Answers Additional Tutorial B, Thermodynamics 2, 2025/2026

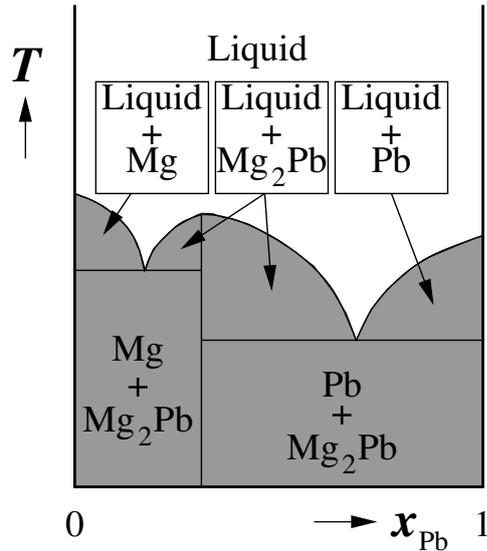## Exercise B1

a) The phase diagram is outlined in figure 1.

Figure 1: The Mg-Pb phase diagram.

b) The phase diagram is outlined in figure 2.
Gibbs' phase rule for $C = 2$ and given pressure becomes $F' = C - P + 1 = 2 - P + 1 = 3 - P$, such that for the case of a two-phase regime there is merely one free variable. The corresponding areas are hatched and we can apply the lever rule there.
Eutectic points are present at compositions $x_{\text{FeCl}_2} = 0.38$ and $x_{\text{FeCl}_2} = 0.54$. Only for these points, on passing via a cooling isopleth, starting in the liquid phase only two solids are formed with compositions that do not change anymore. The lever rule gives their relative amounts.
$K_2\text{FeCl}_4$ melts incongruently at 380 °C, implying that it decomposes into a liquid phase and solid KCl.

c) On cooling a liquid with composition $x_{\text{FeCl}_2} = 0.36$ starting at 500 °C on reaching the liquidus the first $K_2\text{FeCl}_4(\text{s})$ is formed and on further cooling the system enriches in FeCl_2 until at 351 °C the liquid disappears and also $\text{KFeCl}_3(\text{s})$ is formed. The lever rule can be used to find the relative amounts of the two solids $K_2\text{FeCl}_4(\text{s})$ and $\text{KFeCl}_3(\text{s})$.

Exercise B2

a) There is no other work than volume work $(\text{d}W' = 0)$, so the change in Gibbs free energy can be written as
$\text{d}G = V\text{d}P - S\text{d}T + \mu\text{d}n$.

b) From this equation the following Maxwell relation can be derived
$\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \left(\frac{\partial V}{\partial n}\right)_{P,T}$
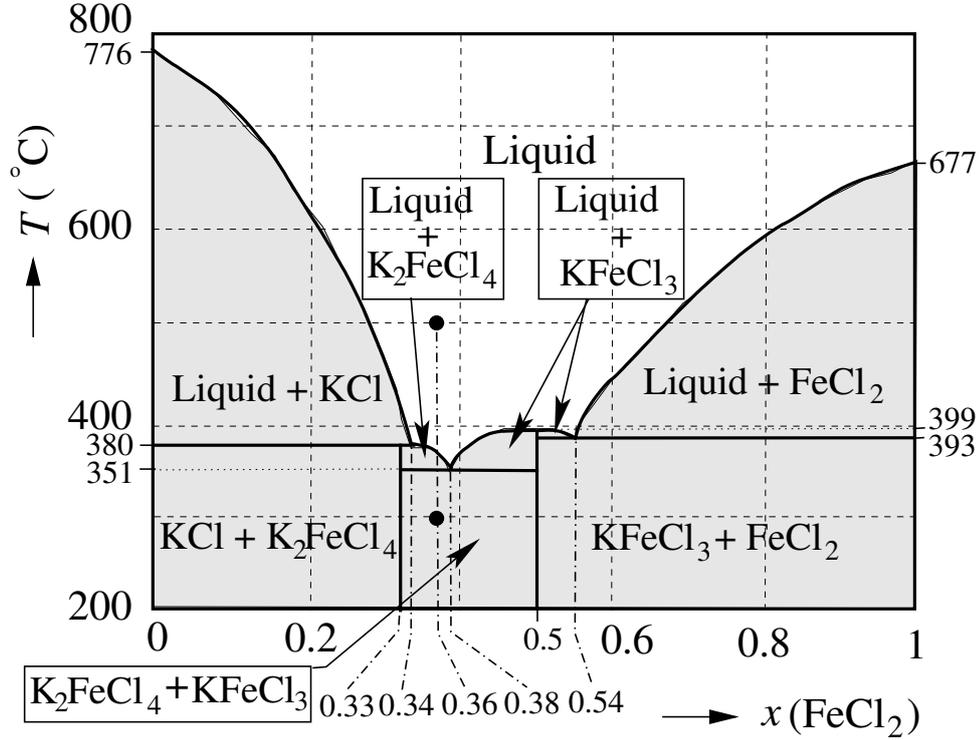$\left(\frac{\partial \mu}{\partial P}\right)_{T,n}$ describes the pressure dependence of the chemical potential.

