

CHEM 3410: Physical Chemistry I — Fall 2009

November 6, 2009

Lecture 27: Introduction to chemical kinetics

References

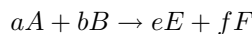
1. Levine, *Physical Chemistry*, Sections 16.1–4

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 tell us about the steps involved in a reaction, what do our experimental results mean

- For a general reaction:



we can write the rate in terms of the concentration of a species:

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{e} \frac{d[E]}{dt} = \frac{1}{f} \frac{d[F]}{dt}$$

- Sometimes we can obtain an empirical relationship for the rate that is a function of several variables:

$$\text{rate} = k[A]^\alpha[B]^\beta[L]^\lambda$$

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:

$$\text{rate} = \underbrace{k(T)}_{\text{rate constant}} \times \underbrace{f\{[\]\}}_{\text{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.