

Solution for 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 the test charge? Explain the difference to real charges.
 - (e) Under what conditions does the Gibbs free energy, G , determine the equilibrium in a system? Under which conditions should the Helmholtz free energy, F , be used? What are the natural variables of each of these thermodynamics functions?

Solution

- (a) An electrochemical system is a heterogeneous system consisting of several phases. Of particular interest for us are the interfaces, at which we can observe phenomena like charge transfer, double layer charging, and adsorption. Main components of electrochemical systems are charged particles. Distributions of these particles depend on local values of the electrostatic potential (the Galvani potential). Distributions of particles are usually non-uniform, in particular in the vicinity of interfaces (e.g. metal|solution interface). We study those systems under equilibrium conditions (no fluxes of species and no net transformation of ionic into electronic flux) and non-equilibrium conditions (current fluxes, overpotentials).
- (b) **Electrical potential:** the potential energy per unit of charge associated with a static electric field, measured in volts. The amount of work to bring a unit point charge from very far to a certain position in an external electric field \vec{E} , $\phi(\vec{r}) = \int \vec{E} \cdot d\vec{r}$.

Chemical potential: the increase of energy by adding 1 mol substance to a homogeneous phase, with entropy and volume remaining unchanged,

$$\mu_i = \left[\frac{dG}{dN_j} \right]_{T, P, N_{j \neq i}}$$

Electrochemical potential: the equivalent quantity to the chemical potential for an electrochemical system; it includes energy contributions due to electrostatic as well as other types of interactions (chemical interactions); electrostatic contributions are added to the chemical potential; amount of work needed or released upon bringing an amount

dN_i of species i from vacuum into system.

$$\tilde{\mu}_i = \left[\frac{d\tilde{G}}{dN_j} \right]_{T,P,N_{j \neq i}} \quad \tilde{\mu}_i = \mu_i + z_i F \phi$$

- (c) **Electrical current:** the magnitude of electric current is defined as the time derivative of the electric charge contained in a phase or transferred across an interface, measured in amperes [A]

$$I = \frac{dQ}{dt}$$

Electrical current density: A vector whose magnitude is the electrical current per cross-sectional area, measured in $A \cdot m^{-2}$.

$$I = \int_S \vec{J} \cdot d\vec{s}$$

$d\vec{s}$ is the element of area whose direction is perpendicular to the surface.

- (d) **Test charge** is a sufficiently small charge that is affected only by the external field and does neither induce charge redistribution nor interact with medium via non-coulombic forces.
Real charges always have internal structure. They always cause their own electric field that distorts the external field to be characterized. They always interact via non-coulombic forces with the medium or phase.
- (e) Gibbs and Helmholtz free energy of electrochemical systems are given by

$$d\tilde{G} = -SdT + VdP + \sum_i \mu_i dN_i + F \sum_i z_i \phi dN_i$$

$$d\tilde{F} = -SdT - PdV + \sum_i \mu_i dN_i + F \sum_i z_i \phi dN_i$$

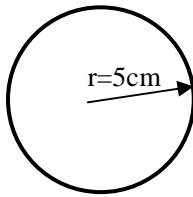
Equilibrium in a system is determined by minimizing the appropriate thermodynamic potential with respect to its variables. At constant T and P , the electrochemical Gibbs free energy is minimal at equilibrium, i.e. T and P are its natural variables. The natural variables of the Helmholtz free energy are T and V .

2. Consider a water-filled sphere, 10 cm in diameter, that contains an excess of 10^{-10} mol of sodium ions.

Solution

- (a) Calculate potential at the surface of the sphere:

Note: linear superposition (no difference between point charge and uniform distribution)



$$\varphi = \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{Q}{r}$$

$$Q = 10^{-10} \text{ mol} \cdot 96485 \frac{\text{C}}{\text{mol}} = 9.6485 \times 10^{-6} \text{ C}$$