Figure 2: The KCl-FeCl$_2$ phase diagram.

$\left(\frac{\partial V}{\partial n}\right)_{P,T} = \overline{V}$, is the partial molar volume, which for a unary (one-component) system is the same as the molar volume $V_m = V/n$.

c) For a perfect gas we have $V = \frac{nRT}{P}$, such that

$\left(\frac{\partial V}{\partial n}\right)_{P,T} = \frac{RT}{P}$, which together with the Maxwell relation leads to $\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \frac{RT}{P}$ or $(\mathrm{d}\mu)_{T,n} = \left(\frac{RT}{P}\mathrm{d}P\right)_{T,n}$

Integrating this relation leads to $\mu(P_2) - \mu(P_1) = RT \ln P_2 - RT \ln P_1$. For the integration constant we choose $\mu^{\ominus} = \mu(P^{\ominus})$ met $P^{\ominus} = 1$ bar, such that the most general solution (with this choice for P) becomes

$\mu(P_2) - \mu^{\ominus} = RT \ln \frac{P_2}{P^{\ominus}}$, or

$\mu(P) = \mu^{\ominus} + RT \ln P$.

Note that $\ln x$ has only meaning for x having no units, so for a scalar. Therefore P has to be interpreted as $\frac{P}{1\,\mathrm{bar}}$ if we specify P in the unit 'bar'.

d) We use the Maxwell relation $\left(\frac{\partial \mu}{\partial P}\right)_{T,n} = \left(\frac{\partial V}{\partial n}\right)_{P,T}$ from part b. This relation leads after integration to

$$\int \mathrm{d}\mu = \int \left(\frac{\partial V}{\partial n}\right)_{P,T} \mathrm{d}P.$$

If we choose $P^{\ominus}$ as reference, we find at pressure P

$$\mu(P) - \mu^{\ominus} = \int_{P^{\ominus}}^{P} \left(\frac{\partial V}{\partial n}\right)_{P,T} \mathrm{d}P$$

To determine the partial molar volume we rewrite the equation of state as a function $V(n)$; neglecting $C(T)$ and higher order terms we find $PV^2 - nRTV - n^2RTB(T) = 0$. This second order

polynomial in V we can solve using the so-called ABC-formula:

$$V = \frac{nRT \pm \sqrt{(nRT)^2 + 4Pn^2RTB(T)}}{2P}.$$

The appropriate sign in this solution we can find by studying the limit of the perfect gas, which we find by taking $B(T) = 0$; in this way we find the perfect gas equation of state for the '+'-sign (the '$-$'-sign results in $V = 0$, which is not a proper solution). For the partial molar volume as a function of P we thus find

$$\left(\frac{\partial V}{\partial n}\right)_{P,T} = \frac{RT}{2P} + \frac{2nR^2T^2 + 8nPRTB(T)}{4P\sqrt{(nRT)^2 + 4Pn^2RTB(T)}} = \frac{RT}{2P} + \frac{\sqrt{(nRT)^2 + 4Pn^2RTB(T)}}{2Pn}.$$

This result we could have obtained also more easily by realising that for a unary stem, whether or not it concerns a perfect gas, the partial molar volume is simply V/n.

