C8862
Free Energy Calculations
exercise

2. Chemical Equilibrium

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Excercise I

1. Determine composition of reaction mixture at equilibrium, which is formed from mixing 500 ml solution of substance A with molar amount of n_A = 0.001 mol and 500 ml solution of substance B with molar amount n_B = 0.01 mol. The volume of the resulting mixture will be 1 L. The substances A and B react together to form C. The reaction is characterized by an equilibrium constant of $K = 10^6$. The volume of the reaction mixture does not change during the reaction. Consider the reaction mixture as an ideal solution at the standard conditions.

$$\mathbf{A + 2\,B \rightleftharpoons C}$$

2. Determine the change in Gibbs energy resulting from mixing of A and B from the task 1.

Excercise II

1. Substance A is titrated with substance B at 298 K. The starting concentration of substance A is $c_{0,A}$ = 4 mM and the concentration does not change during titration. Determine the equilibrium concentrations of A, B, C, and D as a function of $c_{0,B}/c_{0,A}$ in the range of 0 to 2 (i.e., up to twice of the molar equivalent). Consider the reaction mixture as an ideal solution.

$$A + B \rightleftharpoons C \qquad K_1 = 10^6$$

$$A + 2B \rightleftharpoons D \qquad K_2 = 10^6$$

2. Recalculate the equilibrium concentrations of A, C, and D to molar fractions of substance A as a function of $c_{0,B}/c_{0,A}$ in the range of 0 to 2 (i.e., up to twice of the molar equivalent).

Outline of Exercise II Solution

1. Write a set of equations that unambiguously describe the composition of the reaction mixture, which includes
   - relations for equilibrium constants
   - balance equations (take into account the law of mass conservation)
2. The number of equations must be the same (4) as the number of values to be determined (4).
3. Rewrite the equations to form

$$\mathbf{y} = f(\mathbf{x})$$

4. where **x** is the concentration of interest and **y** is a vector that reaches zero when at a solution of the system of equations.
5. The solution can be found using the fsolve method in octave.

$$f(\mathbf{x}) = \mathbf{0}$$

6. Count the titration again in the octave program using the cycle. Use the solution x from the previous step (previous value $c_{0,B}$) for the new value $c_{0,B}$. Store the resulting concentration and molar fraction values in a file.
7. Use gnuplot to view the result.