

## General association problem in one-component systems

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*Abstract: The general problem of homoassociation is solved. The resulting system of equations allows us to calculate the content of each associate in the solution by the value of the difference in Gibbs energies of the formation of this associate and monomer. It is also possible to calculate the Gibbs energies of the formation of all associates and monomer from the known shares of the association.*

**Keywords:** association, solutions, associates, monomers, Gibbs energy

Let us consider a dynamic system, consisting of a finite amount of particles (monomers) denoted by  $X$ . Let particles be able to connect in such a way that associates are formed (denoted by  $X_g$ ), consisting of  $g$  monomers, denoted by  $X$ . According to kinetic considerations, the formation of associates is a result of two-part interactions, expressed in form of the following scheme:



where  $g_{\max}$  is max possible associate divisibility,  $i$  and  $j$  are numbers, running through the values from 1 to ( $g_{\max} - 1$ ). Associates are also formed as a result of combined two-part interactions and mono partial decays, expressed in form of the following scheme:



Thus,  $g_{\max} - 1$  kinds of associates  $X_{i+1}$ . are present in dynamic equilibrium along with the monomer  $X$ . This equilibrium is characterized by the global minimum of the Gibbs free energy of the system.

Let us consider a system, formed by a unit quantity (1 mol) of monomers  $X$ . Let's denote the number of each associate divisibility  $g$  as  $x_g$ . Then, according to the material balance, the quantity of monomers  $X$  will be equal to

$$x_1 = 1 - \sum_{g=2}^{g_{\max}} g \cdot x_g. \quad (3)$$

The chemical potential of monomers and associates was calculated by the equation for ideal mixtures:

$$\mu_g = \mu_g^0 + RT \ln x'_g, \quad (4)$$

where  $x'_g$  is a mole fraction (relative quantity) of a monomer (associate) in the mixture.  $\mu_g^0$  is the chemical potential of the compound consisting of associates with their divisibility being  $g$  only.

$\mu_1^0$  – the chemical potential of the compound consisting of monomers only. As is known from the normalization requirements:

$$\sum_{g=1}^{g_{\max}} x'_g = 1. \quad (5)$$

Taking into the account that the total amount of particles in the system decreases upon reaching the equilibrium, the mole fractions of the monomer (associate) will have the following form:

$$x'_g = \frac{x_g}{1 - \sum_{g=2}^{g_{\max}} g \cdot x_g + \sum_{g=2}^{g_{\max}} x_g} = \frac{x_g}{x_1 + \sum_{g=2}^{g_{\max}} x_g}. \quad (6)$$

The Gibbs free energy of the system will be expressed as follows:

$$\Delta G = \sum_{g=1}^{g_{\max}} x_g \mu_g = \sum_{g=1}^{g_{\max}} x_g (\mu_g^0 + RT \ln x'_g). \quad (7)$$

A necessary condition for the presence of the global minimum  $\Delta G$  as a function  $g_{\max}-1$  of independent variables  $x_g$ , is the following equalities:

$$\frac{\partial \Delta G}{\partial x_g} = 0. \quad (8)$$

This leads to a  $g_{\max}-1$  system of nonlinear equations:

$$\frac{\Delta \mu_g^0}{RT} + \ln \frac{x_g \left( x_1 + \sum_{g=2}^{g_{\max}} x_g \right)^{g-1}}{x_1^g} = \frac{(g-1) \left( \sum_{g=2}^{g_{\max}} x_g - x_g \right)}{x_1 + \sum_{g=2}^{g_{\max}} x_g}. \quad (9)$$

$\Delta \mu_g^0$  – is the difference in chemical potentials.  $\Delta \mu_g^0 = \mu_g^0 - g \mu_1^0$ .

