it depend on, how can we measure
  2. Theory: By what mechanism does a reaction proceed? — what do our experimental results tells us about the steps involved in a reaction, what do our experimental results mean
- For a general reaction:
$$aA + bB \rightarrow eE + fF$$
we can write the rate in terms of the concentration of a species:
$$rate = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{B}\frac{d[B]}{dt} = \frac{1}{e}\frac{d[E]}{dt} = \frac{1}{f}\frac{d[F]}{dt}$$
- Sometimes we can obtain an empirical relationship for the rate that is a function of several variables:
$$rate = k[A]^{\alpha}[B]^{\beta}[L]^{\lambda}$$
where we can make the following general observations:
  - k is the rate constant and is a function of temperature, $k = f(T)$
  - α and β are not stoichiometric coefficients. They are experimentally determined exponents.
  - α, β, and λ can be integers, fractions, or something else?
  - The species L does not appear in the chemical reaction, but can have an impact on the rate of the reaction (as a catalyst, impurity, etc).
  - The empirical expression may only be valid in a limited concentration range. Outside of this range, another law might apply.
- So rate laws are tricky business and in general can be written as:
$$rate = \underbrace{k(T)}_{rate\ constant} \times \underbrace{f\{[\ \ ]\}}_{function\ of\ compositions}$$
- Determining rate laws is tricky business for several reasons: reactions can be very fast or very slow, temperature impacts the rate, there can be reverse/competing reactions, the stoichiometry of the reaction does not give us any insight into the empirical rate law.