# Answers Tutorials 6 Thermodynamics 2, 2025/2026

## Exercise 22

The reaction is

$$\mathrm{HgCl_2(s)} \leftrightharpoons \mathrm{Hg^{2+}(aq)} + 2\mathrm{Cl^-(aq)}.$$

The equilibrium constant is defined as

$$K = \Pi_i a_i^{\nu_i}.$$

We can assume that the activity is equal to the molality for a poorly soluble salt (and we use $a_{\mathrm{HgCl_2(s)}} \approx 1$):

$$K = \frac{a_{\mathrm{Hg^{2+}(aq)}} a^2_{\mathrm{Cl^-(aq)}}}{a_{\mathrm{HgCl_2(s)}}} \approx a_{\mathrm{Hg^{2+}(aq)}} a^2_{\mathrm{Cl^-(aq)}} \approx \frac{b_{\mathrm{Hg^{2+}}}}{b^\ominus} \left(\frac{b_{\mathrm{Cl^-}}}{b^\ominus}\right)^2.$$

The relation between the solubility, $s$, of the salt $\mathrm{HgCl_2(s)}$ and the molalities is $b_{\mathrm{Cl^-}} = 2b_{\mathrm{Hg^{2+}}} = 2s$, so

$$K = \frac{4s^3}{(b^\ominus)^3}, \quad \text{therefore} \quad s = \left(\frac{1}{4}K\right)^{\frac{1}{3}} b^\ominus.$$

$K$ follows from the equilibrium condition $RT\ln K = -\Delta_r G^\ominus$, in which

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\mathrm{Hg^{2+}, aq}) + 2\Delta_f G^\ominus(\mathrm{Cl^-, aq}) - \Delta_f G^\ominus(\mathrm{HgCl_2, s}) = 164.40 - 2\cdot 131.23 + 178.6 = 80.54 \text{ kJ/mol}.$$

From this result the equilibrium constant follows:

$$\ln K = \frac{-80.54\cdot 10^3}{8.314\cdot 298.15} = -32.49, \quad \text{so} \quad K = 7.758\cdot 10^{-15},$$

and therefore

$$s = \left(\frac{1}{4}K\right)^{\frac{1}{3}} b^\ominus = 1.25\cdot 10^{-5} \text{ mol/kg},$$

which indeed corresponds to a very low solubility.

## Exercise 23

$$I = \frac{1}{2}\sum_i z_i^2 \left(\frac{b_i}{b^\ominus}\right) = I_{\mathrm{KCl}} + I_{\mathrm{FeCl_3}}.$$

For a dissolved salt $\mathrm{M}_p\mathrm{X}_q$ with molality $b$ the molalities of the ions are $(b_+/b^\ominus) = p(b/b^\ominus)$ and $(b_-/b^\ominus) = q(b/b^\ominus)$, so we get

$$I = \frac{1}{2}\left[(+1)^2\frac{b_{\mathrm{KCl}}}{b^\ominus} + (-1)^2\frac{b_{\mathrm{KCl}}}{b^\ominus}\right] + \frac{1}{2}\left[(+3)^2\frac{b_{\mathrm{FeCl_3}}}{b^\ominus} + (-1)^2\cdot 3\frac{b_{\mathrm{FeCl_3}}}{b^\ominus}\right].$$

Using the given molalities this results in ($b^\ominus = 1$ mol/kg)

$$I = \frac{1}{2}[0.20 + 0.20] + \frac{1}{2}[9\cdot 0.10 + 3\cdot 0.10] = 0.20 + 0.60 = 0.80.$$

The largest contribution thus comes from the $\mathrm{FeCl_3}$, which has a lower molality but larger charge once dissolved.

# Exercise 24

a) Dissolving 1 mol of AgCl(s) results in 1 mol $Ag^+$ and 1 mol $Cl^-$ in the solution, so $b_{Ag^+} = b_{Cl^-} = s$, where $s$ is the solubility. The equiulibrium constant is given by

$$K = \frac{a_{Ag^+} a_{Cl^-}}{a_{AgCl(s)}} = a_{Ag^+} a_{Cl^-} = \gamma_\pm \left(\frac{b_{Ag^+}}{b^\ominus}\right) \gamma_\pm \left(\frac{b_{Cl^-}}{b^\ominus}\right) = \gamma_\pm^2 \left(\frac{s}{b^\ominus}\right)^2.$$

The ionic strength of the solution is

$$I = \frac{1}{2}\left[(+1)^2 \frac{b_{Ag^+}}{b^\ominus} + (-1)^2 \frac{b_{Cl^-}}{b^\ominus}\right] = \frac{s}{b^\ominus} = 1.274 \cdot 10^{-5}.$$

