

EQUILIBRIUM ELECTROCHEMISTRY

Pre-workshop questions

1. Using the data provided below calculate the standard electrode potential of the cell at 298 K.



	$\Delta H_{f,298}^{\circ}$ (kJ mol ⁻¹)	S_{298}° (J mol ⁻¹ K ⁻¹)
Hg ₂ Cl _{2(s)}	-265.2	192.5
HCl _(aq)	-167.2	56.5
H _{2(g)}	0	130.7
Hg _(l)	0	76.0

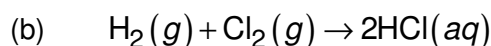
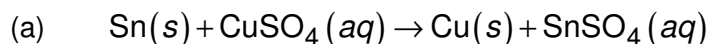
2. Consider a mercury electrode in contact with an aqueous solution of KF. Calculate the Debye length ($1/\kappa$) of the diffuse layer for electrolyte concentrations of 0.0001, 0.001, 0.01 and 0.1 mol dm⁻³. Taking into account that the Helmholtz capacitance is approximately 3.0×10^{-5} F cm⁻², comment on the contribution of the diffuse layer to the total double layer capacitance at the potential of zero charge (pzc).

Hint: At the pzc, $\Delta_{aq}^{\text{OHP}} \phi = 0$, therefore eq. 6.7 of the course is reduced to: $C_{\text{GC}} = \frac{\epsilon_r \epsilon_0}{\kappa^{-1}}$

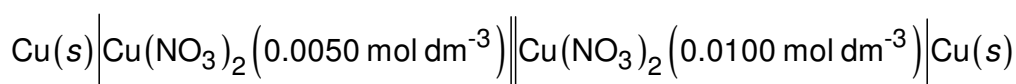
EQUILIBRIUM ELECTROCHEMISTRY

Workshop questions

1. Design electrochemical cells to investigate the following reactions:



2. A student prepared the following cell:



and measured the cell potential at 25°C. The student then mistakenly connected a piece of copper wire between the two copper electrodes and went off to lunch. On returning the student removed the piece of wire and again measured the cell potential. A reading of +0.006 V was obtained.

- Calculate the standard potential of the cell
- Assuming activity coefficients as 1, calculate the cell potential found by the student before lunch.
- Recalculate the cell potential employing *mean ion activities* rather than concentrations. Use the *Debye-Hückel limiting law* ($A = 0.509 \text{ mol}^{-1/2} \text{ dm}^{3/2}$)
- Describe briefly what happened in the cell over lunch.

3. The cation tetrapropylammonium (TPA^+) partitions at the interface between water (W) and 1,2-dichloroethane (O). Considering the Gibbs energy of ion transfer from the aqueous to the organic phase $\Delta G_{\text{TPA}}^{\circ \text{W} \rightarrow \text{O}} = 8.97 \times 10^3 \text{ J mol}^{-1}$, calculate the following quantities at room temperature:

- The standard Galvani potential difference between both liquids
- The partition constant of the ion, i.e. $a(\text{TPA}, \text{O}) / a(\text{TPA}, \text{W})$
- The Galvani potential difference between two electrolyte solution ($\Delta_{\text{O}}^{\text{W}} \phi$) at room temperature with $a(\text{TPA}, \text{W}) = 0.01 \text{ mol dm}^{-3}$ and $a(\text{TPA}, \text{O}) = 0.001 \text{ mol dm}^{-3}$.

Hint. The equilibrium condition is established when the electrochemical potential of the common ion is equal in both electrolyte solutions.

Equilibrium Electrochemistry

List of symbols

$a(i)$	Activity	
a_{\pm}	Extended Debye-Hückel fitting parameter (eqn. 2.17)	m
A	Electrode area Limiting Debye-Hückel constant (eqn. 2.17 and 2.18)	m^2 $0.509 \text{ mol}^{-1/2} \text{ dm}^{3/2}$
B	Extended Debye-Hückel parameter (eqn. 2.17)	$3.3 \times 10^{-9} \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ m}^{-1}$
c	Molar concentration	mol dm^{-3}
C	Capacitance	F
d	Thickness Density	m g dm^{-3}
e	Elementary charge	$1.602 \times 10^{-19} \text{ C}$
E	Electrode potential	V
f	Fugacity	
F	Faraday constant	96485 C mol^{-1}
G	Gibbs Energy	J mol^{-1}
H	Helmholtz Energy	J mol^{-1}
i	Ionic radius	
I_c	Ionic strength (molar scale)	mol dm^{-3}
k_B	Boltzmann constant	$1.38 \times 10^{-23} \text{ J K}^{-1}$
K	Henry's constant	bar
K	Equilibrium constant	
n	Number of electrons transferred in a redox step Number of moles	
N	Number of molecules	
p	Pressure Cation stoichiometry number per unit formula (eq. 2.14)	bar
q	Charge Anion stoichiometry number per unit formula (eq. 2.14)	C
Q	Reaction quotient	
R	Gas constant	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
S	Entropy	J K^{-1}
T	Temperature	K
V_m	Molar volume	$\text{dm}^3 \text{ mol}^{-1}$
x	Mol fraction in condensed phase	
y	Mol fraction in the gas phase	
z	Ionic charge number	

χ	Surface potential of a condensed phase (eqn. 1.20)	V
ϵ_0	Permittivity of free space	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
ϵ_r	Relative permittivity	
ϕ	Galvani potential	V
γ	Activity coefficient	
γ_{\pm}	Mean activity coefficient of a salt	
φ	Fugacity coefficient	
μ	Chemical potential	J mol^{-1}
$\tilde{\mu}$	Electrochemical potential	J mol^{-1}
σ	Electrode surface charge density	C cm^{-2}
ψ	Outer potential (Volta potential)	V