The equation can be simplified to

$$\left(\frac{\partial V}{\partial n}\right)_{P,T} = \frac{RT}{2P} + \sqrt{\left(\frac{RT}{2P}\right)^2 + 2B(T)\frac{RT}{2P}}.$$

The chemical potential now becomes

$$\mu(P) - \mu^\ominus = \int_{P^\ominus}^{P} \left[\frac{RT}{2P} + \sqrt{\left(\frac{RT}{2P}\right)^2 + 2B(T)\frac{RT}{2P}} \right] dP.$$

Choosing a new variable $x = \frac{RT}{2P}$ with $\frac{\partial P}{\partial x} = \frac{\partial P}{\partial \frac{RT}{2P}} = -\frac{2P^2}{RT} = -\frac{RT}{2}\frac{1}{x^2}$, we find

$$\mu(P) - \mu^\ominus = -\frac{RT}{2}\int_{x^\ominus}^{x(P)} \frac{1}{x^2} \left[x + \sqrt{x^2 + 2Bx} \right] dx = -\frac{RT}{2}\int_{x^\ominus}^{x(P)} \left[\frac{1}{x} + \sqrt{\frac{1}{x^2} + \frac{2B}{x^3}} \right] dx.$$

This is a tough integral to solve, but Maple helps us out. The primitive of the integrant turns out to be:

$$\ln(x) + \frac{1}{Bx^2}\left(-\left(x^2 + 2Bx\right)^{3/2} + x^2\sqrt{x^2 + 2Bx} + x^2 B \ln\left(B + x + \sqrt{x^2 + 2Bx}\right) \right)$$

Plotting the chemical potential as a function of P between $P = P^\ominus = 1$ bar and $P = 10P^\ominus$ at $T = 273$ K for the gas CO_2, for which $B(273 \text{ K}) = -142 \text{ cm}^3/\text{mol}$ and $\mu^\ominus = -394.36 \text{ kJ/mol}$, we find the result of figure 3, in which also the perfect gas case is drawn for $B = 0$ as the lower curve. Note that the two curves intersect at the chosen reference pressure $P^\ominus$ because also for the perfect gas case we used the real gas value of $\mu^\ominus = -394.36 \text{ kJ/mol}$. Futhermore μ for the non-perfect case, $B \neq 0$, is less negative as compared to the perfect gas, which is in correspondence with the fact that $B < 0$.

Exercise B3

The net reaction is

$$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$$
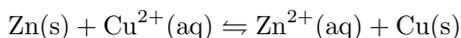
a) Since Zn(s) and Cu(s) are already in their standard state (so $\Delta_f H^\ominus(\text{Cu}) = \Delta_f H^\ominus(\text{Zn}) = 0$), $\Delta_r H^\ominus$ can be calculated using.

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_f H^\ominus(\text{Cu}^{2+}, \text{aq}) = (-153.89 - 64.77)\text{kJ/mol} = -218.66 \text{ kJ/mol}.$$

N.B. $\Delta_f H^\ominus$ is the standard enthalpy of *formation*, not to be confused with the enthalpy of fusion $\Delta_{fus}H$.
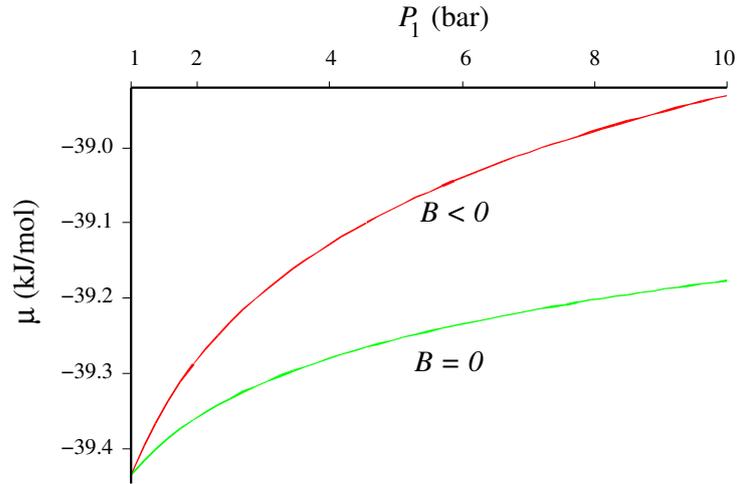
3

Figure 3: The chemical potential as a function of P for the non-perfect gas CO_2, for which $B(273 \text{ K}) = -142 \text{ cm}^3/\text{mol}$ and $\mu^\ominus = -394.36 \text{ kJ/mol}$.