The Debye-Hückel limiting law results in ($A = 0.509$ at 298.15 K)

$$\log \gamma_\pm = -|z_+ z_-| A\sqrt{I} = -0.509 \cdot \sqrt{1.274 \cdot 10^{-5}} = -1.82 \cdot 10^{-3}, \quad \text{which gives} \quad \gamma_\pm = 0.996, \quad \text{so}$$

$$K = 0.996^2 \cdot (1.274 \cdot 10^{-5})^2 = 1.61 \cdot 10^{-10}.$$

b) For a solution with only 0.00200 mol/kg $K_2SO_4$ the ionic strength is

$$I = \frac{1}{2}\left[(+1)^2 \cdot 2 \cdot 0.00200 + (-2)^2 \cdot 0.00200\right] = 0.00600.$$

c) The ionic strength of $K_2SO_4$ in this solution is way bigger than that of AgCl, which means we can neglect the latter for now (Note, that $z_+$ and $z_-$ in the Debye-Hückel limiting law, still refer to $Ag^+$ and $Cl^-$, respectively).

$$\log \gamma_\pm = -|z_+ z_-| A\sqrt{I} = -0.509 \cdot \sqrt{0.00600} = -0.0394, \quad \text{so} \quad \gamma_\pm = 0.9132.$$

d) The equilibrium constant is independent of the composition of the solution because

$$RT \ln K = -\Delta_r G^\ominus$$

and the symbol $\ominus$ refers to the standard state for which all components of the reaction (AgCl(s), $Ag^+$(aq) and $Cl^-$(aq)) are in a (virtual) pure state.
Therefore, we can still use the result for $K$ from part a). The activity coefficient, however, now has the value found in part c), so we find

$$\frac{s}{b^\ominus} = \frac{\sqrt{K}}{\gamma_\pm} = \frac{\sqrt{1.61 \cdot 10^{-10}}}{0.9132} = 1.39 \cdot 10^{-5}, \quad \text{so} \quad s = 1.39 \cdot 10^{-5} \text{ mol/kg},$$

which is larger than the original value for the solubility.

e) Using the equilibrium constant of part a) and the new solubility from part d) we find:

$$I = I_{K_2SO_4} + I_{AgCl} = 0.00600 + 1.39 \cdot 10^{-5} = 0.00601, \quad \text{so} \quad \gamma_\pm = 0.9131, \quad \text{which gives}$$

$$\frac{s}{b^\ominus} = \frac{\sqrt{K}}{\gamma_\pm} = 1.394 \cdot 10^{-5}, \quad \text{which shows that our approximation was very reasonable.}$$

# Exercise 25

a) The electrical work is given by $\mathrm{d}W_e = E\mathrm{d}q$, in which $E$ is the potential difference over which the charge $\mathrm{d}q$ is transfered. This results in the following relation for the Gibbs free energy (at constant pressure)

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mathrm{d}W_e = -S\mathrm{d}T + E\mathrm{d}q.$$

From this characteristic equation the following Maxwell relation can be derived

$$\left(\frac{\partial E}{\partial T}\right)_{q,P} = -\left(\frac{\partial S}{\partial q}\right)_{T,P}.$$

b) The overall reaction is

$$\mathrm{AgCl(s)} + \frac{1}{2}\mathrm{H_2(g)} \leftrightharpoons \mathrm{Ag(s)} + \mathrm{Cl^-(aq)} + \mathrm{H^+(aq)}$$

The standard potential of a standard hydrogen electrode is, per definition, $E^\ominus(\mathrm{Pt|H_2(g)|H^+(aq)}) = 0$ V for any $T$. The standard conditions for this expression are $P = P^\ominus = 1$ bar and $a_{\mathrm{H}^+} = 1$. The standard potential (in V) of the Ag/AgCl/$\mathrm{Cl^-}$ electrode as a function of the temperature at 1 bar is

$$E^\ominus = 0.23659 - 4.8564 \cdot 10^{-4}t - 3.4205 \cdot 10^{-6}t^2 + 5.869 \cdot 10^{-9}t^3.$$

At $t = 25$ °C we find $E^\ominus = 0.2224$ V. Remember that this value is measured with a standard hydrogen electrode as reference.
Per mole of reaction we have a charge transfer of $-N_A e = -F = -96485$ C/mol so

$$\Delta_r G^\ominus = -\nu F E^\ominus = -1 \cdot 96485 \cdot 0.2224 = -21458 \text{ J/mol}$$

