Solutions Additional Exercises Physical Chemistry 1 2021/2022

Exercise add_1

The reaction consists of two equilibria $CO(g) + H_2(g) \leftrightharpoons H_2CO(l)$ and $H_2CO(l) \leftrightharpoons H_2CO(g)$.
For the first reaction $\Delta_r G^\ominus = 28.95$ kJ/mol. For the second reaction it holds that (perfect gas and $a(l) \approx 1$).

$$K(\text{vap}) = \frac{a(g)}{a(l)} = \frac{P}{P^\ominus}.$$

From the equilibrium condition for that second reaction we can find the standard Gibbs free energy of evaporation $\Delta_r G^\ominus(H_2CO(l) \leftrightharpoons H_2CO(g)) = \Delta_{\text{vap}} G^\ominus(H_2CO(l))$ (use $P^\ominus = 1$ bar ≈ 750 Torr)

$$\Delta_{\text{vap}} G^\ominus = -RT \ln K(\text{vap}) = -8.314 \cdot 298 \ln \frac{1500 \text{ Torr}}{750 \text{ Torr}} = -1.72 \text{ kJ/mol}.$$

So for the total reaction, the standard reaction Gibbs free energy is

$$\Delta_r G^\ominus = 28.95 - 1.72 = 27.23 \text{ kJ/mol},$$

resulting in the equilibrium constant of that reaction given by

$$K = \exp\left(-\frac{\Delta_r G^\ominus}{RT}\right) = \exp\left(-\frac{27.23 \cdot 10^3}{8.314 \cdot 298}\right) = 1.69 \cdot 10^{-5}$$

Exercise add_2

The chemical equilibrium reaction is $CaCO_3(s) \leftrightharpoons CaO(s) + CO_2(g)$. Using the assumptions of the exercise we can set the condition for which $CaCO_3(s)$ will dissociate completely in terms of the equilibrium constant at $P = P^\ominus$ being equal to one: $K(P^\ominus) = 1$.
The equilibrium constant is given by (use $a_{CaCO_3(s)} \approx a_{CaO(s)} \approx 1$)

$$K = \frac{a_{CaO(s)} a_{CO_2(g)}}{a_{CaCO_3(s)}} \approx a_{CO_2(g)} = \frac{P_{CO_2}}{P^\ominus} = 1,$$

$\Delta_r G^\ominus$ is defined at $P = P^\ominus$, for a given temperature, so $\Delta_r G^\ominus$ is independent of pressure, but still dependent on the temperature T.
In the tables in Atkins we can find the standard formation Gibbs free energies, $\Delta_f G^\ominus$, at $T = 298$ K, which will differ at other temperatures.
$\Delta_r G^\ominus = -RT \ln K \approx -RT \ln 1 = 0$, so $\Delta_r H^\ominus - T\Delta_r S^\ominus \approx 0$.
Usually the temperature dependence of $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ is rather weak as compared to $\Delta_r G^\ominus$, that is why we use the assumption that the temperature dependence of both $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ is negligible.
Using the tables in Atkins we find

$$\Delta_r H^\ominus = \Delta_f H^\ominus(CaO(s)) + \Delta_f H^\ominus(CO_2(g)) - \Delta_f H^\ominus(CaCO_3(s)) = -635 - 393.5 + 1207 = 178.5 \text{ kJ/mol}.$$

To determine $\Delta_r S^\ominus$ we use the standard molar entropies in the tables:

$$\Delta_r S^\ominus = S_m^\ominus(CaO(s)) + S_m^\ominus(CO_2(g)) - S_m^\ominus(CaCO_3(s)) = 40 + 214 - 93 = 161 \text{ J/molK}.$$

Using these values we find for the estimate of the decomposition temperature

$$T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus} = \frac{178.5 \cdot 10^3}{161} = 1109 \text{ K}$$

Exercise add_3

$$PV = nRT\left(1 + \frac{B}{V_m}\right)$$

with $B = -21.7\ \mathrm{cm^3 mol^{-1}}$. The term carrying B discriminates the gas from a perfect gas. This term discribes the correction to the equation of state, stemming from the finite size of the atoms. As a result of this finite size, the atoms experience a smaller volume V, implying a negative value for B.
For this non-perfect gas we cannot use the perfect gas expressions for the internal energy and the heat capacity.

a) Both processes start with a volume $V_1 = 1.0$ l.
We use the equation of state to find the starting pressure $V_m = V/n$):
$P_1 = \frac{nRT_1}{V_1}\left(1 + \frac{B}{V_{m,1}}\right) = \frac{2.0 \cdot 8.314 \cdot 300}{1.0 \cdot 10^{-3}}\left(1 - \frac{21.7 \cdot 10^{-6}}{1.0 \cdot 10^{-3}/2}\right) = 4.772 \cdot 10^6\ \mathrm{N/m^2}$.

b) Because we do not have an expression for C_P to find ΔH, we use the definition of enthalpy:
$H = U + PV$, so $\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P$.
The difference we have to determine is $\Delta H - \Delta U = \int_{V_1}^{V_2} P\mathrm{d}V + \int_{P_1}^{P_2} V\mathrm{d}P$.

