

CHEM 3410: Physical Chemistry I — Fall 2008

November 19, 2008

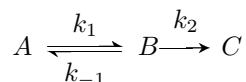
Lecture 33: Pre-equilibrium, competing reactions, and unimolecular reactions

References

1. Levine, *Physical Chemistry*, Chapter 16

Key Concepts

- The steady state approximation (the concentration of an intermediate is constant or time independent) allows us to:
 1. remove intermediate concentrations from rate expressions for reactants or products of the overall reaction
 2. solve algebraic equations as opposed to differential equations
- The steady state approximation is valid in cases where intermediates form slowly but are used up quickly.
- The alternative or reverse case, where the intermediate forms quickly but is used up slowly results in the *pre-equilibrium approximation*.
 - For the generic mechanism:

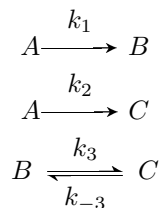


the pre-equilibrium approximation is valid when $k_2 \ll k_{-1}$ and k_2 .

- The kinetic equilibrium is quickly established between A and B. C forms much more slowly. (Kinetic equilibrium before thermodynamic equilibrium).
- We can arrive at the intermediate concentration, [B] by using the equilibrium between A and B:

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[B]}{[A]} \longrightarrow [B] = \frac{k_1}{k_{-1}}[A]$$

- Obtaining an expression for [B] in terms of [A] allows us to again to (1) eliminate [B] from any rate expression and (2) avoid solving differential equations.
- A more complex kinetic mechanism would be having competing reactions with exchange between the products:



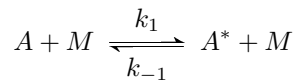
In this case we can have a kinetic and thermodynamic product.

- The relative values of k_1 and k_2 determines the kinetic products (which forms faster).
- The relative values of k_3 and k_{-3} determine which product is thermodynamically more stable (favored at equilibrium).
- The thermodynamic and kinetic product are not necessarily the same.

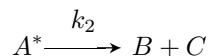
- The Lindemann mechanism describes unimolecular reactions, such as isomerizations and decompositions.



- The mechanism for these types of reactions can be broken up into two elementary steps:
 1. A molecule of species A collides with another molecule (M) to produce an activated a molecules A*. This activated molecule has gained a bit of extra energy that may be enough to allow the molecule to change to products (step 2). The activated molecule can always collide again to return to the original state.



2. The activate A molecule can decay into the products (for example, B and C).



- To determine the overall rate law (what we might observe experimentally), we need to write the rate expressions for the formation of product, B:

$$\frac{d[B]}{dt} = k_2[A^*]$$

However, this expression contains the concentration of an intermediate, which we need to remove. This can be done by employing the steady state approximation ($k_{-1} + k_2 \gg k_1$)

$$\frac{d[A^*]}{dt} = 0$$

By solving for $\frac{d[B]}{dt}$, we can determine the observed rate expression under different conditions, such as high and low pressure.

- Some unimolecular reactions (ex: decomposition of acetaldehyde) do not fit with the above kinetics of unimolecular reactions.