First Year

Trinity Term 2002

Physical Chemistry

Tutorial on Equilibrium Electrochemistry

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Please hand the work in to my pigeon hole in Wadham by 1:00 p.m. on Wednesday of week 4 (15 May 2002).

We will meet for the tutorial in three groups on Friday of week 4 (17 May 2002) at 2:15, 3:45, and 5:15 p.m. in Library Court 6.

Literature
- R G Compton, Handouts for lecture on this subject
- Compton / Saunders, Oxford Primer
- Atkins, Physical Chemistry

Keywords
- Electrochemical cells
- Cell notation
- Salt bridge
- Types of electrochemical cells
- Half cells
- Standard electrode potentials
- Measurement of the emf of a cell
- Activity and activity coefficients
- Nernst equation

Revision and Background

1. Write down *briefly* the definitions / most important facts / equations related to the above keywords.
2. Note: For your general understanding of the present subject it helps to know a little bit about the Debye-Hückel theory (extended and limiting law). At this point, however, we will not use it in the problems.

Problem 1 Equilibrium Constants

Calculate the equilibrium constants for the following reactions at 25 °C in aqueous solutions.

1. $Sn + CuSO_4(aq) \Longleftrightarrow Cu + SnSO_4\ (aq)$
2. $2H_2 + O_2 \Longleftrightarrow 2H_2O$

The standard electrode potentials (SEPs) are

$1/2\ Sn^{2+} + e^- \rightarrow 1/2\ Sn$	-0.136 V
$1/2\ Cu^{2+} + e^- \rightarrow 1/2\ Cu$	$+0.337$ V
$1/4\ O_2 + H^+ + e^- \rightarrow 1/2\ H_2O$	-1.229 V

Problem 2 Cell: Al | Al^{3+}(aq) || Sn^{4+}, Sn^{2+}(aq) | Pt

State or calculate at 25 °C

1. the half equations and the cell reaction
2. the cell emf when all the concentrations are 1.0 M and 0.1 M (ignore activity coefficients)
3. ΔG^0 for the cell reaction in (1.)
4. the equilibrium constant, K, for the cell reaction in (1.)
5. the positive electrode and the direction of electron flow in an external circuit

The SEPs are

$1/2\ Sn^{4+} + e^- \rightarrow 1/2\ Sn^{2+}$	$+0.15$ V
$1/3\ Al^{3+} + e^- \rightarrow 1/3\ Al$	-1.66 V

Problem 3 Cell: Ag| AgCl | Cl_2(g) | Pt

Solid AgCl conducts electricity sufficiently that the above cell is reversible with the AgCl either solid or liquid. The emf of the cell as a function of temperature is given below:

T / K	573	623	673	723	773	823	873
E / V	1.000	0.975	0.949	0.924	0.904	0.887	0.871

Calculate the enthalpy and entropy of fusion and the melting point of AgCl.

Problem 4 Cell: Ag| AgBr(sat.), 0.1 M KBr | AgBr, Ag

The above cell is set up at 25 °C. The saturated solution is made by dropping a little $AgNO_3$ into the KBr solution.

1. Write an expression for the cell emf in terms of SEPs and concentrations (ignore activity coefficients)
2. The cell emf was measured as −0.3681 V. Find the solubility product of AgBr at this temperature

The SEPs are

$AgBr + e^- \rightarrow Ag + Br^-$	−0.095 V
$Ag^+ + e^- \rightarrow Ag$	+0.7991 V

Problem 5 Cell Pt, $H_2(p_1)$ | $HCl(m_1)$ | X | $HCl(m_2)$ | $H_2(p_2)$, Pt

For the above cell X indicates a salt bridge. At 25 °C state or calculate

1. an expression for the cell emf in terms of m_1, m_2, and p_1, p_2 (ignoring activity coefficients)
2. the cell emf when $m_2 = 0.2$ M and $m_1 = 0.1$ M and $p_1 = p_2 = 1$ atm
3. the cell emf when the hydrogen pressure in the RHS is increased to 10 atm, all other concentrations remaining the same
4. the cell reaction

Problem 6 Harned Cell

The emf of each of the following Harned cells is measured at two temperatures:

H_2(1 atm), Pt | HCl(10^{-5} M) | AgCl | Ag $\qquad E_1$
H_2(1 atm), Pt | HA(10^{-2}M), KA(10^{-2}M) | AgCl | Ag $\qquad E_2$

where HA is a weak acid and KA is its salt. The measurements give:

	293 K	303 K
E_1 / V	0.820	0.806
E_2 / V	0.878	0.866

Calculate K_a and ΔH^0 for the dissociation of the weak acid, pointing out any assumptions you make. Comment on the results for ΔH^0.
Hints:
1. You may assume in the second cell that [HA] >> [H^+].
2. Think carefully, in which case you need to use activity coefficients.

Problem 7 Half Cells

The standard electrode potentials of the following half cells are given

I^- | AgI(s), Ag(s) $\qquad E = -0.152$ V
I^- | I_2(s) $\qquad E = +0.536$ V

both at 298 K.

1. Write the cell reaction for a cell consisting of these two electrodes dipping into the same solution of iodide ions (draw the cell to which your equation refers).
2. What is the emf of the cell when the substances are in their standard states ?
3. The emf increases with temperature by 1.0×10^{-4} V/K. Calculate ΔG^0, ΔS^0, and ΔH^0 for the cell reaction at 298 K.