Answers Tutorials 7 Thermodynamics 2, 2023/2024

Exercise 26

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

For a dissolved salt M_pX_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

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

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

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

The largest contribution thus comes from the $FeCl_3$, which has a lower molality but larger charges.

Exercise 27

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 $(A = 0.509 \text{ at } 298.15 \text{ K})$

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

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

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

$$\frac{s}{b^\ominus} = \frac{\sqrt{K}}{\gamma_\pm} = \frac{\sqrt{1.61 \cdot 10^{-10}}}{0.9132} = 1.39 \cdot 10^{-5}, \quad \text{so} \quad s = 1.39 \cdot 10^{-5} \text{ mol/kg}$$
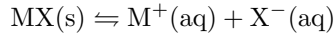
e) Using the equilibrium constant of part a) and the new solubility from part d) we find:

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

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

Exercise 28

The chemical equation for the dissolution of a 1:1 salt MX is

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

Due to the low concentration of a poorly soluble salt we can approximate the mean activity constant of the ions ($\gamma_\pm^2 = \gamma_{M^+}\gamma_{X^-}$) using the Debye-Hückel limiting law:

$$\log \gamma_\pm = -|z_+ z_-| A I^{\frac{1}{2}},$$

in which $z_+ = |z_-| = 1$, $A = 0.509$ and the ionic strength of the solution is $I = \frac{1}{2}\sum_i z_i^2 \frac{b_i}{b^\ominus} = \frac{1}{2}\left(\frac{b_{M^+}}{b^\ominus} + \frac{b_{X^-}}{b^\ominus}\right)$.

For a 1:1 salt we have $b_{M^+} = b_{X^-} = s$ [mol/kg], so $I = s/b^\ominus$ and

$$\ln \gamma_\pm = \frac{{}^{10}\log \gamma_\pm}{{}^{10}\log e} = 2.303 \log \gamma_\pm = -2.303 \cdot 0.509 \sqrt{\frac{s}{b^\ominus}} = -1.172\sqrt{\frac{s}{b^\ominus}}, \quad \text{so} \quad \gamma_\pm = \exp\left(-1.172\sqrt{\frac{s}{b^\ominus}}\right).$$

The equilibrium constant is therefore ($a_{MX(s)} \approx 1$; $b^\ominus = 1$ mol/kg)

$$K_s = \frac{a_{M^+} a_{X^-}}{a_{MX(s)}} = a_{M^+} a_{X^-} = \gamma_{M^+}\frac{b_{M^+}}{b^\ominus}\gamma_{X^-}\frac{b_{X^-}}{b^\ominus} = \gamma_\pm^2 \frac{b_{M^+}}{b^\ominus}\frac{b_{X^-}}{b^\ominus} = \left(\frac{\gamma_\pm s}{b^\ominus}\right)^2,$$

which results in

$$s = \frac{\sqrt{K_s}}{\gamma_\pm}b^\ominus = \sqrt{K_s}\exp\left(1.172\sqrt{\frac{s}{b^\ominus}}\right)b^\ominus.$$

Exercise 29

For two energy states the partition function is

$$q = \sum_i \exp\left[-\beta\epsilon_i\right] = \exp\left[-\beta\epsilon_0\right] + \exp\left[-\beta\epsilon_1\right] = \exp\left[-\beta \cdot 0\right] + \exp\left[-\beta\epsilon_1\right] = 1 + \exp\left[-\beta\epsilon_1\right].$$

We could translate the question to 'at what temperature is the following equation valid':

$$p_1 \equiv \frac{n_1}{N} = \frac{\exp\left(-\beta\epsilon_1\right)}{q} = \frac{\exp\left(-\beta\epsilon_1\right)}{1 + \exp\left(-\beta\epsilon_1\right)} = 0.10,$$

or

$$10\exp\left(-\beta\epsilon_1\right) = 1 + \exp\left(-\beta\epsilon_1\right),$$

or

$$\exp\left(-\beta\epsilon_1\right) = \frac{1}{9}, \quad \text{and} \quad \beta = \frac{1}{kT} = -\frac{1}{\epsilon_1}\ln\left(\frac{1}{9}\right), \quad \text{and} \quad T = \frac{\epsilon_1}{k\ln(9)}.$$