b) $\Delta_r G^\ominus$ can be calculated using

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) - \Delta_f G^\ominus(\text{Cu}^{2+}, \text{aq}).$$

$$\Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) = \Delta_f H^\ominus(\text{Zn}^{2+}, \text{aq}) - T\Delta_f S^\ominus(\text{Zn}^{2+}, \text{aq}) = -153.89 - 298 \cdot (-22.92 \cdot 10^{-3}) = -147.06 \text{kJ/mol},$$

so

$$\Delta_r G^\ominus = (-147.06 - 65.49) = -212.55 \text{ kJ/mol}.$$
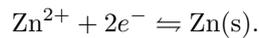
c) We find the standard electrochemical potential for the whole reaction using

$$\Delta_r G^\ominus = -\nu F \left[E^\ominus(\text{Cu}^{2+}/\text{Cu}) - E^\ominus(\text{Zn}^{2+}/\text{Zn}) \right],$$

so

$$E^\ominus(\text{Zn}^{2+}/\text{Zn}) = 0.34 + \frac{-212.55 \cdot 10^3}{2 \cdot 96458.3} = -0.76 \text{ V}.$$

d) For the reaction

$$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn(s)}.$$

we have

$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{Zn(s)}) - \Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) = -\Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) = 147.06 \text{kJ/mol},$$

resulting in the same value as found before:

$$E^\ominus(\text{Zn}^{2+}/\text{Zn}) = -\frac{\Delta_r G^\ominus}{\nu F} = -\frac{147.06 \cdot 10^3}{2 \cdot 96458.3} = -0.76 \text{ V}.$$

Exercise B4

The overall reaction of the two half reactions is

$$\text{PbSO}_4(s) + \text{H}_3\text{O}^+(aq) + \text{PbSO}_4(s) + 5\text{H}_2\text{O}(l) \leftrightarrow \text{Pb}(s) + \text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) + \text{PbO}_2(s) + 3\text{H}_3\text{O}^+(aq) + \text{HSO}_4^-(aq),$$

which simplified becomes

$$2\text{PbSO}_4(s) + 4\text{H}_2\text{O}(l) \leftrightarrow \text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}_3\text{O}^+(aq) + 2\text{HSO}_4^-(aq),$$

with a cell potential of $E^\ominus = -0.356 - 1.685 = -2.041$ V. The battery has 6 of those half cells in series, which gives a total standard potential $E^\ominus_{batt.} = 6 \cdot (-2.041) = -12.25$ V for the battery at a temperature of 298 K.

$E^\ominus_{batt.} < 0$, so the reaction will run spontaneous towards the left. Under standard conditions we have $a_{\text{H}_3\text{O}^+} = 1$, and thus $\text{pH} \equiv -\log a_{\text{H}_3\text{O}^+} = 0$.

a) The charged battery has a potential of $E = -12.65$ V. The '-'sign is a result of the choice of reactants and products in the overall reaction.

$$W_{max} = \Delta_r G = -\nu F E = -2FE = -2 \cdot 9.6485 \cdot 10^4 \cdot (-12.65) = 2441 \text{ kJ/mol}.$$

b) Using the Maxwell relation that we derived in exercise 3 to calculate the entropy

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

we find that per mole of converted lead $\left(\left(\frac{\partial E}{\partial T}\right)_{q,P} = +0.022$ V/K because of the way we defined the overall reaction)

$$\Delta_r S = -\left(\frac{\partial E}{\partial T}\right)_{q,P} \Delta q = -\left(\frac{\partial E}{\partial T}\right)_{q,P} (-\nu F) = -(+0.022) \cdot (-2 \cdot 96485) = 4.25 \cdot 10^3 \text{ J/molK}.$$

c) The E.M.F of the charged battery is $-12.65/6 = -2.108$ V and the standard cell potential is $E^\ominus = -2.041$ V. Using the Nernst equation we find

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q = E^\ominus - \frac{RT}{2F} \ln a^2_{\text{H}_3\text{O}^+} \cdot a^2_{\text{HSO}_4^-},$$

so

$$a^2_{\text{H}_3\text{O}^+} \cdot a^2_{\text{HSO}_4^-} = \exp\left[-\frac{2F(E - E^\ominus)}{RT}\right] = \exp\left[-\frac{2 \cdot 96485 (-2.108 - (-2.041))}{8.314 \cdot 298}\right] = 184.6.$$

We know that the charged battery has $\text{pH} = 1$, and thus $-\log a_{\text{H}_3\text{O}^+} = 1$, so $a_{\text{H}_3\text{O}^+} = 0.1$. When we use this result we find $a_{\text{HSO}_4^-} = 135.9$.

d) The Debye Hückel limiting law gives (on the molality scale)

$$\log \gamma_\pm = -|z_+ z_-| A I^{\frac{1}{2}} \quad \text{and} \quad \mu_i = \mu_i^\ominus + RT \ln a_i = \mu_i^\ominus + RT \ln \frac{b_i}{b^\ominus} + RT \ln \gamma_\pm$$

