Potential Barriers and Tunneling

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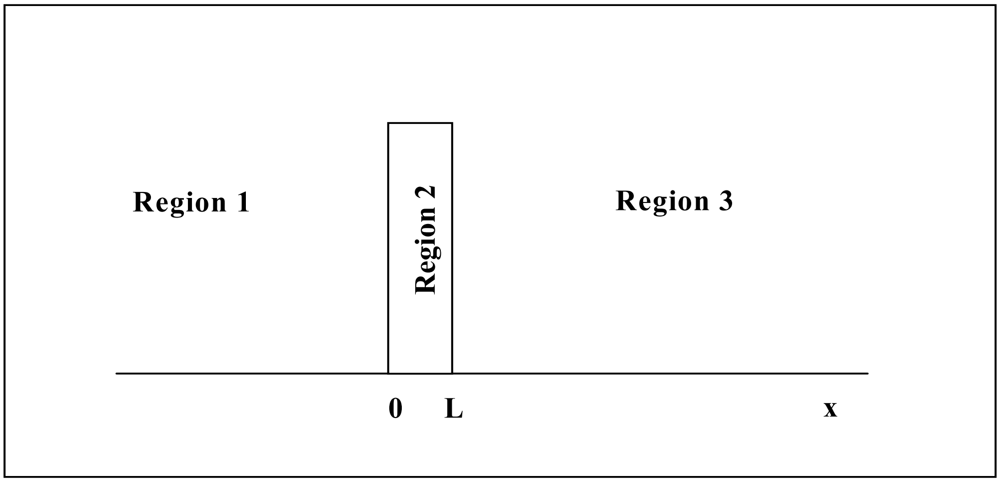
Prerequisites: This worksheet is appropriate for use in Junior-Senior level physical chemistry classes. To use the document you should have some familiarity with Mathcad. In addition, it is recommended that you study the sections of a physical chemistry textbook that relate to the solution of the Schrodinger equation for the particle in a box. This document requires Mathcad 2000 Professional or later.

Introduction: Imagine you placed a ball in a box and gave it a push. For this thought experiment, we will neglect friction and assume that the walls are perfectly rigid, so the ball does not lose energy when it collides with the walls. Thus, once you start the ball moving, it would roll back and forth inside the box until you stopped it. If you didn't give the ball enough energy to get over the sides of the box, would you expect to find it outside of the box? Of course not! The ball is stuck inside of the box until you give it enough energy to get out of the box.

As you know, the world of the atom is different from everyday experience. If an electron is placed inside of an atom-sized box, it has a finite, non-zero probability of being found outside of the box, even if the electron did not have enough energy to get over the walls. This effect is known as *quantum mechanical tunneling* because it is as if the electron tunneled through the wall. This strange phenomenon can explain several observed processes, including some radioactive decay processes and the fusion reaction that powers stars. Tunneling can also explain the observed rates of some chemical reactions and the variation of those rates with different isotopes.

This document will help you explore some of the fundamentals of quantum tunneling. You will first examine the wavefunction and probability distribution function of the particle. You will also explore the effect of particle energy, wall thickness, and particle mass on the tunneling probability.

The scene that is set is a particle that is free to roam from $-\infty$ to 0 in the x-direction (Region 1). At x = 0, the particle encounters a wall. The "wall" is a potential energy barrier, V0, that is greater than the energy of the particle. The wall has a thickness of L (Region 2). To the right of the barrier, the particle is free to roam to $+\infty$ (Region 3). The following illustration depicts this.



First, we define hbar, the mass of the particle, and the range of x for region 1, r1, region 2, r2, and region 3, r3. We must also define the width of the barrier, L.

$$hbar := \frac{6.6260755 \cdot 10^{-34}}{2\pi}$$

$$L := 2 \cdot 10^{-10}$$

This converts from Angstroms to meters. You can change L by changing this number.

Possible values for particle mass are found here.

