Chem132A: Lecture 23

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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**.

$$\begin{aligned} A + A &\longrightarrow A^* + A & \frac{d}{dt}[A^*] &= k_a[A]^2 \\ A + A^* &\longrightarrow A + A & \frac{d}{dt}[A^*] &= -k_a'[A][A^*] \\ A^* &\longrightarrow P & \frac{d}{dt}[A^*] &= -k_b[A^*] \end{aligned} \tag{1}$$

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

$$\begin{aligned} \frac{d}{dt}[A^*] = 0 &= k_a[A]^2 + -k_a'[A][A^*] + -k_b[A^*] \\ [A^*] &= \frac{k_a[A]^2}{kb + k_a'[A]} \end{aligned} \tag{2}$$

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

$$\frac{d}{dt}[P] = k_b[A^*] = \frac{k_a k_b[A]^2}{k_b + k_a'[A]} \tag{3}$$

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.

$$\frac{d}{dt}[P] = k_b[A^*] = \frac{k_a k_b[A]^2}{k_b + k_a'[A]} \approx \frac{k_a k_b[A]}{k_a'} \equiv k_r[A] \tag{4}$$

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

$$A + B \longrightarrow P \tag{5}$$

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).

$$\textbf{Rate} = k_r[A][B] \tag{6}$$

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 (σ). 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

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

Gas Collisions

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

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

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

$$\mu \equiv \frac{m_A m_B}{m_A + m_B} \tag{9}$$

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