We can calculate ϵ_1 using $\epsilon_1 = hc\nu$, with $\nu = 540$ cm^{-1} so

$$T = \frac{hc\nu}{k\ln(9)} = 352.6 \text{ K.}$$

Exercise 30

a) Since we set our lowest energy level to 0, also in a magnetic field, both energy levels are raised by $\frac{1}{2}\mu_B B$, so $\epsilon_0 = 0$ and $\epsilon_1 = \mu_B B$.

$$q = \sum_i \exp\left(-\frac{\epsilon_i}{kT}\right) = 1 + \exp\left(-\frac{\mu_B B}{kT}\right)$$

b) The Boltzmann distribution gives

$$n_i = N\frac{\exp\left(-\frac{\epsilon_i}{kT}\right)}{q} \quad (i = 0, 1),$$

so

$$n_0 = N\frac{1}{1 + \exp\left(-\frac{\mu_B B}{kT}\right)} \quad \text{and} \quad n_1 = N\frac{\exp\left(-\frac{\mu_B B}{kT}\right)}{1 + \exp\left(-\frac{\mu_B B}{kT}\right)}$$

In figure 1, $\frac{n_0}{N}$ and $\frac{n_1}{N}$ are plotted for a magnetic field of $B = 10$ Tesla We can see that occupancy of both levels for $T \to \infty$ goes to 0.5, and that all spins are in the ground state ($n_0(T = 0) = N$ and $n_1(T = 0) = 0$) for $T \to 0$ We can also see that the occupancy of the two states are $\frac{n_0}{N} = 0.731$ and $\frac{n_1}{N} = 0.269$ if $kT = \mu_B B$ (dotted line in the figure).
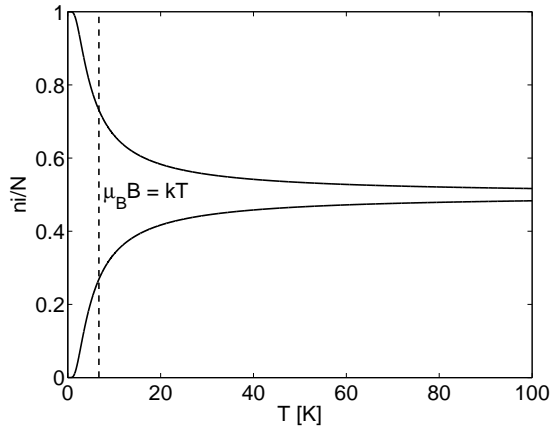

Figure 1: $\frac{n_0}{N}$ and $\frac{n_1}{N}$ for $B = 10$ Tesla

c) The average energy per electron due to the magnetic field is

$$< \epsilon > = \frac{1}{N}\sum_i \epsilon_i n_i = \frac{1}{N}(\epsilon_0 n_0 + \epsilon_1 n_1) = \frac{1}{N}\left(0 \cdot n_0 + \mu_B B N\frac{\exp\left(-\frac{\mu_B B}{kT}\right)}{1 + \exp\left(-\frac{\mu_B B}{kT}\right)}\right)$$

We have to correct for our earlier shift of $+\frac{1}{2}\mu_B B$, however, resulting in

$$< \epsilon > = \mu_B B\frac{\exp\left(-\frac{\mu_B B}{kT}\right)}{1 + \exp\left(-\frac{\mu_B B}{kT}\right)} - \frac{1}{2}\mu_B B.$$

The plot of $< \epsilon >$ has the same shape as the lower line in the graph (apart from the shift of $-\frac{1}{2}\mu_B B$) The effect of the magnetic field thus disappears for $T \to \infty$, because $< \epsilon > \to 0$ (for a finite value of the magnetic field).

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d) Before the 180° pulse we have

$$\frac{n_1}{n_0} = \frac{n_1}{N}\frac{N}{n_0} = \frac{\exp(-\beta\mu_B B)}{q}\frac{q}{1} = \exp(-\beta\mu_B B),$$

The distribution after the pulse is inverted, so we have

$$\left(\frac{n_1}{n_0}\right)' = \frac{n_0}{n_1} = [\exp(-\beta'\mu_B B)]^{-1} = \exp(+\beta\mu_B B)$$

which means $\beta' = -\beta$, corresponding to a negative temperature! This is a system out of equilibrium, which in time will spontaneously return to the original distribution, that is, to the equilibrium state with the positive temperature.