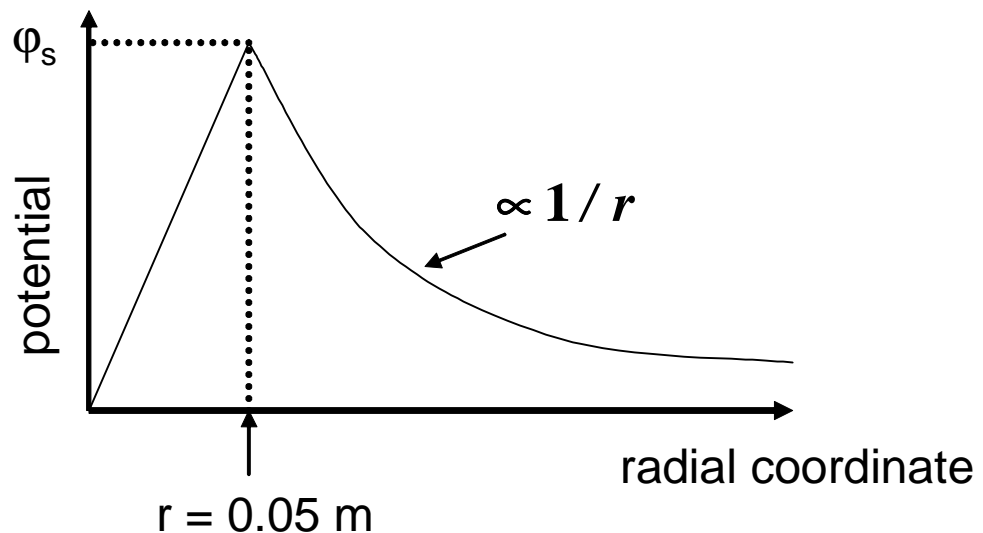
$$\epsilon_0 = 8.8542 \times 10^{-12}, \quad \epsilon_r = 1 \text{ (just outside)}$$

$$r = 0.05 \text{ m}$$

$$\varphi_s = 1.73 \times 10^6 \text{ V}$$

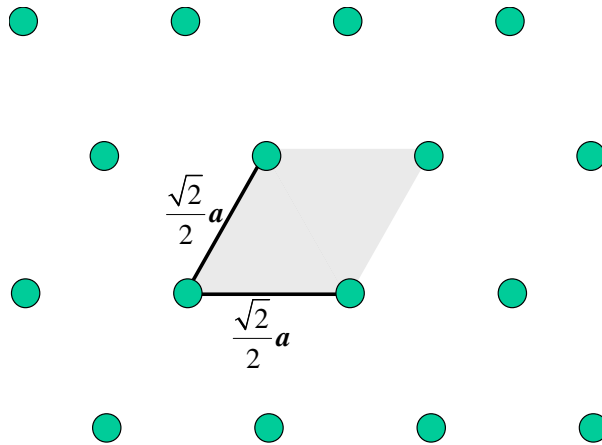
Don't forget units (they are as important for a result as the numbers that you obtain!)

- (b) **Potential variation.** Outside the sphere potential is proportional to $1/r$. How does potential inside the sphere look like? This depends on the detailed charge distribution. Assuming a uniform distribution, the potential will increase linearly with the radial coordinate. Usually, at the surface of the sphere we will also have to deal with so-called image charge effects, which arise at boundaries between media with discontinuous dielectric constants. Assuming the same dielectric constant inside and outside of the sphere the variation of potential looks like



Note on your plots: many of you did not provide any labels or the calculated values at r . No labels, no values,... – the reason why we want to calculate values (e.g. in (a)) or study dependencies, is to actually show them!

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



The lattice constant of Cu is $a = 3.6 \text{ \AA}$. 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 $I = 3 \text{ A}$ is passed for $t = 10 \text{ \mu s}$ to the electrode. The total surface area of the electrode is $A = 1 \text{ cm}^2$.

- What is the excess charge density σ of the metal surface?
- How many excess electrons does each Cu surface atom carry?

Solution

(a) We assume that the current I is constant. The total amount of transferred charge is

$$Q = I \cdot t = 3 \text{ A} \cdot 10 \cdot 10^{-6} \text{ s} = 3 \cdot 10^{-5} \text{ C}$$

and the corresponding surface charge density is thus

$$\sigma = \frac{Q}{A} = \frac{3 \cdot 10^{-5} \text{ C}}{10^{-4} \text{ m}^2} = 0.3 \frac{\text{C}}{\text{m}^2}$$

(b) Area of unit cell:

$$A_{uc} = \left(\frac{\sqrt{2}}{2} a \right)^2 \cdot \frac{\sqrt{3}}{2} = \frac{a^2}{2} \cdot \frac{\sqrt{3}}{2} = \frac{\sqrt{3}}{4} a^2 = 5.6 \cdot 10^{-20} \text{ m}^2$$

Surface atom density:

