Transition State Theory

Consider a reaction in which reactants go to products. The potential of such a reaction can be plotted as a function of reaction coordinate i.e. the path that the reaction takes. Look at your notes for this picture.

In the middle of this plot there is an activation energy barrier. The path shown is the lowest energy path for the reaction. Remember that since molecules have lots of degrees of freedom, the potential will actually have lots of minima and various barriers. However, reactions proceed through the lowest energy path. Suppose we had an atomic microscope and could watch the reactions proceed, how might we calculate the rate of an equilibrium system. Well, we could look put a line at the activation energy barrier. This configuration is called the transition state. We could then watch the configurations that crossed this barrier and record their speed. Averaging all the speeds should give us the rate constant for the reaction.

$$k_{TST} = \frac{1}{2} < |v|\delta(Q - Q^*) >_{Boltzman\ distribution\ over\ reactants}$$

The factor of 1/2 is needed since the delta function does not distinguish whether particles are going to products or reactants.

Since no term depends simultaneously on the positions and velocities, we can separate this average into an average over velocities and on the positions.

$$k_{TST} = \frac{1}{2} < |v| >_{Boltzmann\ distribution\ of\ velocities\ of\ reactants} < \delta(Q - Q^*) >_{Boltzman\ distribution\ of\ positions\ of\ reactants}$$

Let's first do the average over the absolute value of the velocity.

$$< |\mathrm{v}| >_{Boltzman\ distribution\ of\ velocities\ of\ reactants} = \frac{\int_{-\infty}^{+\infty} |\mathrm{v}| e^{-\frac{m\mathrm{v}^2}{2kT}} d\mathrm{v}}{\int_{-\infty}^{+\infty} e^{-\frac{m\mathrm{v}^2}{2kT}} d\mathrm{v}} = \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{+\infty} |\mathrm{v}| e^{-\frac{m\mathrm{v}^2}{2kT}} d\mathrm{v} = 2\sqrt{\frac{m}{2\pi kT}} \int_{0}^{+\infty} \mathrm{v} e^{-\frac{m\mathrm{v}^2}{2kT}} d\mathrm{v} = \sqrt{\frac{m}{2\pi kT}} \frac{2kT}{m} = \sqrt{\frac{2kT}{\pi m}}$$

Now, let's do the average of the delta function:

$$< \delta(Q - Q^*) >_{Boltzman\ distribution\ of\ positions\ of\ reactants} = \frac{\int_{reactants} \delta(Q - Q^*) e^{-\frac{V(Q)}{kT}} dQ}{\int_{reactants} e^{-\frac{V(Q)}{kT}} dQ}$$

$$= \frac{e^{-\frac{V(Q^*)}{kT}}}{\int_{-\infty}^{\infty} e^{-\frac{V(Q_0) + V'(Q_0)(Q - Q_0) + \frac{V''(Q_0)(Q - Q_0)^2}{2}}{kT}} dQ}$$

$$= \frac{e^{-\frac{(V(Q^*) - V(Q_0))}{kT}}}{\int_{-\infty}^{\infty} e^{-\frac{V''(Q_0)(Q - Q_0)^2}{2kT}} dQ} = \sqrt{\frac{V''(Q_0)}{2kT\pi}} e^{-\frac{(V(Q^*) - V(Q_0))}{kT}}$$

In the second equality, we've used the delta function property and assumed a harmonic oscillator potential for the reactants. We also replaced the potential with a taylor expansion about the minimum to second order. For the harmonic oscillator, the first derivative is zero at the minimum. In the third equality, factored out a constant term form the bottom integral and brought it to the top. Finally, in the last equality, we evaluated the bottom integral.

For a harmonic oscillator, we can actually evaluate the second derivative.

$$V(Q) = \frac{1}{2} m\omega^2 (Q - Q_0)^2$$
$$V'(Q) = m\omega^2 (Q - Q_0)$$
$$V''(Q) = m\omega^2$$

Putting all this together, we get:

$$k_{TST} = \frac{\omega}{2\pi} e^{-\frac{(V(Q^*) - V(Q_0))}{kT}} = \frac{\omega}{2\pi} e^{-\frac{E_a}{kT}}$$

This is essential the frequency of oscillation in a harmonic well i.e. the frequency of attempts of a reaction times the probability that any attempt has enough energy to overcome the reaction barrier.

Talk about moving transition state. Add delta function pieces to this.