Solutions Exercise Classes 4 Physical Chemistry 1 2021/2022

Exercise 12

a) First we note that we need a further reaction, number (4) below

(1)	$Ag_2CrO_4(s) + 2e^- \rightarrow 2Ag(s) + CrO_4^{2-}(aq)$	$E^\ominus = +0.45$ 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
(4)	$2H^+(aq) + 2e^- \rightarrow H_2(g)$	$E^\ominus \equiv 0$ V

By inverting and adding (1) and (4), we find the reaction equation

$$H_2(g) + CrO_4^{2-} + 2Ag \leftrightarrows Ag_2CrO_4 + 2H^+ + 4e^-, \qquad E^\ominus = -0.45 - 0 \text{ V} = -0.45 \text{ V}.$$

Adding 2 times (2) to this result, we obtain

$$H_2(g) + CrO_4^{2-} + 2Ag^+ \leftrightarrows Ag_2CrO_4 + 2H^+ + 2e^-, \qquad E^\ominus = -0.45 + 0.7992 = +0.35 \text{ V},$$

and adding twice (3), we finally arrive at the equation we want

$$H_2(g) + CrO_4^{2-} + 2Ag^{2+} \leftrightarrows Ag_2CrO_4 + 2H^+, \qquad E^\ominus = +0.35 + 1.98 = +2.33 \text{ V}.$$

Note, that we should not multiply the potentials by the factor of two we used in the second and third step; this factor is taken care of implicitly by the parameter ν in the Nernst equation.
We, however, have to change the sign of the potential on inverting a chemical equation.

b) The relations between the reaction Gibbs free energy and the potentials in the Nernst equation are given by

$$\Delta_r G = -\nu F E \quad \text{and, therefore, also} \quad \Delta_r G^\ominus = -\nu F E^\ominus.$$

For reaction (2) in the former part we have

$$\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G_i^\ominus = \Delta_f G^\ominus(\text{Ag}) - \Delta_f G^\ominus(\text{Ag}^+) = 0 - \Delta_f G^\ominus(\text{Ag}^+) = -\Delta_f G^\ominus(\text{Ag}^+).$$

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

$$\Delta_f G^\ominus(\text{Ag}^+) = -\Delta_r G^\ominus = \nu F E^\ominus(\text{Ag}^+/\text{Ag}) = 1 \cdot 96485 \cdot 0.7992 = 77.11 \text{ kJ/mol}.$$

c) The definition of Gibbs free energy $G \equiv H - TS$ implies that at constant T we find for any change $\Delta G = \Delta H - T\Delta S$ and therefore also $\Delta_f G = \Delta_f H - T\Delta_f S$, so also $\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta_f S^\ominus$. So at 298 K we find for $Ag^+(aq)$

$$\Delta_f S^\ominus = -\frac{\Delta_f G^\ominus - \Delta_f H^\ominus}{T} = -\frac{77.11 \cdot 10^3 - 105.58 \cdot 10^3}{298} = 95.54 \text{ J/molK}.$$

Assuming $\Delta_f H$ and $\Delta_f S$ to be constant for 298 K $< T <$ 373 K, we find at 373 K

$$\begin{aligned}\Delta_r G^\ominus(373 \text{ K}) &= \Delta_f G^\ominus(\text{Ag}, 373 \text{ K}) - \Delta_f G^\ominus(\text{Ag}^+, 373 \text{ K}) = 0 - \Delta_f G^\ominus(\text{Ag}^+, 373 \text{ K}) \\ &= \Delta_f H^\ominus(\text{Ag}^+) + 373\Delta_f S^\ominus(\text{Ag}^+)) = -105.58 \cdot 10^3 + 373 \cdot 95.54 = -69.94 \text{ kJ/mol}.\end{aligned}$$

d) We use $\Delta_r G^\ominus(373 \text{ K}) = -\nu F E^\ominus(373 \text{ K})$, resulting in a standard electrochemical potential of

$$E^\ominus(\text{Ag}^+(\text{aq})/\text{Ag}, 373 \text{ K}) = -\frac{\Delta_r G^\ominus(373 \text{ K})}{\nu F} = -\frac{-69.94 \cdot 10^3}{1 \cdot 96485} = +0.725 \text{ V}.$$

Compared to $E^\ominus(\text{Ag}^+(\text{aq})/\text{Ag}, 298 \text{ K})$ this corresponds to a potential drop of approximately 1 mV/K, which is in very good agreement with the literature value of −0.989 mV/K.