At *constant volume* ($V_2 = V_1$) we find $\Delta H - \Delta U = V_1 \int_{P_1}^{P_2} \mathrm{d}P = V_1\,(P_2 - P_1)$.
We use the equation state once more to find the final pressure:
$P_2 = \frac{nRT_2}{V_1}\left(1 + \frac{B}{V_{m,1}}\right) = \frac{2.0 \cdot 8.314 \cdot 350}{1.0 \cdot 10^{-3}}\left(1 - \frac{21.7 \cdot 10^{-6}}{1.0 \cdot 10^{-3}/2}\right) = 5.567 \cdot 10^6\ \mathrm{N/m^2}$, resulting in
$\Delta H - \Delta U = 1.0 \cdot 10^{-3} \cdot \left(5.567 \cdot 10^6 - 4.772 \cdot 10^6\right) = 795$ J.

At *constant pressure* we obtain $\Delta H - \Delta U = P_1 \int_{V_1}^{V_2} \mathrm{d}V = P_1\,(V_2 - V_1)$.
The final volume V_2 follows by rewriting the equation of state:
$V^2 - \frac{nRT}{P}V - \frac{nRT}{P}nB = 0$, so $V = \frac{nRT}{2P} \pm \frac{1}{2}\sqrt{\left(\frac{nRT}{P}\right)^2 + 4\left(\frac{n^2RT}{P}\right)B}$
(the negative solution gives no real value for the volume). On substituting the values, we find
$V_2 = \frac{nRT_2}{2P_1} + \frac{1}{2}\sqrt{\left(\frac{nRT_2}{P_1}\right)^2 + 4\left(\frac{n^2RT_2}{P_1}\right)B} = \frac{2.0 \cdot 8.314 \cdot 350}{2 \cdot 4.772 \cdot 10^6} + \frac{1}{2}\sqrt{\left(\frac{2.0 \cdot 8.314 \cdot 350}{4.772 \cdot 10^6}\right)^2 - 4\left(\frac{2.0^2 \cdot 8.314 \cdot 350}{4.772 \cdot 10^6}\right) \cdot 21.7 \cdot 10^{-6}}$.
This results in $V_2 = 1.175 \cdot 10^{-3}\ \mathrm{m^3}$, so
$\Delta H - \Delta U = P_1\,(V_2 - V_1) = 4.772 \cdot 10^6 \cdot \left(1.175 \cdot 10^{-3} - 1.0 \cdot 10^{-3}\right) = 835$ J.

c) For a perfect gas the inital pressure would be $P_1 = 4.99 \cdot 10^6\ \mathrm{N/m^2}$.
For a perfect gas we find for both processes, at a final volume $V_2 = 1.17 \cdot 10^{-3}\ \mathrm{m^3}$,
$\Delta H - \Delta U = nR\Delta T = 2.0 \cdot 8.31 \cdot (350 - 300) = 831$ J.

Exercise add_4

a) The (external) resistance is $R = \frac{E_{term}}{I} = \frac{19}{2.5} = 7.6\ \Omega$. see figure 1.

b) R_i is the internal resistance that causes a decrease of the terminal voltage $E_{term} = E_{EMF} - IR_i \Rightarrow R_i = \frac{E_{EMF} - E_{term}}{I} = \frac{20-19}{2.5} = 0.40\ \Omega$;

c) The transferred charge per mole of electrons is $\Delta q = 1$ F(araday) $= N_A e = 9.6485 \cdot 10^4$ C (e is the elementary charge).
As long as the process is isochoric ($\mathrm{d}V = 0$) there is no mechanical (volume) work. Besides, for such an electrochemical process even under isobaric conditions ($\mathrm{d}P = 0$) we can assume that there is no volume change so that there is no mechanical (volume) work done. So the only work is electrical and at (the given) constant terminal voltage.
If we choose the battery as system, then the system does (electrical) work on the surroundings (the resistance R), or $W < 0$.
In that case $W = -\int E_{term}\mathrm{d}q = -E_{term}\int \mathrm{d}q = -E_{term}\Delta q = -19 \cdot 96485 = -1.83$ MJ/mol.

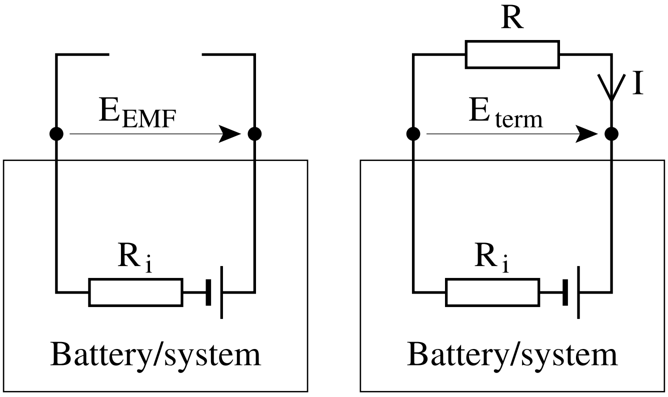


Figure 1: The battery is the system; if there is no external resistance, then the terminal voltage is equal to the maximum voltage of the battery E_{EMF}; if a resistance R is connected the terminal voltage drops with an amount of IR_i to a value of E_{term}.

