Exercise Classes 4 Physical Chemistry 1 2021/2022

Exercise 12

The following standard electrochemical potentials are given at $T = 298$ K

(1)	$Ag_2CrO_4(s) + 2e^- \rightarrow 2Ag + CrO_4^{2-}(aq)$	$E^\ominus = +0.45$ V
(2)	$Ag^+(aq) + e^- \rightarrow Ag(s)$	$E^\ominus = +0.7992$ V
(3)	$Ag^{2+}(aq) + e^- \rightarrow Ag^+(aq)$	$E^\ominus = +1.98$ V

a) Calculate the standard cell voltage at $T = 298$ K for the following cell reaction

$$H_2(g) + CrO_4^{2-}(aq) + 2Ag^{2+}(aq) \leftrightarrows Ag_2CrO_4(s) + 2H^+(aq)$$

b) Calculate the standard formation Gibbs free energy of $Ag^+(aq)$ at $T = 298$ K

c) The standard formation enthalpy of $Ag^+(aq)$ at $T = 298$ K is $\Delta_f H^\ominus(Ag^+(aq)) = +105.58$ kJ/mol. Assuming that formation enthalpies and entropies are only weakly dependent on the temperature, calculate the standard reaction Gibbs free energy of reaction (2) at $T = 373$ K, so just below the boiling temperature of the solution.

d) Determine the standard electrochemical potential of reaction (2) at $T = 373$ K under the same assumption as in the former part and compare the result with the literature value for the temperature coefficient of the redox couple, which is -0.989 mV/K.

Exercise 13

We consider a NiCd-battery at $T = 298$ K. This is a battery that is rechargeable due to a smartly designed cathode and anode, for which the reaction products stick to the electrodes during the discharge.
The redox reaction is in an *aqueous* basic environment, between Cd(s) and $Cd(OH)_2(s)$ with a standard potential $E^\ominus_{Cd} = -0.81$ V and between $NiO_2(s)$ and $Ni(OH)_2(s)$, with a standard potential $E^\ominus_{Ni} = 0.49$ V. These (standard) potentials are in the tables of Atkins specified for the half reactions written as *reduction* half reactions, *i.e.* with the electrons on the left hand side in the chemical equation.

a) Write out the chemical equations for the reactions occurring at the two electrodes as *reduction* half reactions as well as the chemical equation for the net cell reaction.
Note that the molalities of the ions in the two half cells need not be the same.

b) Write out the Nernst equation for the potentials of the two half cells and for the cell voltage as far as possible in terms of the potentials and activities, without plugging in the known values.

c) Determine the cell voltage under standard conditions.

d) The initial state of the half cell is represented by a given molality b_i for the ions and we write the corresponding activities in terms of the activity coefficient γ_i on the molality scale according to $a_i = \gamma_i b_i / b^\ominus$.
Assume that the molalities of the ions in the solvent are so low that, still, $a_{H_2O(l)} \approx 1$.
As a (rough) approximation, we now assume that the activity coefficients are independent of the molality.
Determine the cell voltage at a hydroxide molality of 0.01 mol/kg in the cathode half cell and 0.1 mol/kg in the anode half cell; what can you conclude about the change as compared to the voltage under standard conditions?

e) Determine the cell voltage at a hydroxide concentration of 0.1 mol/kg in both half cells and besides that standard conditions; what is your conclusion?

f) Check whether the cell will produce a spontaneous current when a load (resistance) is connected across the cell terminals for the situations of subproblem d) and e).

Exercise 14

In biological cells the energy that is released upon combustion of food is stored in adenosine triphosphate (ATP). We consider the 'discharge' of this energy storage via the hydrolysis of ATP to adenosine diphosphate (ADP) and an inorganic phosphate P_i^- (e.g. $\mathrm{H_2PO_4^-}$) at 37 °C according to

$$\mathrm{ATP}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{ADP}(aq) + \mathrm{P}_i^-(aq) + \mathrm{H_3O^+}(aq).$$

In such cells pH = 7 is maintained using a buffer. The thermodynamic standard state for the H^+-concentration is the concentration at which the activity $a_{\mathrm{H}^+} = 1$ or pH$= -\log a_{\mathrm{H_3O^+}} = 0$ and furthermore $P = P^{\ominus}$.
The biological standard state is defined differently, namely at pH$= 7$ and all other activities equal to 1 (and $P = P^{\ominus}$). Thermodynamic quantities X in that biological standard state are denoted as $X^{\oplus}$.
Besides this standard, in this exercise we will use the unit calorie instead of Joule (1 cal = 4.184 J).
The reaction Gibbs free energy for the above reaction is $\Delta_r G^{\oplus} = -7.3$ kcal/mol at 37 °C.

a) Use $\mu_{H^+} = \mu_{H^+}^{\ominus} + RT \ln a_{H^+}$ and the definition of pH to determine $\mu_{H^+}^{\oplus}$ in terms of $\mu_{H^+}^{\ominus}$ at 37 °C. Hint: use $\ln x = \frac{\log x}{\log e}$.

b) Then calculate $\Delta_r G^{\ominus}$ of the reaction at 37 °C and compare the result with $\Delta_r G^{\oplus}$
What is your conclusion about the progression of the reaction?

c) Calculate the reaction Gibbs free energy $\Delta_r G$ for the concentrations [ATP] = [ADP] = $[\mathrm{P}_i^-]$ = 1 M and further biological standard conditions.
Assume that we can approximate the activities of the dissolved components by molarities.
What is your conclusion about the progression of the reaction?

d) In a relaxed muscle the concentrations have the following values: [ATP] = 5 mM, [ADP] = 1 mM and $[\mathrm{P}_i^-]$ = 10 mM. Calculate the reaction Gibbs free energy again.

e) What is the ratio [ADP]/[ATP] in equilibrium if $[\mathrm{P}_i^-]$ = 10 mM?