Exercise 13

a) For rechargeable batteries the notions anode and cathode refer to different electrodes depending on whether the battery is charged or discharged.
Make a distinction between the activities of the ions in the two half cells.
Reduction half reactions always have the electrons on the left hand side in the chemical equation, so we write.

$$\mathrm{NiO_2(s) + 2H_2O(l) + 2e^- \leftrightharpoons Ni(OH)_2(s) + 2OH^-_{\mathit{Ni}}(aq)}$$

$$\mathrm{Cd(OH)_2(s) + 2e^- \leftrightharpoons Cd(s) + 2OH^-_{\mathit{Cd}}(aq)}$$

Now, the net cell reaction depends on whether we charge or discharge the battery. We choose the following net reaction and we do not know yet, whether this will correspond to charging or discharging

$$\mathrm{NiO_2(s) + 2H_2O(l) + Cd(s) + 2OH^-_{\mathit{Cd}}(aq) \leftrightharpoons Ni(OH)_2(s) + Cd(OH)_2(s) + 2OH^-_{\mathit{Ni}}(aq)}$$

b)

$$E_{Ni} = E^{\ominus}_{Ni} - \frac{RT}{\nu F}\ln Q_{Ni} = E^{\ominus}_{Ni} - \frac{RT}{\nu F}\ln\frac{a_{\mathrm{Ni(OH)_2}}a^2_{\mathrm{OH^-},Ni}}{a_{\mathrm{NiO_2}}a^2_{\mathrm{H_2O}}}$$

$$E_{Cd} = E^{\ominus}_{Cd} - \frac{RT}{\nu F}\ln Q_{Cd} = E^{\ominus}_{Cd} - \frac{RT}{\nu F}\ln\frac{a_{\mathrm{Cd}}a^2_{\mathrm{OH^-},Cd}}{a_{\mathrm{Cd(OH)_2}}}$$

The net reaction of part a) then corresponds to a cell voltage of

$$E = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{\nu F}\ln Q_{\mathrm{cell}} = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{\nu F}\ln\frac{a_{\mathrm{Ni(OH)_2}}a_{\mathrm{Cd(OH)_2}}a^2_{\mathrm{OH^-},Ni}}{a_{\mathrm{NiO_2}}a^2_{\mathrm{H_2O}}a_{\mathrm{Cd}}a^2_{\mathrm{OH^-},Cd}}$$

c) At standard conditions the cell voltage is

$$E = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} = 0.49 - (-0.81) = 1.30\ \mathrm{V}.$$

d) Use that the activity of solid and liquid components is to a good approximation equal to 1. For higher molalities this will be a rough approximation for the solvent.
An even more rough approximation is chosen to choose the activity coefficients to be independent of the molality.
In both reactions two electrons are transferred ($\nu = 2$).

$$E_{Ni} = E^{\ominus}_{Ni} - \frac{RT}{\nu F}\ln Q_{Ni} = 0.49 - \frac{8.315\cdot 298}{2\cdot 96485}\ln\frac{1\cdot a^2_{\mathrm{OH^-},Ni}}{1\cdot 1}$$

$$E_{Cd} = E^{\ominus}_{Cd} - \frac{RT}{\nu F}\ln Q_{Cd} = -0.81 - \frac{8.315\cdot 298}{2\cdot 96485}\ln\frac{1\cdot a^2_{\mathrm{OH^-},Cd}}{1}$$

The net reaction of part a) then corresponds to a cell voltage of

$$E = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{\nu F}\ln Q_{\mathrm{cell}} = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{2F}\ln\frac{a^2_{\mathrm{OH^-},Ni}}{a^2_{\mathrm{OH^-},Cd}} = E^{\ominus}_{Ni} - E^{\ominus}_{Cd} - \frac{RT}{F}\ln\frac{a_{\mathrm{OH^-},Ni}}{a_{\mathrm{OH^-},Cd}}$$

We assume that γ_i is independent of b_i, such that

$$E = E^{\ominus}_{c} - E^{\ominus}_{a} - \frac{RT}{F}\ln\frac{\gamma_{\mathrm{OH^-}}b_{\mathrm{OH^-},Ni}}{\gamma_{\mathrm{OH^-}}b_{\mathrm{OH^-},Cd}} = 1.30 - \frac{8.315\cdot 298}{96485}\ln\frac{0.01}{0.1} = 1.359\ \mathrm{V}$$

So this is a small change in the cell voltage for a factor 10 change in molality between the two half cells.

e)

$$E = E_c^{\ominus} - E_a^{\ominus} - \frac{8.315 \cdot 298}{96485} \ln \frac{0.1}{0.1} = 1.30 \text{ V}$$

As the Nernst equation for this redox couple shows, an equal molality change in the two half cells has no effect on the cell voltage as compared to the standard cell voltage.

f) For both cases the cell voltage is positive, $E > 0$, so $\Delta_r G < 0$, so the reaction will progress spontaneously and therefore a current will be produced.

Exercise 14

a) For the thermodynamic standard state $a_{H^+} = 1$, or $\ln a_{H^+} = 0$ (and pH$= -\log a_{H^+} = 0$), so

$$\mu_{H^+} = \mu_{H^+}^{\ominus} + RT \ln a_{H^+} = \mu_{H^+}^{\ominus}.$$

Note, that we have defined (in fact set) the standard formation Gibbs free energy and enthalpy of H$^+$ equal to zero for all temperatures:

$$\Delta_f G_{H^+}^{\ominus} = \Delta_f H_{H^+}^{\ominus} = 0 \ \forall_T, \text{ so also } \mu_{H^+}^{\ominus} = G_{m,H^+}^{\ominus} = \Delta_f G_{H^+}^{\ominus} = 0 \ \forall_T.$$

