Additional tutorial B, Thermodynamics 2, 2025/2026

Exercise B1

We consider a binary $s-l$ phase diagram.
In exercise 18 we saw an example of a eutectic phase diagram for which the solid phase was decomposed into two pure solids, which did not form a solid solution for any mole fraction.
In many cases, however, the two components can form a so-called compound phase with the composition A_yB_z. An example is KCl·$FeCl_2$, rather denoted as $KFeCl_3$, in the KCl-$FeCl_2$ phase diagram.
Other well-known and important compounds, in the Fe-O phase diagram, are Fe_2O_3 and Fe_3O_4.
In some cases such compounds melt *incongruently* as we have seen in the lectures. In the SiO_2-CaO phase diagram the compound 3CaO·2SiO_2, e.g., melts incongruently into the solid phase Ca_2SiO_4 and a liquid phase composed of $Ca_3Si_2O_7$ and Ca_2SiO_4.
In case a solid compound phase melts into a liquid phase with the same composition it is said to show *congruent* melting. A pure compound therefore melts always congruently.

a) In fgure 1 the phase diagram of Mg-Pb is sketched in a simplified fashion, showing the case of a congruently melting conpound Mg_2Pb.
Indicate all phases in the diagram and hatch areas appropriately.

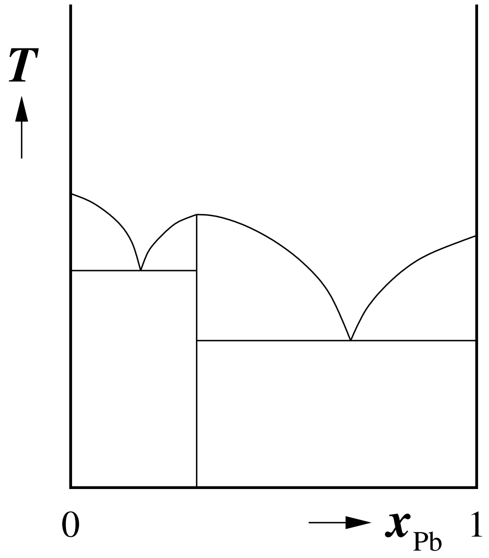

Figure 1: The phase diagram of Mg-Pb

Next we consider the KCl - $FeCl_2$ phase diagram. Use the following data:
$FeCl_2$ ($T_{fus} = 677$ °C) and KCl ($T_{fus} = 776$ °C) form the compounds $KFeCl_3$ and K_2FeCl_4.
$KFeCl_3$ melts congruently at 399 °C and K_2FeCl_4 melts incongruently at 380 °C.
Eutectica are present at ($x_{\text{FeCl}_2} = 0.38$, 351 °C) and ($x_{\text{FeCl}_2} = 0.54$, 393 °C).
The melting curve (liquidus) of KCl intersects the K_2FeCl_4 curve for $x_{\text{FeCl}_2} = 0.34$.
In the solid phase KCl and K_2FeCl_4 are mutually in equilibrium for $x_{\text{FeCl}_2} \leq 0.33$, while $KFeCl_3$ and $FeCl_2$ are mutually in equilibrium for $x_{\text{FeCl}_2} \geq 0.50$.

b) Sketch the phase diagram, indicate all phases in the diagram and hatch areas appropriately.

c) Discuss what happens and which phases are in equilibrium on cooling a melt with composition $x_{\text{FeCl}_2} = 0.36$, starting at 500 °C down to 300 °C.

Exercise B2

To get an impression of the complexity of the pressure dependence of the chemical potential of a pure non-perfect gas we consider the case of a real gas for which the equation of state is expressed as deviating from the perfect gas case in terms of so-called virial coefficients according to

$$P = \frac{nRT}{V}\left[1 + \frac{nB(T)}{V} + \frac{n^2C(T)}{V^2} + \cdots\right],$$

where the virial coefficients $B(T), C(T), \cdots$ are only dependent on the temperature.

a) First determine the chemical potential as a function of the pressure for a single component (so pure) system by writing the characteristic equation for the Gibbs free energy of an open system for a single component.

b) Find a Maxwell relation between μ, P, V and n.
Give an interpretation for both coefficients in this Maxwell relation.

c) Integrate this Maxwell relation between P_1 en P_2 for a *perfect* gas leading to the dependence $\mu(P)$, which we are seeking. Integration is always exacct up to a constant with a value depending on a boundary condition.
Choose as boundary condition the lower value of the integration and choose it to be equal to $P^{\ominus} = 1$ bar.

d) Then determine $\mu(P)$ with respect to the reference value $\mu^{\ominus}$ for the non-perfect gas up to the first virial coefficient, that is, neglect $C(T)$. Work out the result as far as possible.