If we take the external resistance as system then this work is done by the surroundings (battery) on the resistance and is $W = 1.83$ MJ/mol, so positive.

d) Moreover, if the process proceeds reversibly with an infinitely high external resistance, the process indeed takes infinitely long, but $E_{term} = E_{EMF}$, since the current is infinitely small. The work then becomes $W = -\int E_{EMF} \mathrm{d}q = -E_{EMF}\Delta q = -20 \cdot 96485 = -1.93$ MJ/mol.

e) The maximum terminal voltage is $E_{EMF} = 20$ V, so the maximum work per mole of transferred electrons is $W = -\int E_{EMF} \mathrm{d}q = -E_{EMF}\Delta q = -20 \cdot 96485 = -1.93$ MJ/mol, or the work in case the battery delivers current reversibly.

Of course there is a practical limit here, since the E_{EMF} is only realized for (very) small currents, so for a very small amount of power per time unit.

Exercise add_5

a) We assume that at the standard temperature (298 K) the water is formed in its liquid state, whereas oxygen and hydrogen are present in gaseous form, each with standard pressure. The cell reaction then becomes

$$\mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \leftrightharpoons \mathrm{H_2O(l)},$$

with as standard reaction energy ($\Delta_f G^\ominus(\mathrm{H_2}(g)) = \Delta_f G^\ominus(\mathrm{O_2}(g)) = 0$)

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\mathrm{H_2O(l)}) - \Delta_f G^\ominus(\mathrm{H_2}(g)) - \frac{1}{2}\Delta_f G^\ominus(\mathrm{O_2}(g)) = \Delta_f G^\ominus(\mathrm{H_2O(l)}) = -237.13 \text{ kJ/mol}.$$

The reaction quotient Q is given by ($P(\mathrm{O_2}(g)) = P(\mathrm{H_2}(g)) = P^\ominus$ and $a(\mathrm{H_2O(l)}) = 1$)

$$Q = \frac{a(\mathrm{H_2O(l)})}{a(\mathrm{H_2}) \cdot a^{\frac{1}{2}}(\mathrm{O_2})} = \frac{a(\mathrm{H_2O(l)})}{\left(\frac{P(\mathrm{H_2})}{P^\ominus}\right)\left(\frac{P(\mathrm{O_2})}{P^\ominus}\right)^{\frac{1}{2}}} = 1.$$

In this reaction two electrons are transferred ($\nu = 2$ becomes clear from the half reaction $\mathrm{H_2(g)} \leftrightharpoons 2\mathrm{H^+} + 2\mathrm{e^-}$). The EMF of such a cell then is

$$E = E^\ominus - \frac{RT}{\nu F}\ln Q = E^\ominus = -\frac{\Delta_r G^\ominus}{\nu F} = \frac{237.13 \cdot 10^3}{2 \cdot 96485} \text{ V} = 1.23 \text{ V}.$$

b) The standard reaction energy now becomes

$$\Delta_r G^\ominus = \Delta_f G^\ominus(H_2O(g)) = -228.57 \text{ kJ/mol}.$$

The reaction quotient is still $Q = 1$ since all partial pressures are equal to $P^\ominus$, such that

$$E = E^\ominus - \frac{RT}{\nu F}\ln Q = E^\ominus = -\frac{\Delta_r G^\ominus}{\nu F} = \frac{228.57 \cdot 10^3}{2 \cdot 96485} \text{ V} = 1.18 \text{ V}.$$

c) We use the same design. For this cell the reaction is

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \leftrightharpoons 4CO_2(g) + 5H_2O(l),$$

with as standard reaction Gibbs free energy

$$\Delta_r G^\ominus = 4\Delta_f G^\ominus(CO_2(g)) + 5\Delta_f G^\ominus(H_2O(l)) - \Delta_f G^\ominus(C_4H_{10}(g)) = \\ -4 \cdot 394 - 5 \cdot 237 + 17.0 = -2744 \text{ kJ/mol}.$$

We find the number of electrons that is transferred during this reaction as follows. If the H^+-ions are responsible for the transport of charge between the electrodes in the cell, then one of the half cell reactions is

$$\frac{13}{2}O_2(g) + 26e^- + 26H^+(aq) \rightarrow 13H_2O(l)$$

Apparently, a part of the formed water is then used for the other half reaction:

$$C_4H_{10}(g) + 8H_2O(l) \rightarrow 4CO_2(g) + 26e^- + 26H^+(aq).$$

We find the total reaction as the sum of the first (reduction) and the second (oxidation) half reaction. So the number of transferred electrons is apparently $\nu = 26$, such that we find

$$E^\ominus = -\frac{\Delta_r G^\ominus}{\nu F} = \frac{2744 \cdot 10^3}{26 \cdot 96485} \text{ V} = 1.09 \text{ V}.$$

d) The alternative design has an oxygen-ion electrolyte with as cathode reaction

$$13\ O_2 + 52\ e^- \rightarrow 26\ O^{2-}$$

and as anode reaction

$$8\ CO_2 + 10\ H_2O + 52\ e^- \rightarrow 2\ C_4H_{10} + 26\ O^{2-}.$$

Naturally, the total reaction remains the same, just like the number of transferred electrons. Thus this cell supplies the same EMF under standard circumstances as the one from part c).

e) For a reversible process at constant temperature and pressure $\Delta_r G = W_e$ and the efficiency of the fuel cell is thus $\eta = 100$ %, irrespective of the temperature and the pressure ($\Delta_r G$ is the reaction Gibbs free energy at that temperature and pressure).
The cell can only do external work reversibly at infinitely small current I, since then the internal resistance is negligibly small.

