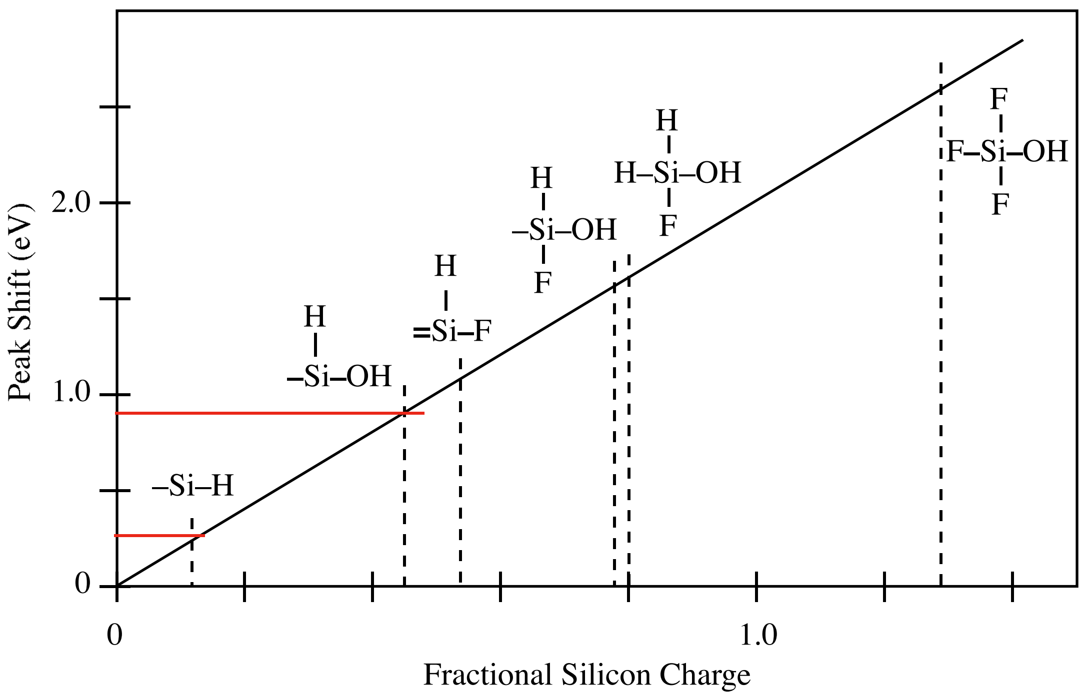
Fundamentals of Electrochemistry
CHEM*7234 CHEM 720
Assignment 5

ANSWERS

1 (a) This is a simple linear graph with a slope of 2. The given charge densities identify the corresponding peak shifts.



The candidate species are located by the fractional charge density values taken from the theoretical calculations and shown as dotted lines. The experimental measurements are located by the red lines from the measured peak shifts. Some points to remember when making these measurements:
A single Si atom produces the two peak structure (it is a doublet p state with mj = 3/2 and 1/2, but all you need to know is that a peak shift is measured only from the purple curve to a corresponding point on the green curve and on the orange curve).
Make the measurements from the top of the largest peak. Doing this we find that the peak shift for the green curve is about 0.264 eV while the peak shift for the orange peak is about 0.903 eV. These are then located on the curve above. From these measurements it is clear that the two surface species must be Si-H and S(H)-OH. The predominant species is clearly the silicon hydride. Sincethe Si is the same in both molecules, we can directly compare the peak area.
Many different ways are possible. Some of you have split the peaks into triangles and summed the areas. One technique I was thinking to do is to photocopy the curves with magnification and then cut out each curve (correctly account for the baseline!) and then simply weigh the two pieces of paper. SInce the paper has a uniform density (we hope), the ratio of the mass is the same as the ratio of the areas. Just with your eyes, you should be able to assess that the area ratio is much smaller than a factor of, say 25 but also that it is considerably larger than a factor of, say 3. SOmething in the vicinty of 8 is acceptable. This suggests that there is 8 times as much hydride as their are hydroxylated Si atoms.

2. (a) You need the values of the physical constants used and conversino factors between eV and J and between Å and m. These values are:
m = 9.1094 x 10^{-31} kg
h = h/2π = 6.626-75 x 10^{-34} J s/2π = 1.054573 x 10^{-34} J s