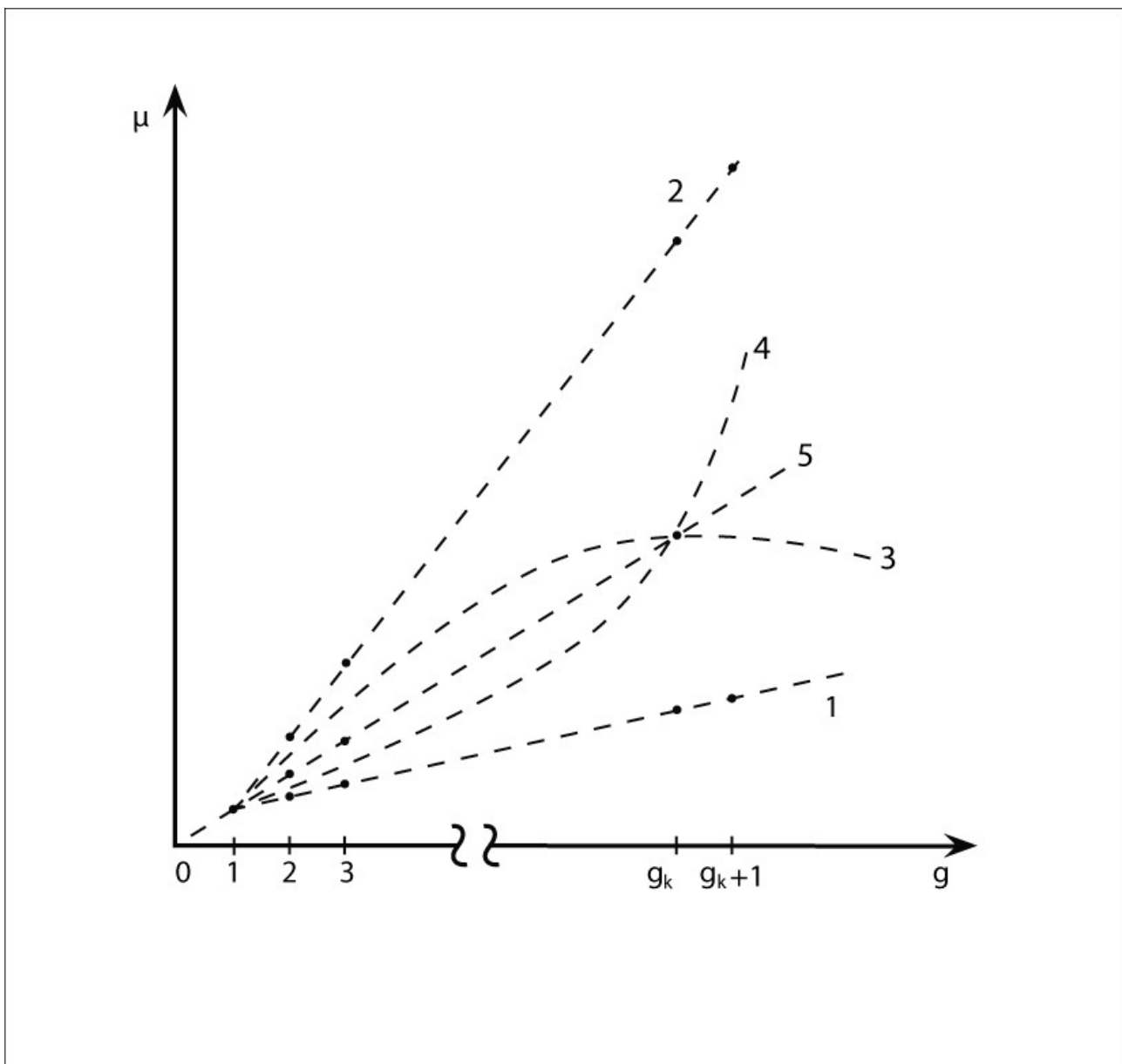
At  $g_{\max} = 2$ , that is, when only one kind of the equilibrium is possible in the system:



Which leads to the presence of a monomer and dimer particles only, we have one equation

$$\frac{\mu_2^0 - 2\mu_1^0}{RT} + \ln \frac{x(1-x)}{(1-2x)^2} = 0, \quad (11)$$

where  $x$  is the amount of dimer particles,  $1-2x$  is the amount of monomer in the equilibrium. This exactly corresponds with the law of the mass action in Sommerfeld's formulation [1], expressed by the formula for ideal mixtures.