f) For a current I through a resistance R the dissipation (electrical energy that is completely transformed into heat) is determined by the power $P = I^2R$; cf. exercise 4. The electrical work done per time unit Δt on the external resistance then is $W_L = I^2R_L\Delta t$, whereas the work done per time unit Δt on the internal resistance is equal to $W_i = I^2R_i\Delta t$, in which $W_L + W_i = \Delta_r G$. The efficiency therefore becomes

$$\eta = \frac{W_L}{\Delta_r G} = \frac{W_L}{W_L + W_i} = \frac{I^2R_L\Delta t}{I^2R_L\Delta t + I^2R_i\Delta t} = \frac{R_L}{R_L + R_i} = \frac{10}{11}.$$

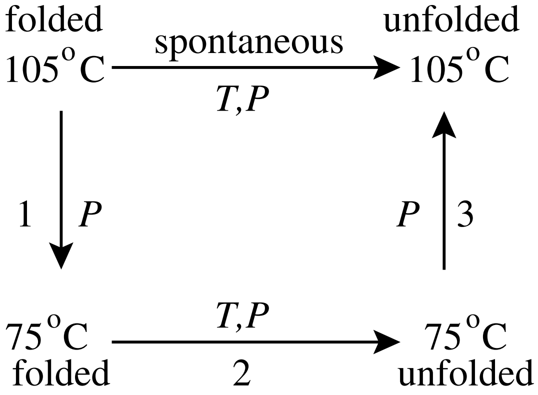
So in practice the internal resistance R_i of the cell decreases the efficiency. In general the internal resistance increases with the current I and therefore it is not a normal 'ohmic' resistance. R_i has different causes:

- The resistance of the electrolyte (membrane) for the ion transport. If the diffusion of ions through the membrane is not fast enough for larger currents I a concentration gradient of ions arises, resulting in a potential difference over that gradient (called polarisation), that decreases the terminal voltage (and thus the efficiency).
- The redox reaction can have too slow kinetics also on the electrodes, due to which again a gradient arises in the ion density around the electrode; The consequence is again a polarisation against the EMF, or a decrease in efficiency. Using a catalyst as electrode can improve the kinetics.
- Transport of unwanted ions through the membrane (e.g. O^{2-} in part a)) causes a current leakage, that does not contribute to the external electrical work. Strictly speaking a leakage does not affect the internal resistance.

Exercise add_6

a) At 75°C there is a (dynamic) equilibrium between the folded and the unfolded state such that at that constant temperature and pressure $0 = \mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T = \mathrm{d}H - T\mathrm{d}S$, such that $\Delta H = T\Delta S$, or $\Delta S = \frac{\Delta H}{T_{unfold}} = \frac{509 \cdot 10^3}{348.2} = 1.46$ kJ/molK.

b) The unfolding process at 105 °C is irreversible (spontaneous). If we add two reversible isobars between 105 °C and 75 °C to the already reversible unfolding process at 75 °C, then we find the following diagram. So we choose the processes 1, 2 and 3 to be reversible.



c) $\Delta c_P = c_P(unfolded) - c_P(folded) = 6.28$ kJ/molK and we consider it to be independent of T between 75 °C and 105 °C.
H is a state function so ΔH is independent of the path. Obviously, we choose the path 1-2-3 as reversible alternative for the spontaneous unfolding process.
For (reversible) isobars $\mathrm{d}H = \mathrm{d}Q + V\mathrm{d}P = \mathrm{d}Q$, such that $\mathrm{d}H = c_P\mathrm{d}T$.
•Process 1 is isobaric, so $\mathrm{d}H_1 = c_P(folded)\mathrm{d}T$, such that $\Delta H_1 = c_P(folded) \cdot (75 - 105)$. ($c_P$ is independent of temperature and of course we can express ΔT in both K and °C).
•Process 3 is isobaric, so $\mathrm{d}H_3 = c_P(unfolded)\mathrm{d}T$, such that $\Delta H_3 = c_P(unfolded) \cdot (105 - 75)$.
•Process 2 is isothermal and $\Delta H_2 = \Delta H_{unfold}(75\ °C) = 509$ kJ/mol.
Therefore $\Delta H_{unfold}(105°C) = c_P(folded) \cdot (75 - 105) + c_P(unfolded) \cdot (105 - 75) + 509 \cdot 10^3 = (105 - 75)\Delta c_P + 509 \cdot 10^3 = 30 \cdot 6.28 \cdot 10^3 + 509 \cdot 10^3 = 697.4$ kJ/mol.

d) S is a state function, so ΔS is also independent of the path.
•Process 1 is isobaric, so $\mathrm{d}Q = \mathrm{d}Q_P = \mathrm{d}H$ and reversible, hence $\mathrm{d}S = \frac{\mathrm{d}Q_{rev}}{T} = \frac{\mathrm{d}H}{T} = \frac{C_P\mathrm{d}T}{T}$.
The temperature changes, so $\Delta S = c_P(folded)\int_{378.2\text{ K}}^{348.2\text{ K}} \frac{\mathrm{d}T}{T} = c_P(folded)\ln\frac{348.2}{378.2}$.
•Process 3 is reversible and isobaric, so $\Delta S = c_P(unfolded)\int_{348.2\text{ K}}^{378.2\text{ K}} \frac{\mathrm{d}T}{T} = c_P(unfolded)\ln\frac{378.2}{348.2}$.