$Me := 9.1093897 \cdot 10^{-31}$ Mass of an electron

$Mp := 1.6726231 \cdot 10^{-27}$ Mass of a proton

$MH := 1.6738245 \cdot 10^{-27}$ Mass of H atom

Return to STM

Return to STM questions

Return to Reaction

Return to Reaction questions

$$m := Me$$

$$x := -1 \cdot 10^{-8}, -9.95 \cdot 10^{-9} .. 1 \cdot 10^{-8} \qquad r1 := -1 \cdot 10^{-8}, -9.95 \times 10^{-9} .. 0$$

$$r2 := 0, 5 \cdot 10^{-11} .. L \qquad r3 := L, \left(L + 5 \cdot 10^{-11}\right) .. 10^{-8}$$

Now we define the energy of the particle and the potential height of the barrier. This document considers only the situation in which the energy of the particle is less than the barrier height. If, in your exploration, you set E > V0, your results will not be reliable!

The energy of the particle

$$E := 4.0\left(1.60217733 \cdot 10^{-19}\right)$$

The height of the barrier

$$V0 := 5.0 \cdot \left(1.60217733 \cdot 10^{-19}\right)$$

The factor in parentheses converts the energy and barrier height from eV to Joules. You can change the numbers in front to change these values.

In Regions 1 and 3, the Schrodinger equation is $\frac{d^2}{dx^2}\psi + \frac{2m}{hbar^2}E \cdot \psi = 0$. In Region 2, the Schrodinger equation is $\frac{d^2}{dx^2}\psi + \frac{2m}{hbar^2}(E - V0) \cdot \psi = 0$. The solutions to these equations will be given soon. They involve some constants that must be defined first.

$$k_1 := \sqrt{\frac{2m \cdot E}{hbar^2}} \qquad k_2 := \sqrt{\frac{2 \cdot m \cdot (V0 - E)}{hbar^2}}$$

$$k_1 = 1.025 \times 10^{10} \qquad k_2 = 5.123 \times 10^{9}$$

Each wavefunction will be multiplied by a constant. The constants ensure that the wavefunction is continuous across the three different regions. The constants are defined here.

$$A := \left[\left(k_2^{\,2} - k_1^{\,2} + 2i \cdot k_1 \cdot k_2\right)e^{-k_2 \cdot L} + \left(k_1^{\,2} - k_2^{\,2} + 2i \cdot k_1 \cdot k_2\right)e^{k_2 \cdot L}\right] \cdot \frac{e^{i \cdot k_1 \cdot L}}{4i \cdot k_1 \cdot k_2}$$

$$C := \frac{\left(k_2 + i \cdot k_1\right) \cdot e^{i \cdot k_1 \cdot L}}{2 \cdot k_2 \cdot e^{k_2 \cdot L}} \qquad D := \frac{\left(k_2 - i \cdot k_1\right) \cdot e^{i \cdot k_1 \cdot L}}{2 \cdot k_2 \cdot e^{-k_2 \cdot L}} \qquad B := C + D - A$$

Region 1 is the range to the left of the barrier is a box that stretches to - ∞. The wavefunction for Region 1 is found by solving the Schrodinger equation for Region 1 (see, for example, McQuarrie and Simon, *Physical Chemistry: A Molecular Approach*, pp. 140-4):

$$\psi 1(r1) := A \cdot e^{i \cdot k_1 \cdot r1} + B \cdot e^{-i \cdot k_1 \cdot r1}$$

The probability distribution of finding the particle in Region 1 is just the complex conjugate of the wavefunction times the wavefunction.

$$Prob1(r1) := \overline{\psi 1(r1)} \cdot \psi 1(r1)$$

Region 2 is the region within the barrier, ranging from x=0 to x=L. The wavefunction and probability distribution for this region are given by:

$$\psi 2(r2) := C \cdot e^{k_2 \cdot r2} + D \cdot e^{-k_2 \cdot r2} \qquad Prob2(r2) := \overline{\psi 2(r2)} \cdot \psi 2(r2)$$