For the individual (mean) activities we then find

$$a_{\text{H}_3\text{O}^+} = \gamma_\pm \frac{b_{\text{H}_3\text{O}^+}}{b^\ominus} \quad \text{and} \quad a_{\text{HSO}_4^-} = \gamma_\pm \frac{\text{HSO}_4^-}{b^\ominus}.$$

Substituting in the results ($b_{\text{H}_3\text{O}^+} = b_{\text{HSO}_4^-} \equiv b$, according to the reaction equation)

$$\log \gamma_\pm = -1 \cdot 1 \cdot 0.509 \left[\frac{1}{2} \frac{b_{\text{H}_3\text{O}^+}}{b^\ominus} + \frac{1}{2} \frac{b_{\text{HSO}_4^-}}{b^\ominus}\right]^{\frac{1}{2}} = -0.509 \left[\frac{b}{b^\ominus}\right]^{\frac{1}{2}},$$

5

so ($b^{\ominus} = 1$ mol/kg)

$$a_{\mathrm{H_3O^+}} = b \cdot 10^{-0.509 \cdot b^{\frac{1}{2}}} \quad \text{and} \quad a_{\mathrm{HSO_4^-}} = b \cdot 10^{-0.509 \cdot b^{\frac{1}{2}}}.$$

If we use this in the Nernst equation (part c) we find

$$E = E^{\ominus} - \frac{RT}{\nu F} \ln \left[b \cdot 10^{-0.509 \cdot b^{\frac{1}{2}}} \cdot b \cdot 10^{-0.509 \cdot b^{\frac{1}{2}}} \right]^2 = E^{\ominus} - 4\frac{RT}{\nu F} \ln \left[b \cdot 10^{-0.509 \cdot b^{\frac{1}{2}}} \right],$$

so

$$b \cdot 10^{-0.509 \cdot b^{\frac{1}{2}}} = \exp\left[-\frac{\nu F(E - E^{\ominus})}{4RT} \right] = \exp\left[-\frac{2 \cdot 96485 \left(-2.108 - (-2.041) \right)}{4 \cdot 8.314 \cdot 298} \right] = 3.686.$$

This equation cannot be solved analytically. If we plot the left part as a function of b, we find a function with a maximum at $b \approx 3$ mol/kg with a value of just under 0.4. In other words: there is no solution to this equation. The Debye Hückel limiting law only works with reasonable certainty for solutions with very low concentrations (typically $b \leq 0.01$ mol/kg).
If we are to trust the theory for a value of $b = 0.01$ mol/kg, the left part becomes $9 \cdot 10^{-3}$. If we use this value, we find a corresponding terminal voltage of $E = E^{\ominus} + 0.243 = -1.798$ V, so for the whole battery $6 \cdot (-1.798) = -10.8$ V. If we measure such a low voltage, it is probably about time to call the road service to recharge the battery.

Exercise B5

a) We work at constant pressure and temperature so G is the most appropriate state function. For the heat we need a state function in terms of dQ and for example dP, which is the enthalpy H.
We have an additional (elektrical) work term $dW_e = Edq$, where E is the EMF (ElectroMotive Force or cell voltage) and dq the charge transferred by the cell (the system), so
$dH = VdP + TdS + Edq$.
For a reversible process in the cell $TdS = dQ^{rev}$ such that $dH = VdP + dQ^{rev} + Edq$.
P is constant ($dP = 0$), so $\Delta H = Q^{rev} + E\Delta q$, or $Q^{rev} = \Delta H - E\Delta q$.
The cell (the system) delivers current to the surroundings, so the elektrical work is negative and
$W_e = E\Delta q = -E\nu F = -0.046 \cdot 2 \cdot 9.6485 \cdot 10^4 = -8.88$ kJ/mol, so the heat is
$Q^{rev} = 11.08 - (-8.88) = 19.96$ kJ/mol. This heat is positive so the cell delivers current but has to take up heat from the surrounding to keep the temperature constant, so formally, the heat *produced* by the cell is negative:
$Q^{rev}_{produced} = -19.96$ kJ/mol.