Realize that the *choice* to set the standard potential of the standard hydrogen electrode to zero for all temperatures, does not mean that the standard potential of other electrodes are also independent of the temperature.
Because of that choice for $E^\ominus(\mathrm{Pt|H_2(g)|H^+(aq)})$, only the Ag/AgCl/$\mathrm{Cl^-}$ electrode determines the temperature dependence for this cell. Under standard conditions we thus find for the standard potential ($t$ [°C] $= T - 273.15$ [K] so $\partial/\partial T = \partial/\partial t$):

$$\left(\frac{\partial E^\ominus}{\partial T}\right)_{q,P} = \left(\frac{\partial E^\ominus(\mathrm{Ag/AgCl/Cl^-})}{\partial T}\right)_{q,P} = -4.8564 \cdot 10^{-4} - 2 \cdot 3.4205 \cdot 10^{-6}t + 3 \cdot 5.869 \cdot 10^{-9}t^2 \quad \text{[V/K]},$$

so $\left(\frac{\partial E^\ominus}{\partial T}\right)_{q,P} = -6.457 \cdot 10^{-4}$ V/K.
Using the Maxwell relation we find for the standard reaction entropy

$$\Delta_r S^\ominus = -\left(\frac{\partial E^\ominus}{\partial T}\right)_{q,P} \Delta q = -(-6.457 \cdot 10^{-4}) \cdot (-96485) = -62.30 \text{ J/molK},$$

so

$$\Delta_r H^\ominus = \Delta_r G^\ominus + T\Delta_r S^\ominus = -21458 + 298.15 \cdot (-62.30) \text{ J/mol} = -40.03 \text{ kJ/mol}.$$

c) Although $\mathrm{Cl^-}$ ions are added, charge neutrality ensures that the amount of $\mathrm{H^+}$ ions will not change and therefore $E^\ominus(\mathrm{Pt|H_2(g)|H^+(aq)}) = 0$, per definition for any $T$, still holds and still $a_{\mathrm{H}^+} = 1$. Nevertheless the activity $a_{\mathrm{Cl}^-}$ will change, because of the added KCl, but also because of the higher temperature.
Using the temparature dependence of the standard potential of the (Ag/AgCl/$\mathrm{Cl^-}$) couple we find at $T = 323.2$ K (50 °C) $E^\ominus(\mathrm{AgCl/Ag,\ Cl^-(aq)}) = 0.2045$ V, so for the total cell without added KCl we take the **sum** of the two half cell potentials at standard conditions (so $^\ominus \equiv a_i = 1$)

$$E^\ominus(323.2 \text{ K}) = (0.2045 - 0) - \frac{8.314 \cdot 323.2}{96485} \ln a^\ominus_{\mathrm{Cl}^-} a^\ominus_{\mathrm{H}^+} = 0.2045.$$

For the total cell with added KCl we find analogously (still $a_{\mathrm{H}^+} = 1$)

$$E(323.2 \text{ K})' = 0.2045 - \frac{8.314 \cdot 323.2}{96485} \ln a'_{\mathrm{Cl}^-} a'_{\mathrm{H}^+} = 0.2045 - \frac{8.314 \cdot 323.2}{96485} \ln \frac{b_{\mathrm{Cl}^-}}{b^\ominus} \cdot 1 \cdot \gamma_\pm^2.$$

So the change in cell potential of $\Delta E$ is given by

$$\Delta E = E(323.2 \text{ K})' - E^\ominus(323.2 \text{ K}) = -\frac{8.314 \cdot 323.2}{96485} \ln \frac{b_{\mathrm{Cl}^-}}{b^\ominus}\gamma_\pm^2, \text{ so } \ln \frac{b_{\mathrm{Cl}^-}}{b^\ominus}\gamma_\pm^2 = -35.91\Delta E.$$

Because $b_{\mathrm{Cl^-}}$ can be written as $b_{\mathrm{Cl^-}} = b^{\mathrm{added}}_{\mathrm{Cl^-}} + b^{\ominus}_{\mathrm{Cl^-}} = b^{\mathrm{added}}_{\mathrm{Cl^-}} + b^{\ominus} = b^{\mathrm{added}}_{\mathrm{K^+}} + b^{\ominus}$, we rewrite this to

$$\ln\left(\frac{b^{\mathrm{added}}_{\mathrm{K^+}}}{b^{\ominus}} + \frac{b^{\ominus}}{b^{\ominus}}\right)\gamma_{\pm}^2 = \ln\left(b^{\mathrm{added}}_{\mathrm{KCL}} + 1\right)\gamma_{\pm}^2 = -35.91\Delta E, \text{ so } \ln\frac{b^{\mathrm{added}}_{\mathrm{KCL}}}{b^{\ominus}} + 2\ln\gamma_{\pm} = -35.91\Delta E.$$