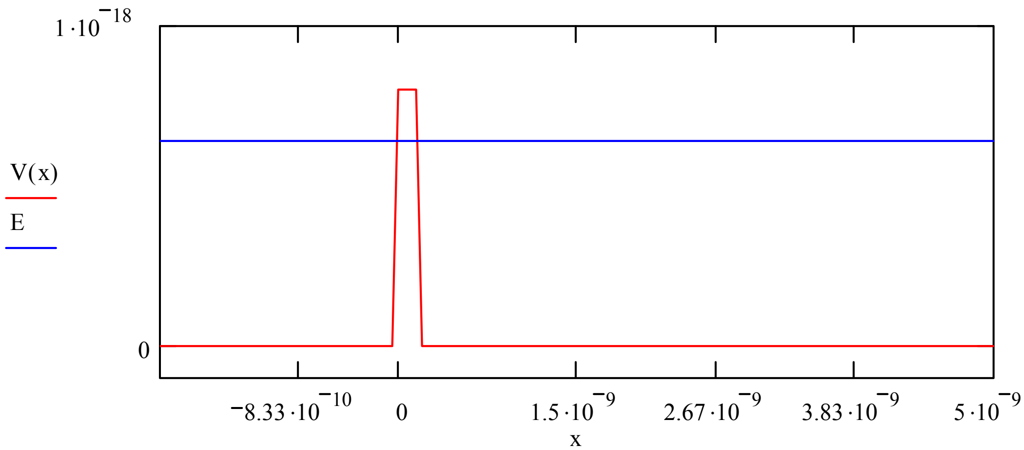
Region 3 is the region to the right of the barrier, ranging from x=L to x= ∞. The wavefunction and probability distribution for this region are given by:

$$\psi 3(r3) := 1 \cdot e^{i \cdot k_1 \cdot r3} \qquad Prob3(r3) := \overline{\psi 3(r3)} \cdot \psi 3(r3)$$

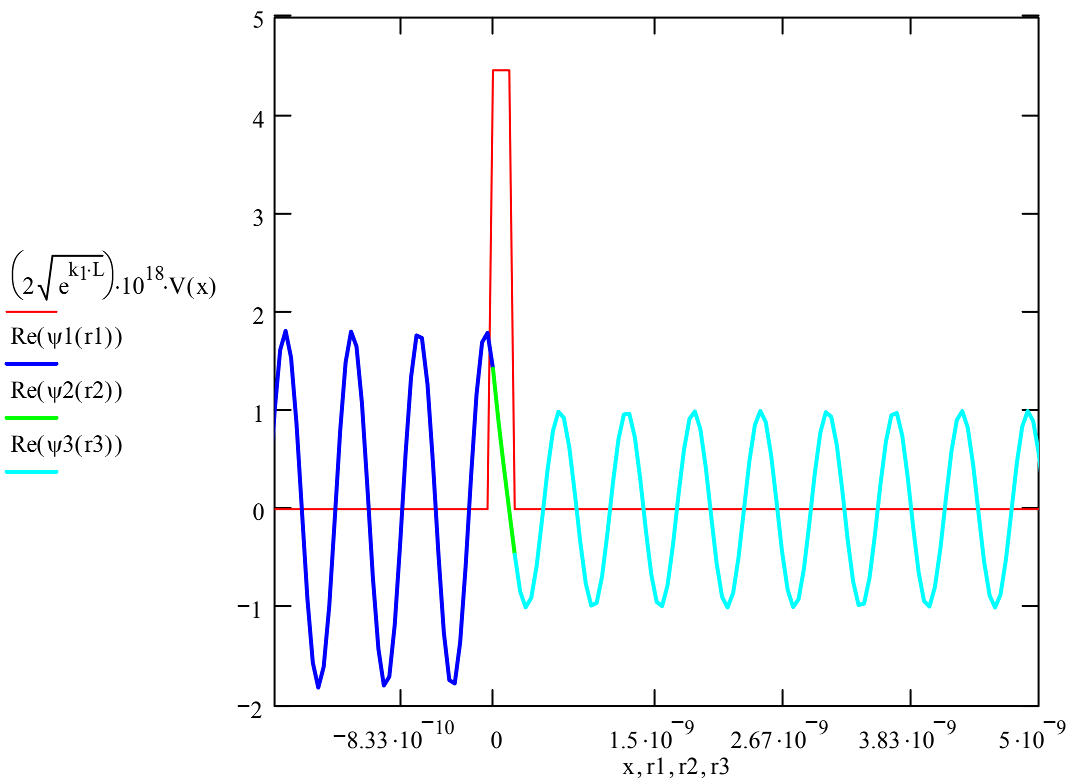
The potential barrier is defined here:

$$V(x) := \begin{cases} V0 & \text{if } (x < L) \wedge (x > 0) \\ 0 & \text{otherwise} \end{cases}$$

