

Answers Additional Tutorial B, Thermodynamics 2, 2023/2024

Exercise B1

- a) The phase diagram is outlined in figure 1.

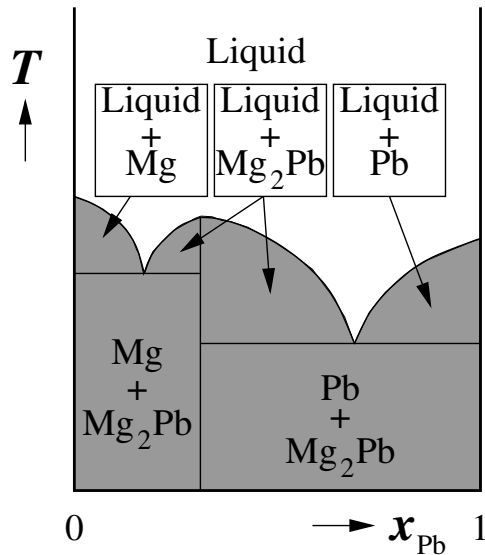


Figure 1: The Mg-Pb phase diagram.

- 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_2FeCl_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 $\text{K}_2\text{FeCl}_4(\text{s})$ 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 $\text{K}_2\text{FeCl}_4(\text{s})$ and $\text{KFeCl}_3(\text{s})$.

Exercise B2

- a) There is no other work than volume work ($dW' = 0$), so the change in Gibbs free energy can be written as

$$dG = VdP - SdT + \mu dn.$$
- 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.

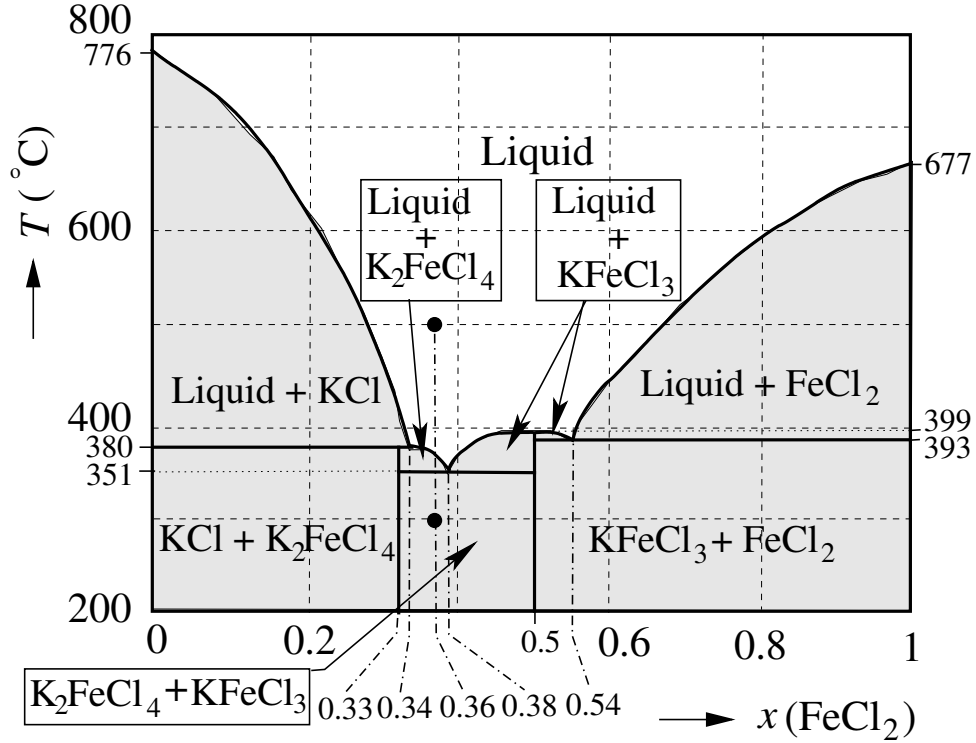


Figure 2: The KCl-FeCl₂ phase diagram.