•Process 2 is isothermal and reversible, so $\Delta S = \frac{Q_{rev}}{T_2} = \frac{509 \cdot 10^3}{348.2} = 1462$ J/mol.
So $\Delta S = c_P(folded) \ln \frac{348.2}{378.2} + c_P(unfolded) \ln \frac{378.2}{348.2} + 1462 = \Delta c_P \ln \frac{378.2}{348.2} + 1462 = 6.28 \cdot 10^3 \ln \frac{378.2}{348.2} + 1462 = 519.0 + 1462 = 1981$ J/molK.

e) The heat during the isobaric process, $\Delta H_{unfold}(105°C)$, is delivered to the surroundings.
$\Delta S_{env} = \frac{-Q}{T_{env}} = \frac{-\Delta H_{unfold}(105°C)}{T_{env}} = \frac{-697.4 \cdot 10^3}{378.2} = -1844$ J/molK.
The second law of thermodynamics requires that $\Delta S_{tot} > 0$ for a spontaneous process.
$\Delta S_{tot} = \Delta S + \Delta S_{env} = 1981 - 1844 = 137$ J/molK.
Thus the total entropy increases, such that the process proceeds indeed spontaneously.

Exercise add_7

The equilibrium constant is given by (we denote $\Delta G = \Delta_r G$, etc. for the sake of simplicity)

$$\Delta G^{\ominus} = -RT \ln K \quad \text{or} \quad \ln K = -\frac{\Delta H^{\ominus}}{RT} + \frac{\Delta S^{\ominus}}{R}.$$

For a temperature independent change of the reaction enthalpy and entropy, the relation between $\ln K$ and $\frac{1}{T}$ is a straight line in a Van 't Hoff-plot with as slope $-\frac{\Delta H^{\ominus}}{R}$ and as offset $\frac{\Delta S^{\ominus}}{R}$. For an isobaric exothermic reaction $\Delta H^{\ominus} < 0$ while for an endothermic reaction $\Delta H^{\ominus} > 0$.
This results in figure 2 below

a) $\ln K$ is positive for all T, so $K > 1$ for all T.

b) For $\frac{1}{T} > \frac{1}{T_o}$ or $T < T_o$ one finds $K > 1$, while $0 < K < 1$ for $T > T_o$,
N.B.: T_o should not be confused with standard conditions. T_o is the temperature at which the equilibrium constant $K = 1$. Since $\Delta G^{\ominus} = -RT \ln K = 0$ at that temperature, $\Delta H^{\ominus}$ and $-T_o \Delta S^{\ominus}$ must exactly compensate each other, there.

c) For $T < T_o$ one finds $0 < K < 1$, wile $K > 1$ for $T > T_o$.

d) $0 < K < 1$ for all T.

K is the equilibrium constant, or $K = Q_{eq}$. Outside equilibrium $Q \neq K$; in case $Q < K$ the reaction proceeds to the right and when $Q > K$ the reaction proceeds to the left.

Exercise add_8

We work isothermally so the temperature does not change.
The cell supplies current until the concentrations in the half cells are such that the cell voltage has become equal to zero; this is the equilibrium situation for the cell.
Only the hydroxide molalities play a role here. From the chemical equations from part 18a) it becomes clear that during current supply every decrease of the hydroxide molality in the anode half cell will result in an equal increase of the hydroxide molality in the cathode half cell.
To make the calculation not too complicated we will assume that, given the low concentrations of hydroxide ions, the consumption of H_2O in the cathode compartment has a negligible influence on the molality of the hydroxide.

a) We start with molalities $b_{\mathrm{OH}^-,c} = b_{\mathrm{OH}^-,a} = b_0$. So at every moment during discharge

$$b_{\mathrm{OH}^-,c} = b_0 + \Delta b \quad \text{and} \quad b_{\mathrm{OH}^-,a} = b_0 - \Delta b,$$

which, using the Nernst-equation, results in a cell voltage given by

$$E = E_c^{\ominus} - E_a^{\ominus} - \frac{RT}{F} \ln \frac{\gamma_{\mathrm{OH}^-}(b_0 + \Delta b)}{\gamma_{\mathrm{OH}^-}(b_0 - \Delta b)}$$

In equilibrium the cell voltage is equal to 0 V; in other words

$$0 = 1.30 - \frac{8.315 \cdot 298}{96485} \ln \frac{(b_0 + \Delta b)}{(b_0 - \Delta b)} = 1.30 - 2.568 \cdot 10^{-2} \ln \frac{(b_0 + \Delta b)}{(b_0 - \Delta b)},$$

such that we find

$$\frac{(b_0 + \Delta b)}{(b_0 - \Delta b)} = \exp \frac{1.30}{2.568 \cdot 10^{-2}} = 9.67 \cdot 10^{21}.$$

From this it follows that

$$\Delta b = b_0 \frac{9.64 \cdot 10^{21} - 1}{9.64 \cdot 10^{21} + 1} \approx b_0.$$