This graph shows the potential barrier. The value of the energy of the particle is shown as a straight line for comparison to the barrier.



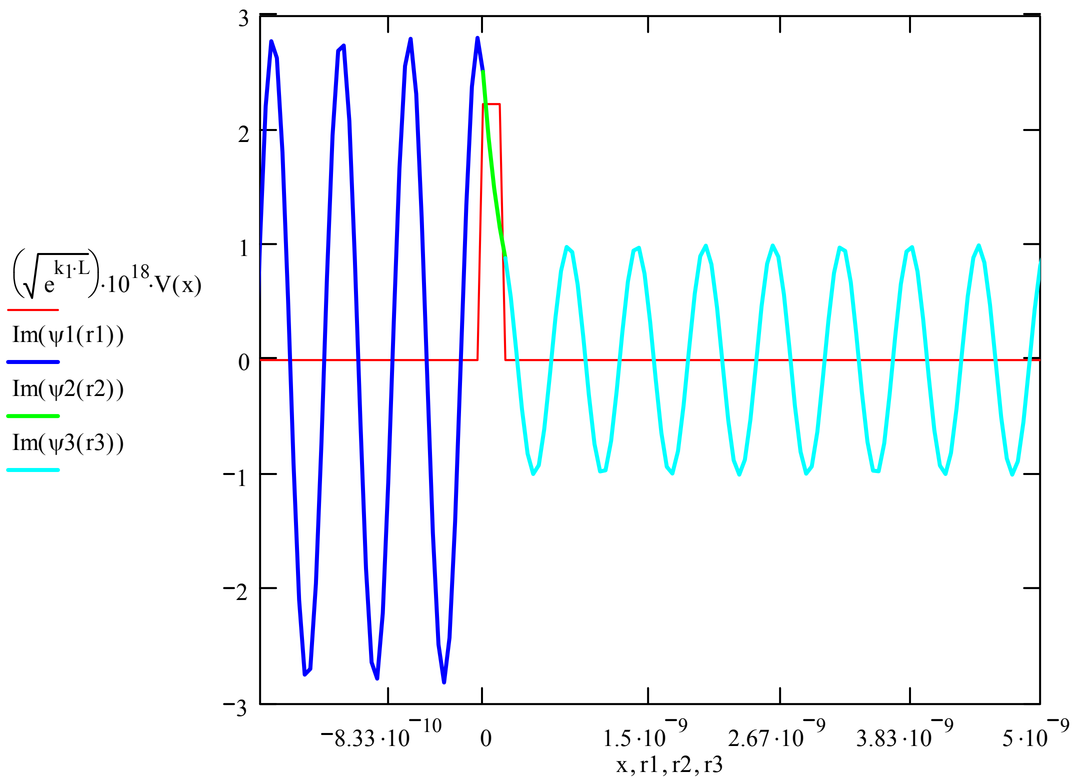
The following graph shows the real parts of the wavefunctions. The wavefunctions are color-coded by region. The barrier is shown to help demonstrate the different wavefunctions for the different regions. The vertical scale of the barrier has been adjusted to allow it to be shown on the same graph as the wavefunctions.



Describe the behavior of the real part of the wavefunction for each region.