$\left(\frac{\partial V}{\partial n}\right)_{P,T} = \bar{V}$, 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 $(d\mu)_{T,n} = \left(\frac{RT}{P} dP\right)_{T,n}$

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

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

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

Note that $\ln x$ has only meaning for x having no units, so for a scalar. Therefore P has to be interpreted as $\frac{P}{1 \text{ bar}}$ 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

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

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

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

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

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

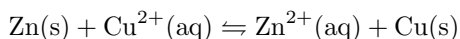
This is a tough integral to solve, but Maple helps us out. The primitive of the integrand turns out to be:

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

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 $\mu^\ominus = -394.36 \text{ kJ/mol}$. Furthermore 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



- 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 $\Delta_{fus} H$.

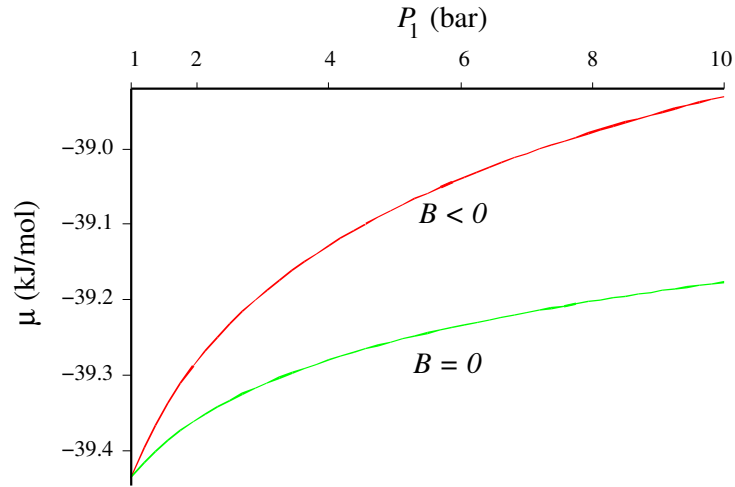


Figure 3: The chemical potential as a function of P for the non-perfect gas CO_2 , for which $B(273 \text{ K}) = -142 \text{ cm}^3/\text{mol}$ and $\mu^\ominus = -394.36 \text{ kJ/mol}$.

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

$$\Delta_r G^\ominus = (-147.06 - 65.49) = -212.55 \text{ kJ/mol}.$$

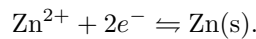
c) We find the standard electrochemical potential for the whole reaction using

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

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



we have

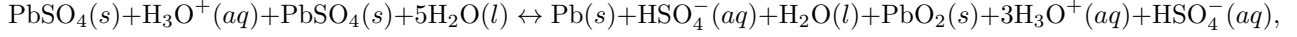
$$\Delta_r G^\ominus = \Delta_f G^\ominus(\text{Zn(s)}) - \Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) = -\Delta_f G^\ominus(\text{Zn}^{2+}, \text{aq}) = 147.06 \text{ kJ/mol},$$

resulting in the same value as found before:

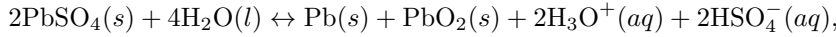
$$E^\ominus(\text{Zn}^{2+}/\text{Zn}) = -\frac{\Delta_r G^\ominus}{\nu F} = -\frac{147.06 \cdot 10^3}{2 \cdot 96458.3} = -0.76 \text{ V}.$$

Exercise B4

The overall reaction of the two half reactions is



which simplified becomes



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 $E_{batt.}^\ominus = 6 \cdot (-2.041) = -12.25$ V for the battery at a temperature of 298 K.

$E_{batt.}^\ominus < 0$, 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.