b) In this case the mixture is the system. The reaction proceeds in the mixture and it proceeds spontaneously, because $E > 0$. In this case no current is delivered to the surroundings, so $dq = 0$. Furthermore there is no measurable cell voltage, so we put $E = 0$. This might suggest wrongly that $dG = VdP - SdT + Edq = 0$. Because of the spontaneous reaction $dG < 0$ must hold. Furthermore we could still use E to determine whether the reaction proceeds spontaneously or not.
In general the characteristic equation of the Gibbs free energy is $dG = VdP - SdT + \sum_i \mu_i dn_i$. We van no longer replace the term $\sum_i \mu_i dn_i$ with the term Edq, as we do for the case of an electrochemical cell.
For the enthalpy we now have to write $dH = VdP + dQ^{rev} + \sum_i \mu_i dn_i$. H is a state function and per mole reacted silver ΔH is therefore independent of whether we are dealing with the mixture or the cell of part a), so also in this case $\Delta H = 11.08$ kJ/mol. The pressure is constant and equal to $P_{ext.} = 1$ bar, so still $dP = 0$ and the change in enthalpy is equal to the irreversibele reaction heat in the system, $Q = 11.08$kJ/mol, which is positive; the heat is taken up by the mixture to keep the temperature constant. So, again formally, the heat *produced* by the cell is negative:
$Q^{irr}_{produced} = -11.08$ kJ/mol.

c) For the Gibbs energy we have $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + E\mathrm{d}q = V\mathrm{d}P - S\mathrm{d}T + \sum_i \mu_i \mathrm{d}n_i$.
So $\Delta G_{P,T} = E\Delta q = -0.046 \cdot 2 \cdot 9.6485 \cdot 10^4 = -8.88$ kJ/mol.
G is a state function, so also independent of the cell situation or the mixture.
In both cases $\Delta G = -8.88$ kJ/mol.

d) To determine $\left(\frac{\partial E}{\partial T}\right)_{P,q}$ we choose the variables T, P and q as independent variables, so the Gibbs function with $\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + E\mathrm{d}q$.
At constant pressure this becomes $\mathrm{d}G = -S\mathrm{d}T + E\mathrm{d}q$. G is a state function so
$\left(\frac{\partial^2 G}{\partial T \partial q}\right)_P = \left(\frac{\partial^2 G}{\partial q \partial T}\right)_P$, so we can use the Maxwell relation
$\left(\frac{\partial E}{\partial T}\right)_{P,q} = -\left(\frac{\partial S}{\partial q}\right)_{P,T}$ to find
$\left(\frac{\partial E}{\partial T}\right)_{P,q} = -\frac{1}{T}\left(\frac{\partial Q^{rev}}{\partial q}\right)_{P,T} = -\frac{1}{300}\frac{19.90 \cdot 10^3}{-2 \cdot 9.6485 \cdot 10^4} = 3.43 \cdot 10^{-4}$ V/K.
$\left(\frac{\partial E}{\partial T}\right)_{P,q} = 3.43 \cdot 10^{-4}$ V/K.

Exercise B6

a) We are searching a redox couple with a reduction potential which is more negative than $E^{\ominus}(\text{Eu}^{3+}/\text{Eu})$ but less negative than $E^{\ominus}(\text{Yb}^{3+}/\text{Yb})$, such that only Eu precipitates. Such a couple should therefore have -1.991 V $< E^{\ominus} < -2.19$ V.
The data section of Atkins shows that scandium ($E^{\ominus}(\text{Sc}^{3+}/\text{Sc}) = -2.09$ V) is possible candidate.

b) To have only Eu precipitated spontaneously we need to have

$$E_{\text{Eu/Sc}} > 0 \quad \text{for} \quad \text{Eu}^{3+} + \text{Sc} \to \text{Eu} + \text{Sc}^{3+}$$
$$E_{\text{Yb/Sc}} < 0 \quad \text{for} \quad \text{Yb}^{3+} + \text{Sc} \to \text{Yb} + \text{Sc}^{3+}$$

We use the Nernst equation to find the potentials:

$$E_{\text{Eu|Sc}} = E^{\ominus}_{\text{Eu|Sc}} - \frac{RT}{3F}\ln\frac{a_{\text{Sc}^{3+}}}{a_{\text{Eu}^{3+}}} > 0, \quad \text{or} \quad \frac{a_{\text{Sc}^{3+}}}{a_{\text{Eu}^{3+}}} < \exp\left(\frac{3FE^{\ominus}_{\text{Eu|Sc}}}{RT}\right)$$

$$E_{\text{Yb|Sc}} = E^{\ominus}_{\text{Yb|Sc}} - \frac{RT}{3F}\ln\frac{a_{\text{Sc}^{3+}}}{a_{\text{Yb}^{3+}}} < 0, \quad \text{or} \quad \frac{a_{\text{Sc}^{3+}}}{a_{\text{Yb}^{3+}}} > \exp\left(\frac{3FE^{\ominus}_{\text{Yb|Sc}}}{RT}\right)$$