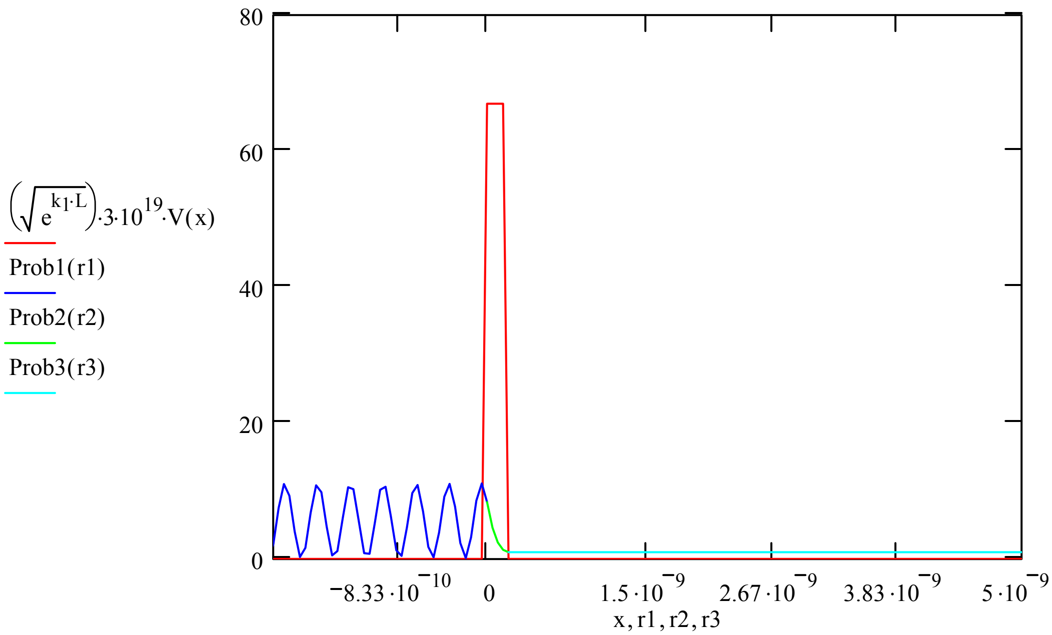
What does the fact that the wavefunction is not zero in the barrier indicate?

The imaginary parts of the wavefunctions are shown in the following graph. Again, the barrier is shown but is not to scale.



Describe the behavior of the imaginary part of the wavefunction for each region.

Finally, the probability distributions are graphed here.



What does this graph indicate to you about the relative probability of finding the particle to the left of the barrier?

What is the classical probability for finding the particle to the right of the barrier? Based on the graph, is the relative quantum probability equal to the classical probability?

The probability that the particle will be found to the right of the barrier is the *tunneling probability*. Mathematically, the tunneling probability related to the coefficient of the wavefunction for Region 3 divided by the coefficient of the wavefunction for Region 1. **Can you explain why?** Specifically, for our example, the tunneling probability, T= $\frac{1}{\overline{A} \cdot A}$.

For these conditions (energy, barrier height, barrier width, and particle mass), the tunneling probability is:

$$T := \frac{1}{\overline{A} \cdot A} \qquad T = 0.30292$$

For E=4 eV, V0=5 eV, L=5 Angstroms, and m=Me, what is the tunneling probability?

What is the tunneling probability if the conditions are the same but the particle is a proton? (set m=Mp). Double-click <u>here</u> to change mass.

For E=4 eV, V0=5 eV, L=5 Angstroms, and m=Me, what is the tunneling probability?

How narrow must you make the barrier for a proton to have the same tunneling probability as the electron did?

What can you conclude about the effect of particle mass on the tunneling probability? Is the relationship linear?

Set m=Me, V0=5 eV, and L=5 Angstroms. What are the tunneling probabilities at E=1, 2, 3, and 4.9 eV?

What can you conclude about the effect of particle energy on the tunneling probability? Is the relationship linear?

Set the energy at one-half of the barrier height. What are the tunneling probabilities for L=1, 3, 5, and 7 Angstroms?

Set the energy at 85% of the barrier height. What are the tunneling probabilities for L=1, 3, 5, and 7 Angstroms?

For a fixed energy, how does the tunneling probability depend on the barrier width?

Tunneling is important for an instrument called the scanning tunneling microscope (STM). For some chemical reactions, atoms can tunnel through the activation barrier to reaction, allowing for a faster-than-anticipated reaction rate. The following two examples allow you to apply your basic understanding of tunneling to better understand these relevant chemical phenomena.