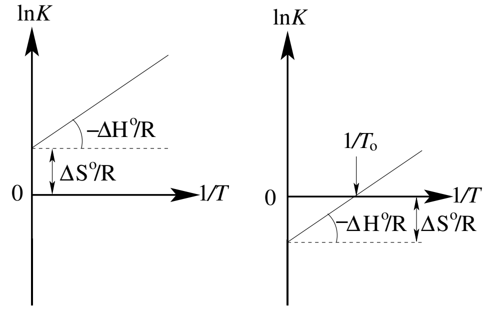
So in equilibrium we find for the molalities of the hydroxide $b_{\mathrm{OH}^-,a} \approx 0$ and $b_{\mathrm{OH}^-,c} \approx 2b_0$.

b) The cell potential decreases in time so that also the current and the delivered power decrease. This is approximately an exponential function in time. The cell voltage at time $t = 0$ is equal to $E_0 = E^{\ominus} = 1.30$ V.
The delivered electrical power at time t is given by

$$P(t) = E(t)I(t) = \frac{E(t)^2}{R_{tot}} = \frac{\left(E_0 \exp\left[-\frac{2RT}{F^2 R_{tot}} \frac{b^{\ominus}}{b_0} t\right]\right)^2}{R_{tot}}.$$

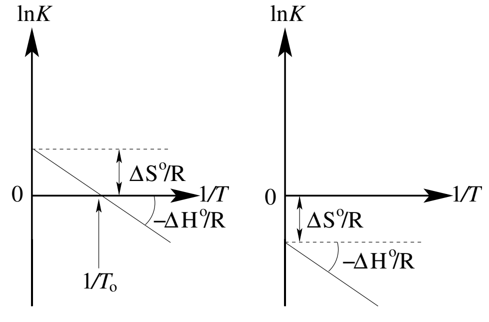
The total delivered electrical work is thus

$$W = \int_0^\infty P(t)\mathrm{d}t = \int_0^\infty \frac{\left(E_0 \exp\left[-\frac{2RT}{F^2 R_{tot}} \frac{b^{\ominus}}{b_0} t\right]\right)^2}{R_{tot}} \mathrm{d}t = \frac{E_0^2}{R_{tot}} \int_0^\infty \exp\left[-2\frac{2RT}{F^2 R_{tot}} \frac{b^{\ominus}}{b_0} t\right] \mathrm{d}t,$$



(a) $\Delta H^{\ominus} < 0$ and $\Delta S^{\ominus} > 0$

(b) $\Delta H^{\ominus} < 0$ and $\Delta S^{\ominus} < 0$



(c) $\Delta H^{\ominus} > 0$ and $\Delta S^{\ominus} > 0$

(d) $\Delta H^{\ominus} > 0$ and $\Delta S^{\ominus} < 0$

Figure 2: The four situations for $K(T)$ in a Van 't Hoff-plot.

or

$$W = \frac{E_0^2}{R_{tot}} \left[-\frac{F^2 R_{tot}}{4RT} \frac{b_0}{b^{\ominus}} \exp\left(-\frac{4RT}{F^2 R_{tot}} \frac{b^{\ominus}}{b_0} t \right) \right]_0^{\infty} = \frac{E_0^2 F^2 R_{tot}}{R_{tot} 4RT} \frac{b_0}{b^{\ominus}} = \frac{E_0^2 F^2}{4RT} \frac{b_0}{b^{\ominus}}.$$

Substituting all values results in (use the result of exercise 18e)

$$W = \frac{1.30^2 \cdot 96485^2 \cdot 0.1}{4 \cdot 8.314 \cdot 298 \cdot 1} = 1.59 \cdot 10^5 \text{ J}.$$

This value is independent of the resistance, since we determined the total power, including the energy dissipated in the cell which latter is delivered to the surroundings as heat.

c) The heat that is generated in the battery must be transfered to the surroundings as a result of the isothermal conditions. This negative heat Q is thus equal to the electrical power P_i that has been dissipated in the internal resistance R_i of the battery. The voltage over the internal resistance at every moment is given by $E_i(t) = E(t) - I(t)R_L = E(t)\left(1 - \frac{R_L}{R_{tot}}\right)$ (see Study Guide, p.20), such that we find

$$Q = -\int_0^{\infty} P_i(t)\mathrm{d}t = -\int_0^{\infty} \frac{E_i(t)^2}{R_i}\mathrm{d}t = -\frac{\left(1 - \frac{R_L}{R_{tot}}\right)^2}{R_i} \int_0^{\infty} E(t)^2 \mathrm{d}t.$$

If we use the result of the integral from the previous part we find

$$-\frac{\left(1 - \frac{R_L}{R_{tot}}\right)^2}{R_i} \frac{E_0^2 F^2 R_{tot}}{4RT} \frac{b_0}{b^{\ominus}} = -\frac{E_0^2 F^2}{4RT} \frac{b_0}{b^{\ominus}} \frac{R_i}{R_{tot}} = -W \frac{R_i}{R_{tot}} = -1.59 \cdot 10^5 \frac{1}{11} = -1.45 \cdot 10^4 \text{ J}.$$

d) We use the result of the previous part, from which it becomes clear that the fraction $\frac{R_i}{R_{tot}}$ of W should be considered as loss, so that the fraction $1 - \frac{R_i}{R_{tot}} = \frac{R_L}{R_{tot}}$ of W is useful (there is no further work done). The efficiency then is

$$\eta = \frac{W_L}{W} = \frac{R_L}{R_{tot}} = \frac{10}{11} = 0.909 \quad \text{or} \quad 90.9\ \%$$