Combining these two conditions, we find

$$\frac{a_{\text{Yb}^{3+}}}{a_{\text{Eu}^{3+}}} < \exp\left(\frac{3FE^{\ominus}_{\text{Eu|Sc}}}{RT} - \frac{3FE^{\ominus}_{\text{Yb|Sc}}}{RT}\right) = \exp\left(\frac{3FE^{\ominus}_{\text{Eu|Yb}}}{RT}\right).$$

The standard potentials of the half reactions are:

$$E_{\text{Eu|Yb}} = -1.991 - (-2.19) = +0.20 \text{ V},$$

so the condition becomes

$$\frac{a_{\text{Yb}^{3+}}}{a_{\text{Eu}^{3+}}} < \exp\left(\frac{3 \cdot 96485 \cdot 0.20}{8.3145 \cdot 298}\right) = 1.4 \cdot 10^{10}.$$

Exercise B7

a) There are n amino acids and thus $(n-1)$ peptide bonds in the polypeptide chain. Every peptide bond has two rotational degrees of freedom, the torsion angles ϕ and ψ, which each have three positions so there are $3^2 = 9$ torsional states per peptide bond (see figure 4).
Thus for the n peptides of the entire molecule there are $N_c = 3^{2(n-1)} = 9^{(n-1)}$ conformations.
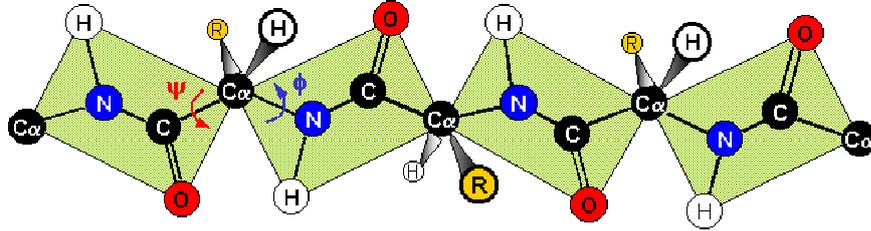
Figure 4: Completely unfolded polypeptide chain; ϕ and ψ each have 3 preferred states.

b) $\Delta S = k \ln W_u - k \ln W_n$, in which the number of conformations is $W_n = 1$ for the folded (native) state, whereas part a) shows that $W_u = N_c = 3^{2(n-1)}$ for all unfolded states. With this we find $\Delta S = k \ln 3^{2(n-1)} - k \ln 1 = k \ln 3^{2 \cdot 99} - 0 = 2 \cdot 99 k \ln 3 = 218k = 3.0 \cdot 10^{-21}$ J/K. This is the entropy per molecule. The molar entropy thus becomes $\Delta S_m = N_A \Delta S = 1.8$ kJ/mol K.

c) The torsional degrees of freedom in an ethane molecule result in an entropy gain per mol ethane of $\Delta S = N_A k \ln 3 = R \ln 3 = 9.1$ J/mol K.

d) The conformational torsional entropy per group in the molecule for the polypeptide molecule is $\frac{\Delta S}{100} = 18$ J/mol K, which is twice as much as for the ethane molecule. The factor two is a consequence of the number of torsion angles (ϕ and ψ). The huge difference between the two cases of part b) and c) is the result of the large difference in possible molecular conformations.

Exercise B8

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)

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

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, $PV = NkT$,

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

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

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

This is exactly the same result as found in Lecture 7.
If we would have considered the atoms of the gas to be distinguishable, we would have found

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

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

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

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

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

Exercise B9

a) There are three relevant reaction equations according to

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{1}$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{2}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \tag{3}$$

b) We determine the thermodynamic equilibrium constants for the equations using $RT\ln K_i = -\Delta_{r_i}G^{\ominus}$ ($i = 1, 2, 3$). We calculate $\Delta_r G_i^{\ominus}$ using the data from Atkins' tables for $\Delta_f G_j^{\ominus}$, where j denotes the components of reaction i. This results in the following table ($T = 298.15$ K).