Scanning Tunneling Microscopy

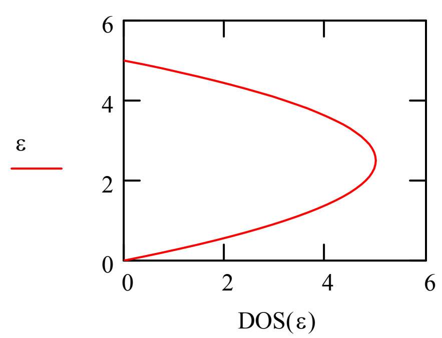
In a scanning tunneling microscope (STM), a metal tip is brought very close (within 10 Angstroms) to a surface of a conducting or semiconducting sample. A voltage is applied between the sample and the tip, so electrons will tunnel between the sample and the tip. Commonly, the tip is held at a positive voltage relative to the tip, so electrons will tunnel from the sample to the tip. The flow of electrons from the sample to the tip is the *tunneling current.*

In a STM, Region 1 from the above example corresponds to the sample, Region 2 to the gap (usually vacuum) between the tip and sample, and Region 3 to the tip. Instead of a single particle in a single energy state, the sample has many (~10^{23}) electrons in many energy states. The distribution of energy states is called the *density of states* (DOS), which is proportional to the square of the wavefunction in Region 1. Essentially, there are a large number of energy states of similar energies. We can make a simple model of the DOS of a sample here:

Set V0=5. Double-click here to return to the region in which the variables are defined.

$V0 := 5 \qquad m := Me$

$\varepsilon := 0, 0.1 .. 5 \qquad DOS(\varepsilon) := 5 - \frac{20}{V0^2}\cdot\left(\varepsilon - \frac{V0}{2}\right)^2$



This is a fairly representative DOS for common samples.

The tunneling current is found to depend exponentially on the distance between the tip and the sample. The decay constant, k(ε), is related to the mass of the electron and its energy, as shown in the equation below:

$$k(\varepsilon) := \sqrt{\frac{2m\cdot\varepsilon\cdot 1.60217733\cdot 10^{-19}}{hbar^2}}$$

$L := 5.0\cdot 10^{-10}$ This is the barrier width.

This is different than our first example in which their was one particle with a specific energy. Now, the sample has many electrons, each of which could tunnel, at a variety of different energies. At a given energy, the tunneling current is proportional to the number of energy states at that energy (the DOS) times the probability of tunneling with that energy (e^{-2kL}). The total tunneling current is the sum of the tunneling current from each state. Thus, the total tunneling current will be proportional to the sum over the DOS. For more information, see *Introduction to Scanning Tunneling Microscopy* by C. Julian Chen.

$$I := \sum_{\varepsilon} \left(DOS(\varepsilon) \cdot e^{-2\,k(\varepsilon)\cdot L} \right)$$

This is the total tunneling current. (We have neglected the proportionality constants because we will be interested in relative differences in tunneling currents.)

$$I = 0.57279$$

For a gap (L) of 5 Angstroms, what is the tunneling current? What is the percent change in tunneling current if the gap is changed by 0.1 Angstroms?

The STM scans over the sample in constant current mode. That is, piezoelectric crystals move it across the sample, and the tip-sample distance is maintained by keeping the tunneling current at a constant value. A computer controls a feedback loop so that if tip approaches a bump, the current increases, and the computer responds by pulling the tip away so that a constant distance (and therefore tunneling current) is maintained. This produces a topographical map of the surface, and the vertical resolution is determined by the computer's ability to regulate the tunneling current. A nice variety of STM images can be viewed on the web at:
http://www.almaden.ibm.com/vis/stm/gallery.html

If the electronics can maintain a tunneling current to within 1%, what is the vertical resolution of the STM? That is, what displacement of the tip causes a 1% change in the tunneling current?

What aspect of tunneling allows STM to have such good vertical resolution?