Exercise B3

Consider, at $T = 298$ K, the reaction

$$\mathrm{Zn(s)} + \mathrm{CuSO_4(aq)} \leftrightharpoons \mathrm{ZnSO_4(aq)} + \mathrm{Cu(s)}.$$

Some relevant data are given in the table below for a temperature of $T = 298$ K.

	$\Delta_f H^{\ominus}$(kJ/mol)	$\Delta_f S^{\ominus}$(J/molK)	$\Delta_f G^{\ominus}$(kJ/mol)	$E^{\ominus}$(V)
Cu^{2+}(aq)	64.77		65.49	
Zn^{2+}(aq)	-153.89	-22.92		
SO_4^{2-}(aq)	-909.27		-744.53	
Cu^{2+}(aq)/Cu				+0.34

a) Calculate the standard reaction enthalpy $\Delta_r H^{\ominus}$ for the reaction.

b) Calculate the standard reaction Gibbs free energy $\Delta_r G^{\ominus}$ for the reaction.

c) Use the latter result to show that the standard electrochemical potential of the redox couple Zn^{2+}/Zn is equal to $E^{\ominus}(Zn^{2+}/Zn)$ = -0.76 V.

d) Verify that the same result can be found by using $\Delta_r G^{\ominus}$ for the reaction

$$\mathrm{Zn^{2+}} + 2e^- \leftrightharpoons \mathrm{Zn(s)}.$$

Exercise B4

Lead-acid batteries are used in cars and have the following half reactions ($T = 298$ K)

$$\mathrm{PbSO_4}(s) + \mathrm{H_3O^+}(aq) + 2e^- \leftrightarrow \mathrm{Pb}(s) + \mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \quad \text{with} \quad E^{\ominus} = -0.356 \text{ V}$$

$$\mathrm{PbO_2}(s) + 3\mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq) + 2e^- \leftrightarrow \mathrm{PbSO_4}(s) + 5\mathrm{H_2O}(l) \quad \text{with} \quad E^{\ominus} = 1.685 \text{ V}$$

A car battery has six of those half cell combinations in series. When it is charged, the terminal voltage is $E = 12.65$ V at a pH of 1.00.
The EMF changes by -0.022 V/K upon increasing the temperature.

a) Calculate the maximum work per mole of converted lead for the charged sextuple battery at 298 K.

b) Calculate the entropy change per mole of converted lead for the charged sextuple battery at 298 K.

c) Calculate the activity of $\mathrm{HSO_4^-}(aq)$ in the cells of the charged sextuple battery.

d) Use the Debye Hückel limiting law to estimate the molality of $\mathrm{H_3O^+}(aq)$ in the cells of the charged sextuple battery and discuss whether the result is reasonable.

Exercise B5

We consider the reaction 2Ag(s) + $\mathrm{Hg_2Cl_2}$(s) → 2Hg(l) + 2AgCl(s).
At 27 °C and 1 bar the change in enthalpy is 11.08 kJ/mol.
Th cahnge in volume during the reaction can be considered as negligible.
An electrochemical cell, which delivers a current according to the same reaction has an ElectroMotive Force (EMF) of 0.046 V at the given temperature and pressure.
Calculate for these conditions

a) The heat produced by the cell in case the current is delivered reversibly; what is the system and what are the surroundings of your choice?

b) The heat produced if the reaction would proceed in a mixture of silver and calomel, making up the system, at an external pressure $P_{ext.} = 1$ bar.

c) The change in Gibbs free energy for the cases a) and b).

d) The temperature coefficient at constant pressure and charge $\left(\frac{\partial E}{\partial T}\right)_{P,q}$ of the EMF of the cell.

Exercise B6

If we consider the series of lanthanides, europium has the least negative reduction standard electrochemical potential ($E^{\ominus} = -1.991$ V) of the $\mathrm{M^{3+}/M}$ couples in strong acids (pH = 0.000), followed by ytterbium with $E^{\ominus} = -2.19$ V.

a) What are the criteria for a reductor in a strong acid (pH = 0.000), at standard conditions to have only europium being precipitated as a metal for any lanthanide? Find such a reductor in the data section of Atkins.

b) Determine for non-standard conditions the relation between the activities of the europium en ytterbium ions to have only europium being precipitated as a metal for the choice of the reductor of part a).

Exercise B7

Given is a polypeptide with n amino acids.
We estimate the conformational entropy of a completely unfolded polypeptide compared to that in completely folded state. We assume that the difference is only determined by the difference in torsional degrees of freedom.
In unfolded state the peptide groups can rotate around the N-C$_\alpha$ and the C$_\alpha$-CO bond axes, namely over the two angles ϕ and ψ, respectively. These rotations each have three positions in which the torsion energy is minimal, therefore these three torsion angles occur often. For the conformations of the polypeptide molecule we limit ourselves to those torsion positions (see figure 2).

