Excercises for an improved intuitive understanding

After working through these problems you should have developed a good overview of how partition constants can be applied to solve quantitative partition problems. But do you also have a good ´intuitive´ understanding of how partition systems respond to changes of one or several variables? If you change the volume of a phase or a partition constant then some of the system responses (like changes in equilibrium concentrations, mass fractions) are proportional to the changed variable while others are not. An example for a non-linear response is the fact that you will need 10 times more solvent to extract 99% of a chemical out of a water sample than if you wanted to extract only 90% (see problem Organic pollutants in water). The following exercise is intended to train your intuitive understanding of partition processes (corresponds to Box 3 in the script).

Exercise for a better understanding of the system response of a simple partition system:

Use sheet 1 of the Mehr-Phasensystem.xls to calculate the equilibrium state of 1 ng of a compound i in the following partition system: 1 ml air, 1 ml water and a $K_{i\,aw}$ of 0.1 [L_{water} / L_{air}]. Try to estimate (not calculate yet) how the concentrations of i and the mass fraction of i in both phases change if you change the system as follows:

What will happen if Henry's law constant is reduced by factor 10 in comparison to the initial situation?

Answer:

The mass distribution will be shifted even more towards the water phase. However, not too much of a change is possible because much of the compound is already in the water phase and more than 100% of the compound cannot go there. Therefore, water concentration can´t change very much (at the most it can increase to somewhat below 1 ng/L). As a consequence the air concentration must change by almost a factor 10 because otherwise the factor 10 change in the Henry´s Law constant would not come about. This, in turn, means that also the mass of the pollutant in air must be reduced by a factor 10. Consequently, the mass of the pollutant in water must now be close to 100%. Compare this with the exact solution to the problem (calculated with the spread sheet).

The above questions were quite abstract. A concrete application might look as follows: you have calculated the partitioning of compound i between air and aerosols by assuming an average value for the aerosol content of the air. The true aerosol content can vary by a factor 3-5 though depending on the location and whether conditions. Of course you can do the all the calculations again for another aerosol content but if your are listening to a presentation and you want to check the plausibility of the arguments or you are dealing with a much more complex problem of which the aerosol partitioning is just a small piece then it is very helpful if you can estimate the effect of such changes without much effort. This also helps if you want to check the results of a spreadsheet that you may have just set-up for doing partition calculations.
Often one also encounters the situation that the partition constants that one is using are subject to an uncertainty of a factor 3 -10 or even more (see chapter VI in the textbook). Then it is good to know how sensitive a given partition equilibrium will react on such uncertainties.

Box 3 in the script provides a general discussion of the response of a partition system to changes in the partition constant. You can access the program for creating the graphics in Box 3 here (Massenverteilung.xls) and recalculate them with different phase volumes if you wish.