

# Chem132A: Lecture 23

Shane Flynn (swflynn@uci.edu)

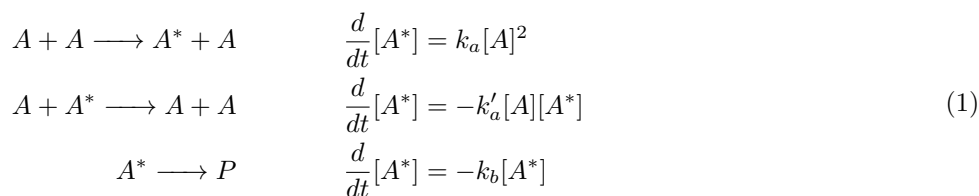
12/1/17

## Final Exam

The final exam will be on Friday, December 15 from 8am-10am.

## Uni-Molecular Reactions

Consider some simple reaction like  $A \longrightarrow P$ . We do not know if this is an elementary reaction. One proposed mechanism is the **Lindemann-Hinshelwood Mechanism**.



Applying our steady state approximation to the intermediate  $A^*$  we find

$$\begin{aligned} \frac{d}{dt}[A^*] = 0 &= k_a[A]^2 + -k'_a[A][A^*] + -k_b[A^*] \\ [A^*] &= \frac{k_a[A]^2}{k_b + k'_a[A]} \end{aligned} \quad (2)$$

We can then substitute in the intermediate concentration at steady state to our product formation rate and find.

$$\frac{d}{dt}[P] = k_b[A^*] = \frac{k_a k_b [A]^2}{k_b + k'_a [A]} \quad (3)$$

If we assume the decay of  $A^*$  to  $P$  is the slow step in the mechanism than we could write  $k'_a[A][A^*] > k_b[A^*]$ . We can use this to simplify our product rate equation.

$$\frac{d}{dt}[P] = k_b[A^*] = \frac{k_a k_b [A]^2}{k_b + k'_a [A]} \approx \frac{k_a k_b [A]}{k'_a} \equiv k_r[A] \quad (4)$$

In this limit (slow step assumption) we see that the reaction would look first order wrt  $A$ .

## Collision Theory

Using **Collision Theory** we can try to predict the rate of a reaction via probability. Consider a bi-molecular reaction



We would assume that the rate of this reaction is proportional to the number of collisions that occur between  $A$  and  $B$  molecules (assuming no complicated underlying mechanism but a simple elementary reaction).

$$\text{Rate} = k_r[A][B] \quad (6)$$

From intuition, if we assume a reaction occurs through a collision, we need some type of cross section associated with the sizes of the atoms ( $\sigma$ ). We also know the average velocities must be accounted for. From Maxwell-Boltzmann

Statistics we know the dependence is  $\langle V \rangle \propto \sqrt{\frac{T}{M}}$ . If we stick in an exponential activation energy dependence and a **Steric Factor** to account for proper orientation upon collision we find

$$k \approx P\sigma\sqrt{\frac{T}{M}}e^{-\frac{E_a}{RT}} \quad (7)$$

## Gas Collisions

Recall from our previous discussions, the collision rate for a gas is given by.

$$\begin{aligned} Z_{AB} &= \sigma \sqrt{\left(\frac{8k_B T}{\pi \mu}\right)} N_A^2 [A][B] \\ \sigma &= \pi d^2 \\ d &= \frac{1}{2}(d_A + d_B) \end{aligned} \quad (8)$$

We have also defined the reduced mass  $\mu$  which essentially replaced the two different masses with an average value (so we do not need to keep track of both).

$$\mu \equiv \frac{m_A m_B}{m_A + m_B} \quad (9)$$

Next class we will further elaborate this model, we will propose the cross section is a function of energy  $\sigma(E)$  with an intrinsic **Collision Energy** (associated with the collision) that must be overcome by the collision if a reaction is to occur.