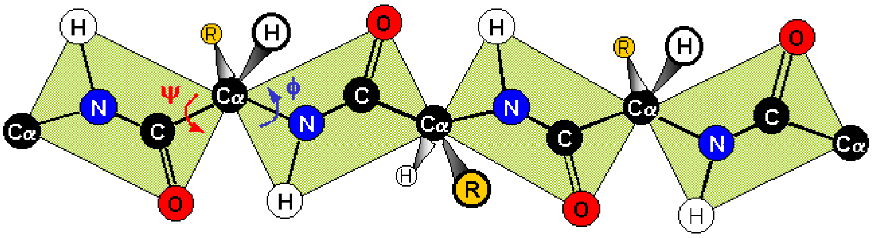

Figure 2: Completely unfolded polypeptide chain. The torsion angles ϕ and ψ each have 3 preferred states.

In the folded state there is one torsion position for both ϕ and ψ.

a) Determine the number of possible conformations N of the polypeptide molecule in the unfolded state.

b) Use the Boltmann definition of the entropy to calculate the molar entropy difference ΔS between all possible unfolded states on one hand and the completely folded state on the other hand for a polypeptide with $n = 100$ amino acids.

c) Make a similar estimation of the entropy as a consequence of the torsion freedom in an ethane molecule, again assuming that three torsion positions can be occupied.

d) How can you reconcile the results of parts b) and c)?

Exercise B8

In statistical thermodynamics the indistinguishability character of the particles in a system plays an important role, not for the internal energy or the enthalpy, but for the entropy and therefore also for the free energy. A perfect gas is a good example of a system, in which the particles are indistinguishable. In a crystal, however, the particles are distinguishable, because they are located at fixed positions.
We will consider the effect of the indistinguishability of atoms for a perfect gas. To that end, we use the so-called Sackur-Tetrode equation, that is based on quantum mechanics

$$S_{indistinguishable} = Nk \ln\left[\frac{kT}{P\Lambda^3}\mathrm{e}^{\frac{5}{2}}\right] \quad \text{with} \quad \Lambda = \frac{h}{\sqrt{2\pi m k T}},$$

and describes the entropy of a perfect atomic gas. In this expression m is the mass of the atoms, h is Planck's constant, $\mathrm{e} = \exp(1)$ and the other symbols have their usual meaning. If the indistinguishability character of the atoms would not be taken into account, this equation would have the following form.

$$S_{distinguishable} = Nk \ln \left[\frac{NkT}{P\Lambda^3} e^{\frac{3}{2}} \right] \quad \text{with} \quad \Lambda = \frac{h}{\sqrt{2\pi mkT}},$$

a) Discuss, without using formulas, whether the indistinguishability character of the atoms results in a larger or a smaller entropy.

b) Calculate the entropy of 1 mol helium at $T = 298$ K and $P = P^{\ominus}$.

c) Calculate the difference $S_{indistinguishable} - S_{distinguishable}$, and compare the answer with the result of part a).

d) In Lecture 7 we found that for the isothermal expansion of n mol of a perfect mono-atomic gas from a volume V_1 to a volume $V_2 = 2V_1$, the entropy change is equal to $\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln 2$. Verify whether the same result is found with the Sackur-Tetrode equation; do this for both the distinguishable and the indistinguishable case.

Exercise B9

The oceans play an important role in the reduction of greenhouse gasses because they can dissolve huge amounts of CO_2 gas. We make an estimate of the maximal amount of carbon the oceans can dissolve in an equilibrium situation.

a) Find the three relevant chamical equilibrium reactions for the absorption of CO_2 in water.

b) Use the data given below (from the data section of Atkins) to find the equilibrium constants of these reactions

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

c) Define α_i as the mole fraction of the carbon containing component i as fraction of the total of carbon containing components.
Find an expression for the conservation of carbon mass for the three reactions in terms of α_i and use this expression to determine the fraction α_{CO_2} of CO_2 as function of the pH; assume that the activities of the various components can be approximated by their mole fractions.
Use this to calculate α_i for all carbon containing components at pH = 7.4.

d) Use the result of the former part c) to find the total amount of carbon containing components, assuming that the solution behaves as ideal. Use for that the Henry constant of CO_2 in water at $T = 298K$: $K_{CO_2} = 1.25 \cdot 10^6$ Torr and the concentration of CO_2 in the air, which amounts to merely 0.033 %, to find the mole fraction x_{CO_2}. The total volume of the oceans is $V_{\text{oceans}} = 1.37 \cdot 10^{18}$ m^3.