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

- 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 ($(\frac{\partial E}{\partial T})_{q,P} = +0.022$ 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

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

so

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

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)

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

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

$$a_{\text{H}_3\text{O}^+} = b \cdot 10^{-0.509 \cdot b^{\frac{1}{2}}} \quad \text{and} \quad a_{\text{HSO}_4^-} = b \cdot 10^{-0.509 \cdot b^{\frac{1}{2}}}.$$

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

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

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 $b \approx 3 \text{ mol/kg}$ 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 $b \leq 0.01 \text{ mol/kg}$).

If we are to trust the theory for a value of $b = 0.01 \text{ mol/kg}$, the left part becomes $9 \cdot 10^{-3}$. If we use this value, we find a corresponding terminal voltage of $E = E^\ominus + 0.243 = -1.798 \text{ V}$, so for the whole battery $6 \cdot (-1.798) = -10.8 \text{ V}$. 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 $W_e = E\Delta q = -E\nu F = -0.046 \cdot 2 \cdot 9.6485 \cdot 10^4 = -8.88 \text{ kJ/mol}$, so the heat is $Q^{rev} = 11.08 - (-8.88) = 19.96 \text{ kJ/mol}$. 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:

$$Q_{produced}^{rev} = -19.96 \text{ kJ/mol}.$$

- 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 can 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 $\Delta H = 11.08 \text{ kJ/mol}$. The pressure is constant and equal to $P_{ext.} = 1 \text{ bar}$, so still $dP = 0$ and the change in enthalpy is equal to the irreversible reaction heat in the system, $Q = 11.08 \text{ kJ/mol}$, 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:

$$Q_{produced}^{irr} = -11.08 \text{ kJ/mol}.$$

- c) For the Gibbs energy we have $dG = VdP - SdT + Edq = VdP - SdT + \sum_i \mu_i dn_i$.
 So $\Delta G_{P,T} = E\Delta q = -0.046 \cdot 2 \cdot 9.6485 \cdot 10^4 = -8.88 \text{ kJ/mol}$.
 G is a state function, so also independent of the cell situation or the mixture.
 In both cases $\Delta G = -8.88 \text{ kJ/mol}$.
- 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 $dG = VdP - SdT + Edq$.
 At constant pressure this becomes $dG = -SdT + Edq$. 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
 $\left(\frac{\partial E}{\partial T}\right)_{P,q} = -\frac{1}{T} \left(\frac{\partial Q^{rev}}{\partial q}\right)_{P,T} = -\frac{1}{300} \frac{19.90 \cdot 10^3}{-2.9.6485 \cdot 10^4} = 3.43 \cdot 10^{-4} \text{ V/K}$.
 $\left(\frac{\partial E}{\partial T}\right)_{P,q} = 3.43 \cdot 10^{-4} \text{ V/K}$.

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 $-1.991 \text{ V} < E^\ominus < -2.19 \text{ V}$.
 The data section of Atkins shows that scandium ($E^\ominus(\text{Sc}^{3+}/\text{Sc}) = -2.09 \text{ V}$) is possible candidate.
- b) To have only Eu precipitated spontaneously we need to have

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

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

We use the Nernst equation to find the potentials:

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

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

Combining these two conditions, we find

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

The standard potentials of the half reactions are:

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

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 three relevant reaction equations according to



- b) We determine the thermodynamic equilibrium constants for the equations using $RT \ln K_i = -\Delta_r G_i^\ominus$ ($i = 1, 2, 3$). 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 ($T = 298.15 \text{ K}$).

Component	H ₂ CO ₃ (aq)	CO ₂ (aq)	H ₂ O(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) $\alpha_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_C}$, etc, where n_C is the total amount of carbon containing components ($n_C = n_{\text{CO}_2} + n_{\text{H}_2\text{CO}_3} + n_{\text{HCO}_3^-} + n_{\text{CO}_3^{2-}}$). Conservation of carbon massa implies that

$$\alpha_{\text{CO}_2} + \alpha_{\text{H}_2\text{CO}_3} + \alpha_{\text{HCO}_3^-} + \alpha_{\text{CO}_3^{2-}} = 1.$$

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 ($a_i = \gamma_i x_i \approx x_i = \frac{n_i}{n_{\text{tot}}}$)):

Reaction (1): $a_{\text{H}_2\text{CO}_3} = K_1 a_{\text{CO}_2}$, or $\alpha_{\text{H}_2\text{CO}_3} \frac{n_C}{n_{\text{tot}}} = K_1 \alpha_{\text{CO}_2} \frac{n_C}{n_{\text{tot}}}$, so $\alpha_{\text{H}_2\text{CO}_3} = K_1 \alpha_{\text{CO}_2}$.