Component	H_2CO_3(aq)	CO_2(aq)	H_2O(l)	H^+(aq)	HCO_3^-(aq)	CO_3^{2-}(aq)
$\Delta_f G_j^{\ominus}$ (kJ/mol)	-623.08	-385.98	-237.13	0	-586.77	-527.81

Reaction	1	2	3
$\Delta_r G^{\ominus}$ (kJ/mol)	0.03	36.31	58.96
K	0.988	$4.31 \cdot 10^{-7}$	$4.68 \cdot 10^{-11}$

c) $\alpha_{CO_2} = \frac{n_{CO_2}}{n_C}$, etc, where n_C is the total amount of carbon containing components ($n_C = n_{CO_2} + n_{H_2CO_3} + n_{HCO_3^-} + n_{CO_3^{2-}}$). Conservation of carbon massa implies that

$$\alpha_{CO_2} + \alpha_{H_2CO_3} + \alpha_{HCO_3^-} + \alpha_{CO_3^{2-}} = 1.$$

From the definition of the thermodynamic equilibrium constant we find (assume that the activities of the carbon containing components can be approximated by the mole fractions ($a_i = \gamma_i x_i \approx x_i =$

$\frac{n_i}{n_{tot}}$)):

Reaction (1): $a_{H_2CO_3} = K_1 a_{CO_2}$, or $\alpha_{H_2CO_3} \frac{n_C}{n_{tot}} = K_1 \alpha_{CO_2} \frac{n_C}{n_{tot}}$, so $\alpha_{H_2CO_3} = K_1 \alpha_{CO_2}$.

Reaction (2): $a_{HCO_3^-} = K_2 a_{H_2CO_3}/a_{H^+}$, ofwel $\alpha_{HCO_3^-} = K_2 \alpha_{H_2CO_3}/a_{H^+}$.

Reaction (3): $a_{CO_3^{2-}} = K_3 a_{HCO_3^-}/a_{H^+}$, or $\alpha_{CO_3^{2-}} = K_3 \alpha_{HCO_3^-}/a_{H^+}$.

Substituting these results we find α_{CO_2} van CO_2:

$$\alpha_{CO_2} = \frac{1}{1 + K_1 + \frac{K_1 K_2}{a_{H^+}} + \frac{K_1 K_2 K_3}{a_{H^+}^2}}.$$

Because the pH is defined as pH = $-^{10}$log a_{H^+} we can plot the fraction as function of the pH. The result is given in figure 5; the values are not exactly the same as the ones we found.
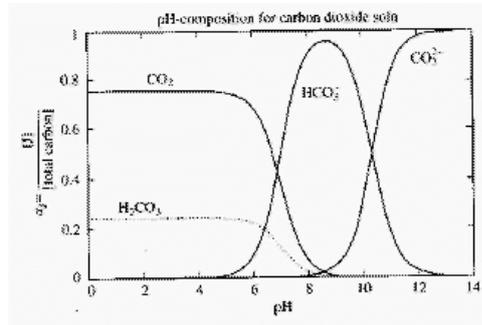

Figure 5: α_{CO_2} as a function of pH for the relevant components.

For pH = 7.4 we find $\alpha_{CO_2} = 0.0789$. The other fractions we can find using the relations between the activities and the equilibrium constants given above:

α_{CO_2}	$\alpha_{H_2CO_3}$	$\alpha_{HCO_3^-}$	$\alpha_{CO_3^{2-}}$
0.0789	0.0780	0.861	0.00103

d) We use the Henry constant of CO_2 and its vapour pressure in the atmosphere to determine the mole fraction x_{CO_2} in the oceans.

$$x_{CO_2} = \frac{P_{CO_2}}{K_{CO_2}} = \frac{3.3 \cdot 10^{-4} \text{ atm}}{1.25 \cdot 10^6 \text{ Torr}} \frac{760 \text{ Torr}}{1 \text{ atm}} = 2.006 \cdot 10^{-7}.$$

This mol fraction we can rewrite in terms of α_{CO_2} and the total amount of carbon containing components n_C:

$$x_{CO_2} = \frac{n_{CO_2}}{n_{tot}} \approx \frac{n_{CO_2}}{n_{H_2O}} = \frac{\alpha_{CO_2} n_C}{n_{H_2O}}.$$

$n_{H_2O} = [H_2O]V_{oceanen} = (1 \text{ g/cm}^3)(1 \text{ mol/18 g})(1.37 \cdot 10^{18} \text{ m}^3) = 7.61 \cdot 10^{22}$ mol, with the following result

$$n_C = \frac{x_{CO_2} n_{H_2O}}{\alpha_{CO_2}} = \frac{2.006 \cdot 10^{-7} \cdot 7.61 \cdot 10^{22}}{0.0789} = 1.9 \cdot 10^{17} \text{ mol}.$$