Exercise add_9

a) Because the atoms in the perfect gas are indistinguishable, the number of realization possibilities W in the Boltzmann-expression for the entropy, $S = k \ln W$, will be smaller. For example an exchange of two atoms that are in different energy states is indistinguishable from the situation before the exchange. The same holds for an exchange of their positions.

b) The mass of helium is $m = 4u = 4 \cdot 1.66 \cdot 10^{-27}$ kg, so $\Lambda = \frac{6.63 \cdot 10^{-34}}{\sqrt{2\pi 4 \cdot 1.66 \cdot 10^{-27} \cdot 1.38 \cdot 10^{-23} \cdot 298}} = 50.6$ pm. For 1 mol $N = N_A$, so

$$S_{indist.} = 6.02 \cdot 10^{23} \cdot 1.38 \cdot 10^{-23} \ln \left[\frac{1.38 \cdot 10^{-23} \cdot 298}{1 \cdot 10^5 \cdot (50.6 \cdot 10^{-12})^3} \cdot 2.718^{\frac{5}{2}} \right] = 126.0 \text{ J/molK}.$$

c)

$$S_{indist.} - S_{dist.} = Nk \ln \left[\frac{kT}{P\Lambda^3} \mathrm{e}^{\frac{5}{2}} \right] - Nk \ln \left[\frac{NkT}{P\Lambda^3} \mathrm{e}^{\frac{3}{2}} \right] = Nk \ln \left[\frac{\mathrm{e}}{N} \right] = -446.6 \text{ J/molK}.$$

In other words, the indistinguishability character of the gas decreases the entropy significantly.

d) First we write the Sackur-Tetrode equation in terms of the volume V using the equation of state for a perfect gas, $PV = NkT$,

$$S_{indist.} = Nk\ln\left[\frac{kT}{P\Lambda^3}\mathrm{e}^{\frac{5}{2}}\right] = Nk\ln\left[\frac{V}{N\Lambda^3}\mathrm{e}^{\frac{5}{2}}\right].$$

For an isothermal expansion from V_1 to $2V_1$ this equation results in an entropy change given by

$$\Delta S = Nk\ln\left[\frac{2V_1}{N\Lambda^3}\mathrm{e}^{\frac{5}{2}}\right] - Nk\ln\left[\frac{V_1}{N\Lambda^3}\mathrm{e}^{\frac{5}{2}}\right] = Nk\ln\left[\frac{2V_1}{V_1}\right] = Nk\ln 2 = nR\ln 2.$$

This is exactly the same result as that of exercise 25.
If we would have considered the atoms of the gas to be distinguishable, we would have found

$$S_{dist.} = Nk\ln\left[\frac{NkT}{P\Lambda^3}\mathrm{e}^{\frac{3}{2}}\right] = Nk\ln\left[\frac{V}{\Lambda^3}\mathrm{e}^{\frac{3}{2}}\right] \quad \text{and}$$

$$\Delta S = Nk\ln\left[\frac{2V_1}{\Lambda^3}\mathrm{e}^{\frac{3}{2}}\right] - Nk\ln\left[\frac{V_1}{\Lambda^3}\mathrm{e}^{\frac{3}{2}}\right] = Nk\ln\left[\frac{2V_1}{V_1}\right] = Nk\ln 2 = nR\ln 2,$$

so exactly the same result. Even though the number of realization possibilities W has increased by a factor 2^N, which results in $\Delta S = nR\ln 2$ (see exercise 25), this increase is the same for distinguishable and indistinguishable particles and is only determined by the twice as large volume. The difference $S_{indist.} - S_{dist.}$ is only determined by the number of ways in which N particles can be exchanged. That number of permutations is $N!$ with an entropy increase of

$$\Delta S = k\Delta\ln W = -k\ln N! \approx -k(N\ln N - N) = -Nk\ln(\frac{N}{e}) = Nk\ln(\frac{e}{N}),$$

which is equal to the difference $S_{indist.} - S_{dist.}$ as obtained in the former part.

Exercise add_10

The chemical equilibrium reaction is $\frac{1}{2}\mathrm{N_2(g)} + \frac{3}{2}\mathrm{H_2(g)} \leftrightharpoons \mathrm{NH_3(g)}$.

a) We can determine the standard reaction Gibbs free energy at 298 K with

$$\Delta_r G^{\ominus} = \sum_j \nu_j \Delta_f G_j^{\ominus} = +\left(-16.45\cdot 10^3\right) - \frac{1}{2}\cdot 0 - \frac{3}{2}\cdot 0 = -16.45\cdot 10^3 \text{ J/mol}.$$

b) In thermodynamic equilibrium $\Delta_r G = 0$, such that $\Delta_r G^{\ominus} = -RT\ln Q_{eq} = -RT\ln K$, so $K = \exp\left[-\frac{\Delta_r G^{\ominus}}{RT}\right] = \exp\left[-\frac{-16.45\cdot 10^3}{8.314\cdot 298}\right] = 765$.