1 eV = 1.602177 x 10^{-19} J
1 Å = 10^{-10} m

$$\kappa = \frac{\sqrt{2m\phi}}{\hbar} = \frac{\sqrt{2\left(9.1094\times10^{-34}\ \text{kg}\right)\phi(\text{eV})\left(1.602177\times10^{-19}\ \frac{\text{J}}{\text{eV}}\right)}}{1.054573\times10^{-34}\ \text{J s}}$$

$$= 5.12\times10^{9}\ \sqrt{\phi(\text{eV})}\left(\text{m}^{-1}\right)\times10^{-10}\ \frac{\text{Å}^{-1}}{\text{m}^{-1}}$$

$$= 0.512\sqrt{\phi(\text{eV})}\left(\text{Å}^{-1}\right)$$

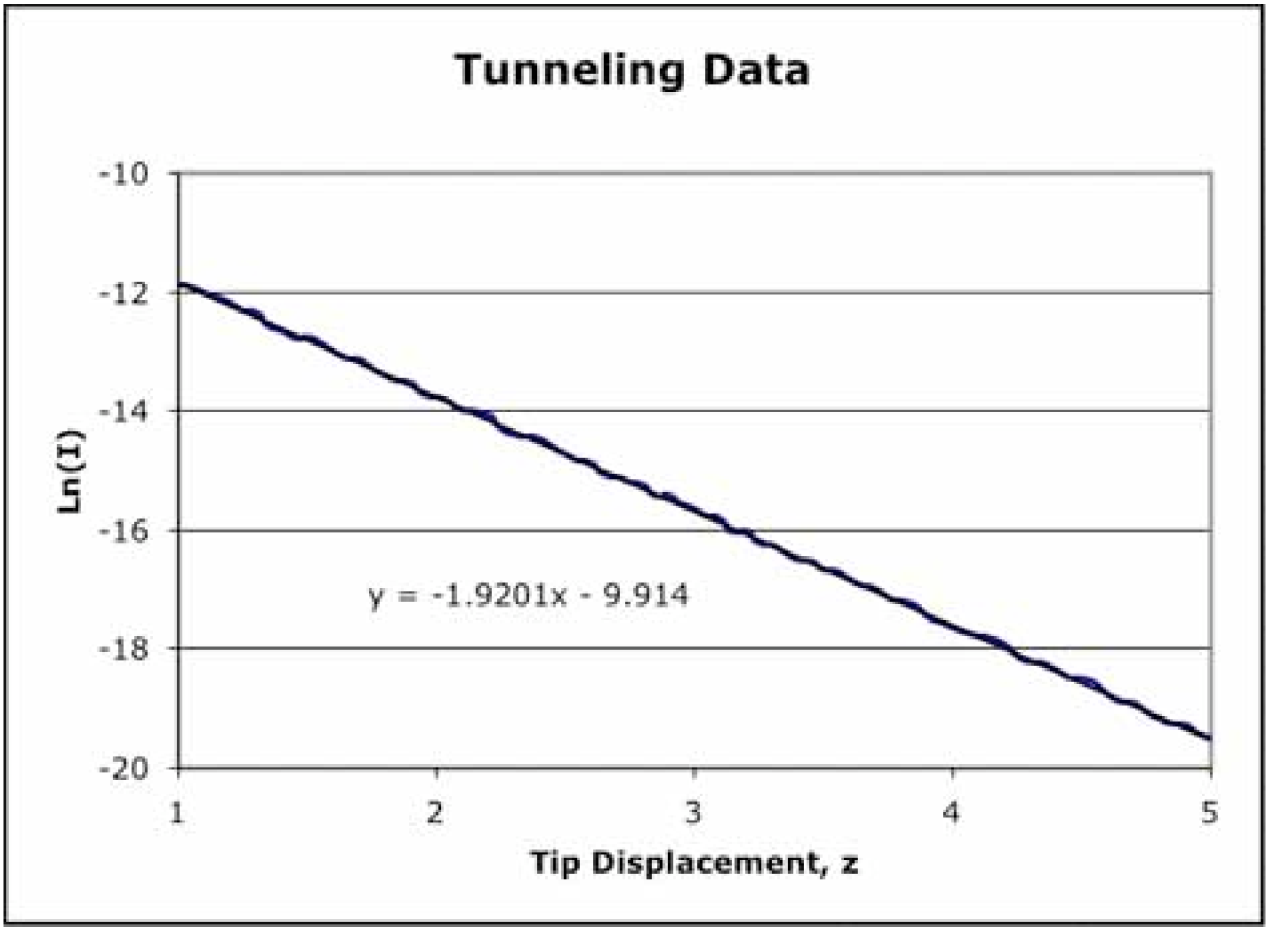
2 (b). The equation needs to be reorganized so that the logarithm can be taken. In doing this, we soon see that the correct plot is that of z vs. ln(I).In doing this, we find a straight line with a slope equal to -2κ. Once having measure the slope, we can readily obtain κ, which then quickly gives us the local barrier height φ.

$$I = V\rho_s \exp(-2\kappa z)$$

$$\frac{I}{V\rho_s} = \exp(-2\kappa z)$$

$$\ln\left(\frac{I}{V\rho_s}\right) = -2\kappa z$$

$$\ln(I) = -2\kappa z + \ln\left(V\rho_s\right)$$



The measured slope from the fit is -1.9201. We solve this for κ and then for ϕ.

$$\text{slope} = -1.9201 = -2\kappa$$

$$\kappa = \frac{-1.9201}{-2} = 0.960 = 0.512\sqrt{\phi}$$

$$\phi = \left(\frac{0.960}{0.512}\right)^2 = 3.52 \text{ eV}$$