To estimate $\gamma_{\pm}$ we use the Debye-Hückel limiting law. The ionic strength $I$ is ($b_{\mathrm{H^+}} = b^{\ominus} \equiv 1\mathrm{mol/kg}$)

$$I = \frac{1}{2}\sum_i z_i^2\frac{b_i}{b^{\ominus}} = \frac{1}{2}\left(z^2_{\mathrm{K^+}}\frac{b_{\mathrm{K^+}}}{b^{\ominus}} + z^2_{\mathrm{Cl^-}}\frac{b_{\mathrm{Cl^-}}}{b^{\ominus}} + z^2_{\mathrm{H^+}}\frac{b_{\mathrm{H^+}}}{b^{\ominus}}\right) = \frac{1}{2}\left(\frac{b_{\mathrm{K^+}}}{b^{\ominus}} + \frac{b_{\mathrm{Cl^-}}}{b^{\ominus}} + 1\right),$$

which can also be written in terms of added KCL:

$$I = \frac{1}{2}\left(\frac{b^{\mathrm{added}}_{\mathrm{K^+}}}{b^{\ominus}} + \frac{b^{\mathrm{added}}_{\mathrm{Cl^-}}}{b^{\ominus}} + 2\right) = \frac{b^{\mathrm{added}}_{\mathrm{KCl}}}{b^{\ominus}} + 1.$$

The temperature dependence in the Debye-Hückel limiting law is also in the constant $A$:

$$A = \frac{F^3}{4\pi N_A \ln 10}\left(\frac{\rho b^{\ominus}}{2\epsilon^3 R^3 T^3}\right)^{\frac{1}{2}}, \text{ so } A' = A(323.2\text{ K}) = A(298.2\text{ K})\left(\frac{298.2}{323.2}\right)^{\frac{3}{2}} = 0.509\left(\frac{298.2}{323.2}\right)^{\frac{3}{2}},$$

which enters the expression for $\gamma_{\pm}$:

$$\log\gamma_{\pm} = -|z_{\mathrm{H^+}} z_{\mathrm{Cl^-}}|A' I^{\frac{1}{2}} = -0.451\left(\frac{b^{\mathrm{added}}_{\mathrm{KCl}}}{b^{\ominus}} + 1\right)^{\frac{1}{2}}, \text{ so } \ln\gamma_{\pm} = \frac{\log\gamma_{\pm}}{\log \mathrm{e}} = \frac{-0.451\left(\frac{b^{\mathrm{added}}_{\mathrm{KCl}}}{b^{\ominus}} + 1\right)^{\frac{1}{2}}}{\log \mathrm{e}}.$$

If we combine this expression with the earlier one for $\Delta E$, we find

$$\ln\frac{b^{\mathrm{added}}_{\mathrm{KCL}}}{b^{\ominus}} + 2\frac{-0.451\left(\frac{b^{\mathrm{added}}_{\mathrm{KCl}}}{b^{\ominus}} + 1\right)^{\frac{1}{2}}}{\log \mathrm{e}} = -35.91\Delta E, \text{ so } \ln\frac{b^{\mathrm{added}}_{\mathrm{KCL}}}{b^{\ominus}} - 2.077\left(\frac{b^{\mathrm{added}}_{\mathrm{KCl}}}{b^{\ominus}} + 1\right)^{\frac{1}{2}} = -35.91\Delta E.$$

For $\Delta E = +0.1000$ V, we find

$$\ln\frac{b^{\mathrm{added}}_{\mathrm{KCL}}}{b^{\ominus}} - 2.077\left(\frac{b^{\mathrm{added}}_{\mathrm{KCl}}}{b^{\ominus}} + 1\right)^{\frac{1}{2}} = -3.591.$$

This still leaves us with a so-called transcendental equation, which is not algebraically solvable, so we will have to find the solution numerically. Plotting the function $f(x) = \ln x - 2.077\,(x+1)^{\frac{1}{2}} + 3.591$ and reading off the value for $f(x) = 0$, we find two values $x = 0.297$ and $x = 5.55$ (see Figure 1). The latter value is unreliable within the limitations of the Debye-Hückel limiting law. The first value leads to an estimate of $b_{\mathrm{KCL}} = 0.297$ mol/kg. This is 297 mmol/kg, which is still quite large to be reliable, but certainly a rough estimate.

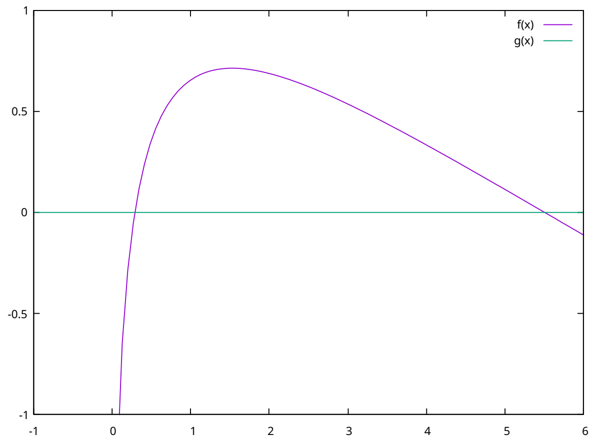


Figure 1: The function $f(x) = \ln x - 2.077\,(x+1)^{\frac{1}{2}} + 3.591$.