Reaction (2): $a_{\text{HCO}_3^-} = K_2 a_{\text{H}_2\text{CO}_3} / a_{\text{H}^+}$, or $\alpha_{\text{HCO}_3^-} = K_2 \alpha_{\text{H}_2\text{CO}_3} / \alpha_{\text{H}^+}$.

Reaction (3): $a_{\text{CO}_3^{2-}} = K_3 a_{\text{HCO}_3^-} / a_{\text{H}^+}$, or $\alpha_{\text{CO}_3^{2-}} = K_3 \alpha_{\text{HCO}_3^-} / \alpha_{\text{H}^+}$.

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

$$\alpha_{\text{CO}_2} = \frac{1}{1 + K_1 + \frac{K_1 K_2}{\alpha_{\text{H}^+}} + \frac{K_1 K_2 K_3}{\alpha_{\text{H}^+}^2}}.$$

Because the pH is defined as $\text{pH} = -\log a_{\text{H}^+}$ we can plot the fraction as function of the pH. The result is given in figure 4; the values are not exactly the same as the ones we found.

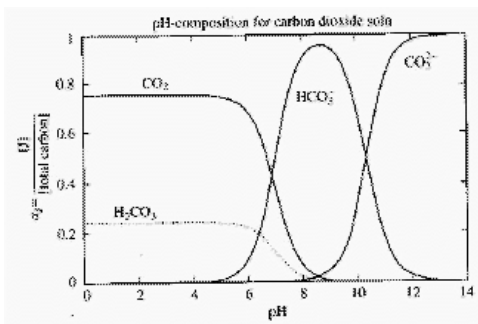


Figure 4: α_{CO_2} as a function of pH for the relevant components.

For $\text{pH} = 7.4$ we find $\alpha_{\text{CO}_2} = 0.0789$. The other fractions we can find using the relations between the activities and the equilibrium constants given above:

α_{CO_2}	$\alpha_{\text{H}_2\text{CO}_3}$	$\alpha_{\text{HCO}_3^-}$	$\alpha_{\text{CO}_3^{2-}}$
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.

$$x_{\text{CO}_2} = \frac{P_{\text{CO}_2}}{K_{\text{CO}_2}} = \frac{3.3 \cdot 10^{-4} \text{ atm}}{1.25 \cdot 10^6 \text{ Torr}} \frac{760 \text{ Torr}}{1 \text{ atm}} = 2.006 \cdot 10^{-7}.$$

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

$$x_{\text{CO}_2} = \frac{n_{\text{CO}_2}}{n_{\text{tot}}} \approx \frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}}} = \frac{\alpha_{\text{CO}_2} n_C}{n_{\text{H}_2\text{O}}}.$$

$n_{\text{H}_2\text{O}} = [\text{H}_2\text{O}]V_{\text{oceanen}} = (1 \text{ g/cm}^3)(1 \text{ mol/18 g})(1.37 \cdot 10^{18} \text{ m}^3) = 7.61 \cdot 10^{22} \text{ mol}$,
with the following result

$$n_C = \frac{x_{\text{CO}_2} n_{\text{H}_2\text{O}}}{\alpha_{\text{CO}_2}} = \frac{2.006 \cdot 10^{-7} \cdot 7.61 \cdot 10^{22}}{0.0789} = 1.9 \cdot 10^{17} \text{ mol}.$$