Q4 In plant cells, organelles called *chloroplasts* (and in animal cells organelles called *mitochondria*) store energy by establishing a concentration gradient of H^+ ions (protons) across their bounding membranes. This energy is used to synthesize adenosine triphosphate (ATP), which in turn provides the energy for other metabolic processes.

a) As a simple model for the aqueous environment take a lattice with Ω sites, and write an expression for the entropy of N protons distributed among the sites. Assume a dilute solution, such that $N << \Omega$, and that both N and Ω are large enough that you may, if you need, use Stirling's approximation $\ln n! = n \ln n - n$.

b) Use your answer to part (a) to calculate the change in entropy when a single proton is exported from the organelle. Show that it can be written as

$$\Delta S = a k_\mathrm{B} \ln \left(\frac{c_{\mathrm{H^+ outside}}}{c_{\mathrm{H^+ inside}}} \right)$$

where $c_{\mathrm{H^+}}$ denotes the proton concentration and a is a numerical constant that you should find.

c) At a temperature of 37C (*i.e.* 310K) a typical pH difference across the membrane is approximately 0.7, being 7.7 inside and 7.0 outside. (Recall that $\mathrm{pH} = -\log_{10} c_{\mathrm{H^+}}$, with $c_{\mathrm{H^+}}$ measured in moles per litre). Assuming that the change in free energy is dominated by the change in entropy, how much free energy can be recovered by allowing a single proton to cross the membrane into the organelle? Express your answer as a multiple of $k_\mathrm{B}T$, and then convert this to eV.

d) In mitochondria an additional contribution to the free energy comes from a potential difference V across the membrane. It is found that the formation of an ATP molecule requires the movement of 4 protons into the mitochondrion. If the free energy needed to create an ATP molecule is approximately $20 k_\mathrm{B}T$, how large must V be?