c) The reaction quotient is (perfect gases and $P^{\ominus} = 1$ bar)

$$Q = \frac{\left(\frac{P_{NH_3}}{P^{\ominus}}\right)}{\left(\frac{P_{N_2}}{P^{\ominus}}\right)^{\frac{1}{2}}\left(\frac{P_{H_2}}{P^{\ominus}}\right)^{\frac{3}{2}}} = \frac{4.0}{3.0^{\frac{1}{2}}\cdot 1.0^{\frac{3}{2}}} = 2.309$$

The reaction Gibbs free energy is

$$\Delta_r G = \Delta_r G^{\ominus} + RT\ln Q = -16.45\cdot 10^3 + 8.314\cdot 298\ln 2.309 = -14.38 \ \text{ kJ/mol}.$$

d) Since $\Delta_r G < 0$ the reaction proceeds spontaneously towards the product.

Exercise add_11

a)

$$\mathrm{cyt}_o + \mathrm{e}^- \to \mathrm{cyt}_r \quad \text{with} \quad E^{\ominus}_{cyt},$$

$$\mathrm{D}_o + \mathrm{e}^- \to \mathrm{D}_r \quad \text{with} \quad E^{\ominus}_{D}.$$

The net reaction becomes

$$\mathrm{cyt}_o + \mathrm{D}_r \leftrightharpoons \mathrm{cyt}_r + \mathrm{D}_o \quad \text{with} \quad E^{\ominus} = E^{\ominus}_{cyt} - E^{\ominus}_{D}.$$

Therefore the Nernst equation for this cell is ($\nu = 1$)

$$E = E^{\ominus} - \frac{RT}{F} \ln \frac{[\mathrm{cyt}_r][\mathrm{D}_o]}{[\mathrm{cyt}_o][\mathrm{D}_r]} \quad \text{with} \quad E^{\ominus} = E^{\ominus}_{cyt} - E^{\ominus}_{D}.$$

b) In equilibrium $E = 0$ such that

$$\ln \frac{[\mathrm{cyt}_r]_{eq}[\mathrm{D}_o]_{eq}}{[\mathrm{cyt}_o]_{eq}[\mathrm{D}_r]_{eq}} = \ln \frac{[\mathrm{D}_o]_{eq}}{[\mathrm{D}_r]_{eq}} - \ln \frac{[\mathrm{cyt}_o]_{eq}}{[\mathrm{cyt}_r]_{eq}} = \frac{F}{RT}\left(E^{\ominus}_{cyt} - E^{\ominus}_{D}\right),$$

or

$$\ln \frac{[\mathrm{D}_o]_{eq}}{[\mathrm{D}_r]_{eq}} = \ln \frac{[\mathrm{cyt}_o]_{eq}}{[\mathrm{cyt}_r]_{eq}} + \frac{F}{RT}\left(E^{\ominus}_{cyt} - E^{\ominus}_{D}\right).$$

This results in a straight line if we plot $\ln \frac{[\mathrm{D}_o]_{eq}}{[\mathrm{D}_r]_{eq}}$ versus $\ln \frac{[\mathrm{cyt}_o]_{eq}}{[\mathrm{cyt}_r]_{eq}}$. The slope is 1 and the intercept is $\frac{F}{RT}\left(E^{\ominus}_{cyt} - E^{\ominus}_{D}\right)$.

c) From the data we determine the logarithm of the concentration ratio.

$\ln \frac{[\mathrm{D}_o]_{eq}}{[\mathrm{D}_r]_{eq}}$	-5.882	-4.776	-3.661	-3.002	-2.593	-1.436	-0.6274
$\ln \frac{[\mathrm{cyt}_o]_{eq}}{[\mathrm{cyt}_r]_{eq}}$	-4.547	-3.772	-2.415	-1.625	-1.094	-0.2120	0.3293

The plot from the previous part with these values results in an intercept of -1.2124, such that at 298 K $E^{\ominus}_{cyt} = \frac{RT}{F} \cdot (-1.2124) + 0.237 = 0.0257 \cdot (-1.2124) + 0.237 = 0.206$ V.

Exercise add_12

For very low concentrations of a dissolved compound (the solute) we can use the simple expression

$$\Pi = [B]RT \quad \text{with} \quad [B] = \frac{n_B}{V} = \frac{c_B}{M_B}$$

for the osmotic pressure. Here M_B is the molar mass and c_B is the mass concentration of the polystyrene. The osmotic pressure is measured as $\Pi = \rho g h$, such that

$$h = \left(\frac{RT}{\rho g M_B}\right) c_B.$$

When we plot $h(c_B)$, the expression between the brackets is the slope. For this plot we can incorporate the point $h(c_B = 0) = 0$; this increases the accuracy since the equation above is most accurate for $c_B \approx 0$. The slope of this plot is 0.29 cmL/g, or

$$\frac{RT}{\rho g M_B} = 0.29 \cdot 10^{-2}\ \mathrm{m}^4/\mathrm{kg}.$$

With that we find for the molar mass of the dissolved polystyrene ($g = 9.81$ m/s^2):

$$M_B = \frac{8.314 \cdot 298.15}{1.004 \cdot 10^3 \cdot 9.81 \cdot 0.29 \cdot 10^{-2}} = 87\ \mathrm{kg/mol} = 87 \cdot 10^3\ \mathrm{g/mol}.$$