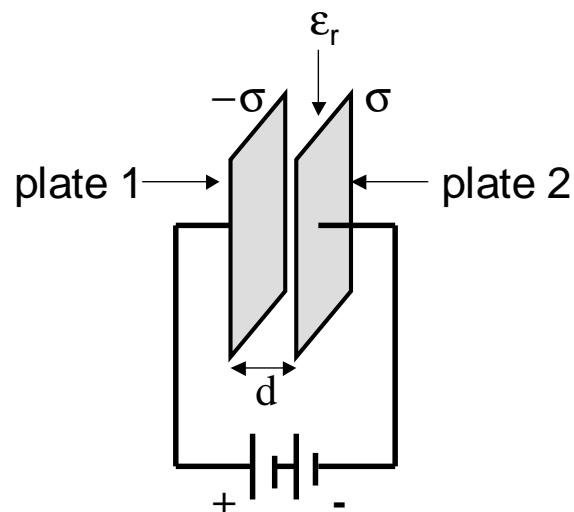
$$\frac{1}{5.6 \cdot 10^{-20} \text{ m}^2} = 1.79 \cdot 10^{19} \text{ m}^{-2} = 1.79 \cdot 10^{15} \text{ cm}^{-2}$$

Excess charge per surface atom:

$$q_{ex} = \sigma A_{uc} = 1.68 \times 10^{-20} \text{ C}$$

$$= 0.105 e_0$$

4. Consider a parallel arrangement of two electrodes with surface area $A = 1 \text{ cm}^2$ at a separation $d = 1 \mu\text{m}$. The space between the electrodes is filled by water with dielectric constant $\epsilon_r = 80$. The surface charge density on one plate is σ (as calculated in problem 2). The opposite plate has the charge density $-\sigma$. This configuration, depicted below, corresponds to a simple parallel plate capacitor.



- Calculate the electric field, E , at a point between the two electrodes.
- Plot the electrical potential ϕ as a function of the lateral coordinate x (perpendicular to the surface of the plate).
- Calculate the potential difference U between a point on plate 1 and a point on plate 2. What is the work performed by the electric field upon moving a test charge from plate A to plate B?
- Derive the relation for the capacitance of an ideal capacitor

$$C = \epsilon_0 \epsilon_r \frac{A}{d}$$

- Water starts to decompose at a voltage is decomposed at the voltage 1.2V. Calculate the maximum energy $E = \frac{1}{2} CU^2$ that could be stored in this capacitor.

Solution

(a) The electric field in a plate capacitor is defined as:

$$E = \frac{\sigma}{\epsilon\epsilon_0}$$
$$= 4.24 \times 10^8 \frac{V}{m}$$

(b) The voltage difference between two plates is given by:

$$\Delta V = E \cdot d = 4.24 \times 10^8 \frac{V}{m} \cdot 1 \times 10^{-6} m = 4.24 \times 10^2 V$$

$$W_{el} = e_0 \Delta V = 6.79 \times 10^{-17} J$$

↑
Suitable test charge: small!
(see problem 1(d)!)

(c)
$$C = \frac{Q}{V}$$

Substitution of $V = Ed$, $E = \frac{\sigma}{\epsilon_r \epsilon_0}$, $\sigma = \frac{Q}{A}$ into above equation gives:

$$\Rightarrow C = \epsilon_r \epsilon_0 \frac{A}{d} = 7.08 \times 10^{-8} F = 71 \mu F$$

(d) The maximum energy that can be store in a capacitor is given by:

$$E_{\max} = \frac{1}{2} C V_{\max}^2$$

V_{\max} is the maximum voltage between two plates of the capacitance.
 $V_{\max} = 1.23 V$ for water

$$E_{\max} = 5.1 \times 10^{-8} J$$

5. Consider a plain metal electrode situated at $z = 0$, with the metal occupying the half-space $z \leq 0$, the solution the region $z > 0$. In a simple model the excess surface charge density σ on the metal surface is balanced by a space charge density $\rho(z) = A \exp(-\kappa z)$, where κ depends on the properties of the solution.
- (a) Determine the constant A from the charge balance condition.
 (b) Calculate the interfacial capacity assuming that κ is independent of σ .

Solution

(a) According to the charge balance equation:

$$-\sigma = \int_0^{\infty} \rho(z) dz = \frac{K}{\kappa}$$

$$\Rightarrow K = -\kappa\sigma$$

$$\rho(z) = -\kappa\sigma \exp(-\kappa z)$$

Note: sign of ρ !

(b) We have to calculate a weighted average of the charge separation from the interface. The weighting function is the charge density, $\rho(z)$. This corresponds to assuming that all charges are located at the distance \bar{d} from the interface.

$$\bar{d} = \frac{\int_0^{\infty} dz z \rho(z)}{\int_0^{\infty} dz \rho(z)} = \frac{\frac{1}{\kappa^2}}{\frac{1}{\kappa}} = \frac{1}{\kappa}$$

$$C = \epsilon_0 \epsilon_r \frac{A}{\bar{d}} = \epsilon_0 \epsilon_r A \kappa$$