A NOTE ON EXCESS GIBBS ENERGY EQUATIONS BASED ON LOCAL COMPOSITION CONCEPT

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The equations based on the local composition concept (Wilson, NRTL *etc.*) are often used for description of thermodynamic behaviour of liquid mixtures. They are regarded as semiempirical equations. In this contribution it is shown, however, that the local composition equation are not consistent with the model from which they were derived and that they should be treated as only empirical ones.

In the last ten years there have been proposed several equations describing the concentration and temperature dependence of molar excess Gibbs energy of liquid mixtures which are theoretically explained by means of the concept of local composition[1-6]. These equations are based on a very simple physical model of liquid which is represented by a three-dimensional fully occupied lattice with coordination number independent of concentration. It is assumed that the potential energy of such lattice is the sum of all interaction energies between pairs of neighbouring particles. Adjustable parameters in final expressions are considered to be characteristics of these interactions and the equations are therefore used for prediction of behaviour of multicomponent systems by means of binary data.

In this contribution it is shown that there is inconsistency in the theoretical basis of local composition equations. Local mole fractions x_{ij} (x_{ij} is mole fraction of component i in the first coordination sphere of a molecule of component j) are related to the overall mole fractions according to

$$\frac{x_{ii}}{x_{ji}} = \frac{x_i}{x_j} W_{ji} , \qquad (1)$$

where weighting function W_{ji} is in local composition equations assumed to be proportional to Boltzmann-type factor $\exp\left[-(g_{ii} - g_{ji})/RT\right]$ when $(g_{ii} - g_{ji})$ is the adjustable parameter (g_{ij} denotes the energy of interaction between $i-j$ pair of molecules).

In binary system

$$x_{ii} + x_{ji} = 1 . \tag{2}$$

Substitution of Eq. (2) into Eq. (1) gives

$$\frac{1}{x_{ji}} - 1 = \frac{x_i}{x_j} W_{ji} \tag{3}$$

and

$$x_j/x_{ji} = x_i W_{ji} + x_j . \tag{4}$$

Simultaneously, the number of pairs $1-2$ in a binary mixture of x_1 mol of component 1 and x_2 mol of component 2 must obey the conservation equation

$$x_2 x_{12} = x_1 x_{21} \tag{5}$$

or alternatively

$$x_2/x_{21} = x_1/x_{12} . \tag{6}$$

Substituting Eq. (4) into Eq. (6) we obtain

$$x_1 W_{21} + x_2 = x_2 W_{12} + x_1 . \tag{7}$$

According to local composition theory it must hold

$$(\partial W_{ij}/\partial x_i)_T = 0 . \tag{8}$$

From condition (7) it follows

$$W_{21} = \frac{(1 - x_1) W_{12} + x_1 - (1 - x_1)}{x_1} = \frac{W_{12}}{x_1} - W_{12} - \frac{1}{x_1} + 2 . \tag{9}$$

Respecting condition (8) Eq. (9) results in

$$\frac{\partial W_{21}}{\partial x_1} = - \frac{W_{12}}{x_1^2} + \frac{1}{x_1^2} = 0 \tag{10}$$

and then

$$W_{ij} = 1 . \tag{11}$$

Local composition theory is thus inconsistent for any nonrandom mixture. Local composition equations must be therefore treated as only empirical ones. The same conclusion holds also for the new equation of Abrams and Prausnitz[7] who used local area fractions.

It is obvious that the probability of finding molecule i in the neighbourhood of central molecule j is not affected only by their mutual interaction g_{ij} but it depends on the interaction of molecule i with all of its neighbours. Potential energy of every particle changes with the composition of mixture and weighting functions W_{ij} in Eq. (1) are therefore generally dependent on concentration as follows from condition (7). This physical view is confirmed also by the new approach of Hiranuma[8], who implicitly considers the number of ways of constructions of linear array through successive adding of interacting molecules to be the combinatorial factor of mixture. This obviously misleading assumption results, for particles of the same size, in Wilson equation.

REFERENCES

1. Wilson G M.: J. Amer. Chem. Soc. *86*, 127 (1964).
2. Orye R. V., Prausnitz J. M.: Ind. Eng. Chem. *57*, 18 (1965).
3. Renon H., Prausnitz J. M.: AIChE J. *14*, 135 (1968).
4. Bruin S., Prausnitz J. M.: Ind. Eng. Chem. Proc. Des. Develop. *10*, 562 (1971).
5. Palmer D. A., Smith B. D.: Ind. Eng. Chem. Proc. Des. Develop. *11*, 114 (1972).
6. Marina J. M., Tassios D. P.: Ind. Eng. Chem. Proc. Des. Develop. *12*, 67 (1973).
7. Abrams D. S., Prausnitz J. M.: AIChE J., in press.
8. Hiranuma M.: Ind. Eng. Chem. Fundam. *13*, 219 (1974).