Tunneling in Chemical Reactions

Most reactions have an activation barrier that the reactants must overcome in order for the reaction to proceed. If the reactants do not have enough energy to surmount the activation barrier, then they will not react. However, it is possible for the reactants to tunnel through the barrier and become products even though they did not have enough energy to classically get over the activation barrier. As you discovered above, the tunneling probability depends strongly on mass, so tunneling is most commonly observed for transfer of H atoms.

Remember that the rate constants of most chemical reactions display Arrhenius behavior. That is, the rate constant k = $A\exp\left(\frac{-E_a}{RT}\right)$, where E_a is the activation energy, and A is the Arrhenius prefactor. For reactions that display this behavior, a plot of ln(k) versus 1/T should yield a straight line. However, for some reactions, at low temperatures k is larger than would be expected based on the Arrhenius model. A possible explanation for this observation is that tunneling contributes to the reaction rate. At low temperatures, where few molecules have enough energy to overcome the activation barrier, some molecules tunnel through the barrier. This would cause more reactions to occur in a given time and cause the rate constant to have a larger value than expected.

One reaction in which tunneling could explain the abnormal behavior of k with temperature is OH + HCl $\rightarrow$ H_2O + Cl. This reaction involves the breaking of the H-Cl bond. The activation energy has been estimated as 2910 J/mol, which is 1.81 eV. Assume that the width of the barrier is about 1.2 Angstroms, which is roughly the equilibrium bond length of HCl. This simple model approximates that the H-Cl bond will be broken at about twice its equilibrium length. (This is not a bad assumption. According to a Morse potential, at twice its equilibrium length, the bond is about 80% of the way to dissociation.) Also assuming that HCl has about 0.20 eV of energy (kinetic plus zero-point vibration),

Estimate the tunneling probability for these conditions. It's probably easiest to return to the beginning of the document to change the values for mass, energy, V0, and L. Click here to return to the variable definitions.

If each molecule makes about 8.65 x 10^{13} attempts to go through the barrier per second (this is the number of vibrations a HCl molecule undergoes per second), what is the tunneling probability per second?

If one mole of molecules is present, how many molecules, on average, tunnel through the barrier per second?

If DCl was used instead of HCl under the same conditions, how many molecules, on average, tunnel through the barrier per second? Assume the mass of deuterium is twice the mass of hydrogen.

Based on your answer, can you suggest an experiment to test whether tunneling is responsible for the observed behavior for the rate constant for this reaction?

Summary Questions

1. On what factors does quantum tunneling depend? Specify how (linearly, exponentially, etc.) the tunneling probability depends on each factor.

2. How is tunneling central to STM?

3. What role does tunneling play in the rate of chemical reactions?

Mathcad Notes for editing the hyperlink tags in this document. These notes are useful for documents written in Mathcad 2001i and 2011. These notes were obtained from the Mathcad help files that accompanied Mathcad 2011 but work for Mathcad 2001i as well. These notes were added by Theresa Julia Zielinski, feature editor of the SymMath column.

1. Before you can link to a specific region in a worksheet, you must mark it with a tag. A tag uniquely identifies a region in a worksheet, allowing you to jump directly to that region. A tag can be any collection of words, numbers, or spaces, but no symbols. A tag can not have a period in it, such as Sec1.1 but you can write Sec1,1 or Sec1-1." You can create a tag as follows:

Creaing a tag

1. Right-click on any region in your worksheet for which you would like to create a region tag. It is best to use a text region.

2. Select Properties from the pop-up menu.

3. In the Properties dialog box, under the Display tab, type a tag in the text box provided and click “OK.”

4. Now you can link to that region from within the worksheet or from any other worksheet.

To create a hyperlink to a region that has been tagged:

1. Write a suitable text phrase in your worksheet. Click on this region in your worksheet, and choose Hyperlink from the Insert menu.

2. Click “Browse” to locate and select the target worksheet, or type the complete path or Internet address (URL) to a worksheet. You must enter the name of the target worksheet even if you are creating a hyperlink to a region within the same worksheet.

3. At the end of the worksheet path type “#” followed by the region tag name. The complete path for your target region will look something like this: C:\filename#region tag

Make further desired specifications in the Hyperlink dialog box and click “OK.”