For clarity we will keep the term $\mu_{H^+}^{\ominus}$ nevertheless in the equations. For the biological standard state pH$= 7$, and we find

$$\mu_{H^+} = \mu_{H^+}^{\ominus} + RT \ln a_{H^+} = \mu_{H^+}^{\ominus} + RT \frac{\log a_{H^+}}{\log e} = \mu_{H^+}^{\ominus} - RT \frac{\text{pH}}{\log e} = \mu_{H^+}^{\ominus} - RT \frac{7}{\log e}$$

or at 37 °C (1 cal = 4.185 J, such that $R = 1.987$ cal/molK)

$$\mu_{H^+}^{\oplus} = \mu_{H^+}^{\ominus} - RT \frac{7}{\log e} = \mu_{H^+}^{\ominus} - RT 16.12 = \mu_{H^+}^{\ominus} - 1.987 \cdot 310 \cdot 16.12 = \mu_{H^+}^{\ominus} - 9.93 \text{ kcal/mol}.$$

b)

$$\text{ATP}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{ADP}(aq) + \text{P}_i^-(aq) + \text{H}_3\text{O}^+(aq)$$

The reaction Gibbs free energy is already specified at 37 °C as $\Delta_r G^{\oplus} = -7.3$ kcal/mol.
Compared to the biological standard state (pH$= 7$), for the thermodynamic state we only have to adjust the contribution of a_{H^+}, such that (ν_{H^+} is the coefficient of H^+ in the reaction)

$$\Delta_r G^{\ominus} = \Delta_r G(\text{pH} = 0) = \Delta_r G^{\oplus} + \nu_{H^+} RT \frac{7}{\log e} = \Delta_r G^{\oplus} + RT \cdot 16.12,$$

which at 37 °C results in

$$\Delta_r G^{\ominus} = -7.3 \cdot 10^3 + 9.93 \cdot 10^3 = +2.6 \text{ kcal/mol},$$

and shows that under standard thermodynamic conditions $\Delta_r G > 0$, whereas under biological conditions $\Delta_r G < 0$, so for biological conditions the reaction will proceed spontaneously.

c)

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln Q = \Delta_r G^{\ominus} + RT \ln \frac{a_{ADP(aq)} a_{P_i^-(aq)} a_{H_3O^+(aq)}}{a_{ATP(aq)} a_{H_2O(l)}},$$

or

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln a_{H_3O^+(aq)} + RT \ln \frac{a_{ADP(aq)} a_{P_i^-(aq)}}{a_{ATP(aq)} a_{H_2O(l)}} = \Delta_r G^{\oplus} + RT \ln \frac{a_{ADP(aq)} a_{P_i^-(aq)}}{a_{ATP(aq)} a_{H_2O(l)}},$$

at pH =7. Furthermore $a_{H_2O(l)} \approx 1$ such that

$$\Delta_r G = \Delta_r G^{\oplus} + RT \ln \frac{a_{ADP(aq)} a_{P_i^-(aq)}}{a_{ATP(aq)}} = \Delta_r G^{\oplus} + RT \ln \frac{\frac{[ADP(aq)]}{[ADP(aq)]^{\oplus}} \frac{[P_i^-(aq)]}{[P_i^-(aq)]^{\oplus}}}{\frac{[ATP(aq)]}{[ATP(aq)]^{\oplus}}},$$

with $[C]^{\oplus} = 1$ mol/L for all components C (except for $H_3O^+(aq)$). Here we approximated the activities using concentration fractions; if all concentrations are 1 mol/L then we find again

$$\Delta_r G = \Delta_r G^{\oplus} + RT \ln 1 = \Delta_r G^{\oplus} = -7.3 \text{ kcal/mol}.$$

This value shows that the hydrolysis of ATP is essentially an irreversible spontaneously progressing chemical reaction.

d)

$$\begin{aligned}\Delta_r G = \Delta_r G^{\oplus} + RT \ln \frac{\frac{[ADP(aq)]}{[ADP(aq)]^{\oplus}} \frac{[P_i^-(aq)]}{[P_i^-(aq)]^{\oplus}}}{\frac{[ATP(aq)]}{[ATP(aq)]^{\oplus}}} &= -7.3 \cdot 10^3 + 1.987 \cdot 310 \ \ln \frac{1 \cdot 10^{-3} \cdot 10 \cdot 10^{-3}}{5 \cdot 10^{-3}} \\ &= -7.3 \cdot 10^3 - 3.83 \cdot 10^3 = -11 \text{ kcal/mol}\end{aligned}$$

e) In equilibrium $\Delta_r G = 0$, such that at $[P_i^-] = 10 \cdot 10^{-3}$ mol/L

$$0 = -7.3 \cdot 10^3 + 1.987 \cdot 310 \ \ln \left[10^{-2} \frac{[ADP(aq)]}{[ATP(aq)]} \right], \text{ or } \quad \frac{[ADP(aq)]}{[ATP(aq)]} = 1.4 \cdot 10^7.$$

This value shows that the hydrolysis of ATP is essentially an irreversible chemical reaction.