**Pic. 1**

## Discussion of results

As practice shows, the associates formation has four types of patterns:

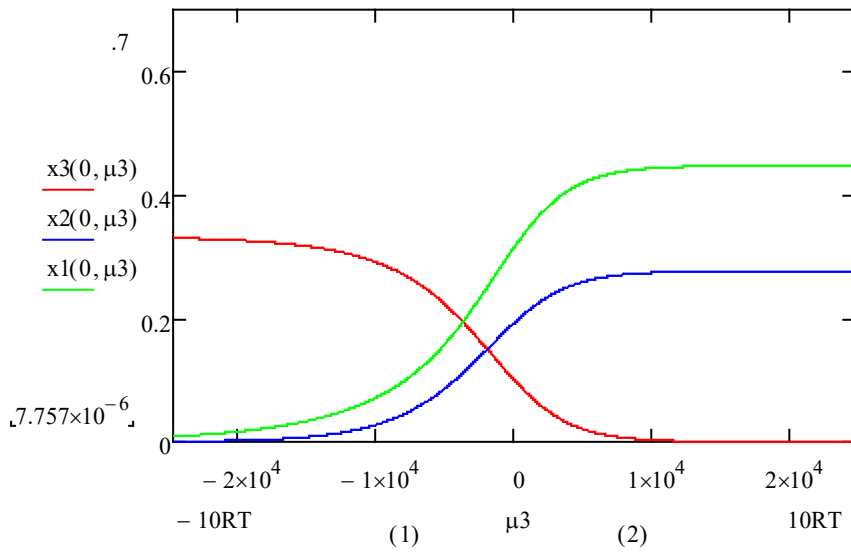
- 1) it is always energetically favorable:  $\Delta\mu_g < 0$  for all values of  $g \geq 2$ ;
- 2) it is always energetically unfavorable:  $\Delta\mu_g > 0$  for all values of  $g \geq 2$ ;
- 3) it is energetically favorable starting with the associate of a definite divisibility  $g_k$ :  
 $\Delta\mu_g > 0$  for  
 $2 \leq g \leq g_k - 1$  and  $\Delta\mu_g < 0$  for  $g \geq g_k$ ;
- 4) it is energetically unfavorable starting with the associate, having divisibility  $g_k$ :  
 $\Delta\mu_g < 0$  for  
 $2 \leq g \leq g_k - 1$  and  $\Delta\mu_g > 0$  for  $g \geq g_k$ .

On the basis of theoretical considerations, the fifth option can be considered when the associates' formation is energetically indifferent  $\Delta\mu_g = 0$  under all possible values of  $g$ . Graphically options (1) - (5) can be represented as follows in Pic. 1.

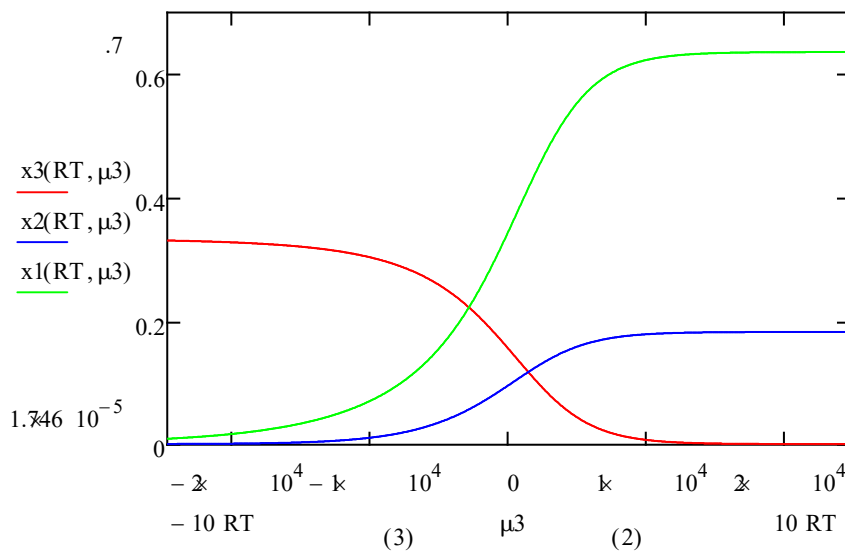
For the quantitative description of the above-mentioned dependence's, a system of two equations was solved numerically, using MATCAD method [2], which corresponds to the formation of dimer particles  $X_2$  and trimer particles  $X_3$  given the presence of monomer  $X$  in the system. According to (9), the system looks as follows:

$$\begin{aligned} \frac{\mu_2^0 - 2\mu_1^0}{RT} + \ln \frac{x_2(1-x-2x_3)}{(1-2x_2-3x_3)^2} &= \frac{x_3}{1-x-2x_3} \\ \frac{\mu_3^0 - 3\mu_1^0}{RT} + \ln \frac{x_3(1-x-2x_3)^2}{(1-2x_2-3x_3)^3} &= \frac{2x_2}{1-x-2x_3} \end{aligned} \quad (12)$$

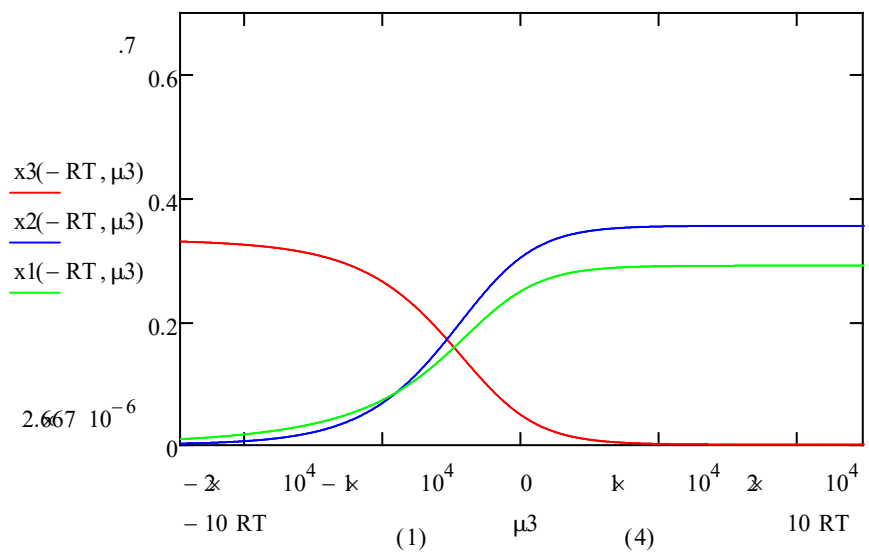
The ratio  $\frac{\Delta\mu_3^0}{RT}$  is determined in the range from  $-10$  up to  $+10$  under values of  $\frac{\Delta\mu_2^0}{RT}$  equal to  $\pm 1$  and  $0$ . The dependence of the amount of monomer and associates  $x_g$  on indicated ratio is expressed in Pictures 2-4.



**Pic. 2**



**Pic. 3**



**Pic. 4**

The solution of the inverse task on Association is of particular interest. It is known, that in addition to the state of the monomer, many liquids are in the state of molecule dimer, molecule trimer, etc. This has been experimentally proven using various methods and, in some cases, quantified. Further, using the values of the chemical potential of the pure solvent  $\Delta G$  and the amounts of monomers and associates  $x_g$ , using formulas (9), it is possible to find the values of  $\Delta\mu_g^0$ . Then, using the formula (7), all  $g_{\max}$  values of  $\mu_g^0$  can be found.

Author states that there is no conflict of interest.

### References

- [1] *Sommerfeld A.* (2002) Vorlesungen über theoretische Physik. 5, Thermodynamik und Statistik. Thun, Deutsch.
- [2] <http://old.exponenta.ru/soft/Mathcad/Mathcad.asp>