Exercise Series 1

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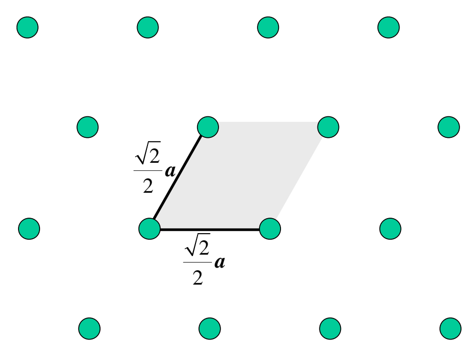
1. Write down explanations of the following terms or answers on the queries
   (a) electrochemical system (main components and characteristics)
   (b) electrical potential, chemical potential, electrochemical potential
   (c) electrical current, electrical current density (in relation to electron flux through metal or ion flux in solution)
   (d) What is a test charge? Explain the difference to real charges.
   (e) Under which conditions does the Gibbs free energy, $\boldsymbol{G}$, determine the equilibrium in a system? Under which conditions should the Helmholtz free energy, $\boldsymbol{F}$, be used? What are the natural variables of each of these thermodynamic functions?

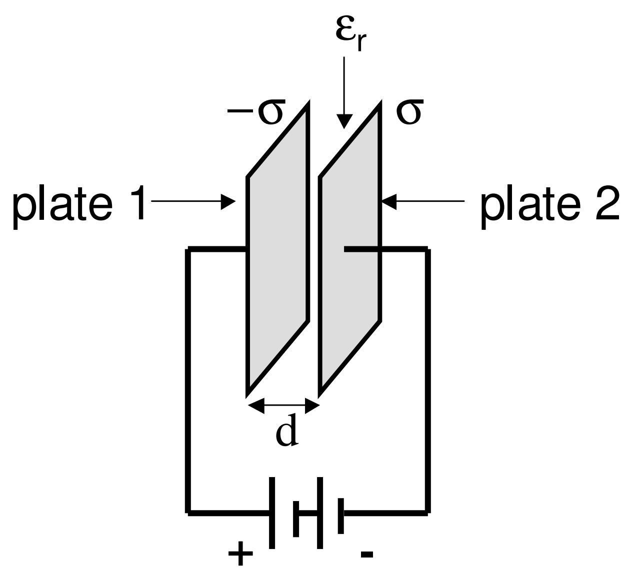
2. Consider a water-filled sphere, 10 cm in diameter, that contains an excess of 10^{-10} mol of sodium ions.
   (a) What is the electrical potential on the surface of the sphere? [Hint: The potential on the surface can be calculated by assuming that the excess charge is located at a point in the center of the sphere. Could you explain why?]
   (b) Plot the electrical potential φ outside of the sphere as a function of the radial coordinate $\boldsymbol{r}$.

3. The Cu(111) electrode surface corresponds to a hexagonal lattice of Cu atoms, as illustrated in the figure below. The primitive unit cell, indicated by the gray area, corresponds to the area occupied by one surface atom.



The lattice constant of Cu is $a = 3.6$ Å. The electrode is in a solution and connected to a galvanostat that can be used to control the flux of an electrical current to or from the electrode. A current of $I = 3$ A is passed for $t = 10$ μs to the electrode. The total surface area of the electrode is $A = 1$ cm^2.
   (a) What is the final excess charge density σ of the metal surface (units $\boldsymbol{C/m^2}$)?
   (b) How many excess electrons does each Cu surface atom carry?

4. Consider a parallel arrangement of two electrodes (of the type considered in problem 3) with surface area $A = 1$ cm^2 at a separation $d = 1$ μm. The space between the electrodes is filled by a dielectric (here: water) with dielectric constant $\varepsilon_r = 80$. The surface charge density on one plate is σ (use the value from problem 2 (a)). The opposite plate has the charge density $-\sigma$. This configuration, depicted below, corresponds to a simple parallel plate capacitor.



(a) Calculate the electric field, E, at a point between the two electrodes.

(b) Calculate the potential difference V between a point on plate 1 and a point on plate 2. What is the corresponding work performed by the electric field upon moving a test charge from plate 1 to plate 2? What is the relation between the electric field, E, calculated in (a), and V?

(c) Use the definition of capacitance, $C = Q/V$ (where Q is the total charge on each of the plates) to derive the relation for the capacitance of an ideal capacitor

$$C = \varepsilon_0 \varepsilon_r \frac{A}{d}.$$

Calculate C for the given configuration.

(d) Water starts to decompose at the voltage 1.2V (due to electrolysis). Calculate the maximum energy $E = \frac{1}{2} C V^2$ that could be stored in this capacitor.

5. Consider a plain metal electrode situated at $z=0$, with the metal occupying the half-space $z \leq 0$, while the solution region occupies $z>0$. In a simple model, the excess surface charge density σ on the metal surface is balanced by a space charge density $\rho(z) = K \exp(-\kappa z)$ in the solution, where κ is a parameter that depends on the properties of the solution.

(a) Determine the constant K from the charge balance condition.

(b) Calculate the interfacial capacitance corresponding to this charge distribution, assuming that κ is independent of σ. [Hint: You must calculate an average plate separation, $\bar{d}$, at which the charge in solution is virtually located. Use the space charge density $\rho(z) = K \exp(-\kappa z)$ as a weighting function in determining $\bar{d}$.]