UFPR	**Universidade Federal do Paraná** **Dep. Química – Curso de Licenciatura e Bacharelado em Química** **Segunda Lista de Exercícios de Físico-Química IV (CQ049)** **Professor Eduardo Lemos de Sá**

Os exercícios abaixo foram retirados do livro Atkins, P. W. & de Paula, J. *Physical Chemistry*, 8ª ed, Oxford University Press

1)

The emf of the cell $Pt(s)|H_2(g, p^{\ominus})|HCl(aq, b)|AgCl(s)|Ag(s)$ at 25°C has the following values:

$b/(10^{-3}\, b^{\ominus})$	3.215	5.619	9.138	25.63
E/V	0.52053	0.49257	0.46860	0.41824

After this, determine the E^0 for the electrochemical reaction involved (see Atkins, Physical-Chemistry, 8ª ed., page 223).

Self-test 7.11 Calculate the solubility constant (the equilibrium constant for the reaction $Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Cl^-(aq)$) and the solubility of mercury(I) chloride at 298.15 K. *Hint.* The mercury(I) ion is the diatomic species Hg_2^{2+}.

[2.6×10^{-18}, 8.7×10^{-7} mol kg^{-1}]

7.14(b) Write the cell reaction and electrode half-reactions and calculate the standard emf of each the following cells:

(a) $Pt|Cl_2(g)|HCl(aq)\|K_2CrO_4(aq)|Ag_2CrO_4(s)|Ag$

(b) $Pt|Fe^{3+}(aq),Fe^{2+}(aq)\|Sn^{4+}(aq),Sn^{2+}(aq)|Pt$

(c) $Cu|Cu^{2+}(aq)\|Mn^{2+}(aq),H^+(aq)|MnO_2(s)|Pt$

7.15(a) Devise cells in which the following are the reactions and calculate the standard emf in each case:

(a) $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

(b) $2\,AgCl(s) + H_2(g) \rightarrow 2\,HCl(aq) + 2\,Ag(s)$

(c) $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$

7.17(a) Calculate the equilibrium constants of the following reactions at 25°C from standard potential data:

(a) $Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2\,Sn^{2+}(aq)$

(b) $Sn(s) + 2\,AgCl(s) \rightleftharpoons SnCl_2(aq) + 2\,Ag(s)$

7.18 Careful measurements of the emf of the cell Pt | H_2(g, $p^\ominus$) | NaOH(aq, 0.0100 mol kg^{-1}), NaCl(aq, 0.01125 mol kg^{-1}) | AgCl(s) | Ag have been reported (C.P. Bezboruah, M.F.G.F.C. Camoes, A.K. Covington, and J.V. Dobson, *J. Chem. Soc. Faraday Trans. I* **69**, 949 (1973)). Among the data is the following information:

θ/°C	20.0	25.0	30.0
E/V	1.04774	1.04864	1.04942

Calculate pK_w at these temperatures and the standard enthalpy and entropy of the autoprotolysis of water at 25.0°C.

7.16(a) Use the Debye–Hückel limiting law and the Nernst equation to estimate the potential of the cell Ag | AgBr(s) | KBr(aq, 0.050 mol kg^{-1}) ‖ Cd(NO_3)$_2$(aq, 0.010 mol kg^{-1}) | Cd at 25°C.

25.13 In an experiment on the Pt | H_2 | H^+ electrode in dilute H_2SO_4 the following current densities were observed at 25°C. Evaluate α and j_0 for the electrode.

η /mV	50	100	150	200	250
j/(mA cm^{-2})	2.66	8.91	29.9	100	335

How would the current density at this electrode depend on the overpotential of the same set of magnitudes but of opposite sign?

7.20 The standard potential of the AgCl/Ag,Cl$^-$ couple has been measured very carefully over a range of temperature (R.G. Bates and V.E. Bowers, *J. Res. Nat. Bur. Stand.* **53**, 283 (1954)) and the results were found to fit the expression

$$E^\ominus/\mathrm{V} = 0.23659 - 4.8564 \times 10^{-4}(\theta/°\mathrm{C}) - 3.4205 \times 10^{-6}(\theta/°\mathrm{C})^2 + 5.869 \times 10^{-9}(\theta/°\mathrm{C})^3$$

Calculate the standard Gibbs energy and enthalpy of formation of Cl$^-$(aq) and its entropy at 298 K.