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Generalization of Guggenheim's combinatorial activity coefficient equation

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ABSTRACT

We revisit Guggenheim's theory to demonstrate that the change in Gibbs energy of athermally mixing molecules can be generalized into a model that requires only the mole fraction, volume and contact area of the various molecules. Subsequently, we obtain a general formula for the combinatorial activity coefficient for mixtures of molecules differing in size and shape.

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1. Introduction

After Huggins [1] and Flory [2] introduced a lattice model to quantify the Gibbs energy of an athermal mixture, i.e. a mixture in which there is no energetic interaction between molecules, Guggenheim [3] refined it. While according to the Flory-Huggins model, small molecules can be placed at random in a lattice, Guggenheim took into account that the placement of mono-segmented molecules in a lattice is influenced by the presence of multi-segmented molecules. Although Guggenheim's model has been applied in many activity coefficient models later, there are two important issues in the Guggenheim model to be aware of. First, Guggenheim considers that all molecules have the same coordination number, while it is known that the coordination number ranges from 6 to 12. Secondly, liquids do not possess a long range order, and therefore the concept of a lattice will limit the number of possible configurations that molecules can make in a liquid. We will touch upon these two issues by going through Guggenheim's derivation and propose a generalized expression for the Gibbs energy of mixing. Finally, we derive a new relation for the combinatorial activity coefficient, which can be applied to mixtures having molecules of arbitrary shape.

2. Theory

2.1. Definition of volume and surface area fractions

We start with a liquid mixture consisting of two components, A and B. When we consider that molecules A and B fit exactly into r_A and r_B lattice cells, respectively, and assume that there are no empty cells, then the total number of lattice cells is given by

$$R_{\text{tot}} = r_A N_A + r_B N_B, \quad (1)$$

where N_j is the number of molecules of type j . On the other hand, we can treat the system as a fluid, which has a total volume defined by the number and molecular volumes of the molecules V_j

$$V_{\text{tot}} = V_A N_A + V_B N_B. \quad (2)$$

In the lattice model, the probability that a lattice cell is populated by a segment of molecule A or B is given by the volume fraction, defined as

$$\phi_A = \frac{N_A r_A}{N_A r_A + N_B r_B} \quad \text{and} \quad \phi_B = \frac{N_B r_B}{N_A r_A + N_B r_B}, \quad (3)$$

respectively, while in the fluid model the volume fractions are expressed by

$$\phi_A = \frac{N_A V_A}{N_A V_A + N_B V_B} \quad \text{and} \quad \phi_B = \frac{N_B V_B}{N_A V_A + N_B V_B}, \quad (4)$$

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respectively. The definition of Eq. (3) is used in the Flory-Huggins model, while Eq. (4) is due to Hildebrand [4], who demonstrated by this that the equation of the Flory-Huggins model does not require a lattice definition. Both methods assume that molecules are randomly positioned in the liquid space.

Guggenheim, Stavermann [5], and Tompa [6] pointed out, however, that the placement of segments cannot be performed randomly, because the segments of chain molecules have a higher probability to be placed aside each other. To correct the volume-based probability, they introduced the surface area fraction to account for the probability to form a contact pair of lattice cells. The surface area fractions can be defined as

$$\theta_A = \frac{N_A z_A q_A}{N_A z_A q_A + N_B z_B q_B} \quad \text{and} \quad \theta_B = \frac{N_B z_B q_B}{N_A z_A q_A + N_B z_B q_B}. \quad (5)$$

In this generalized Guggenheim expression, z_j is the coordination number of the lattice of the pure component j and q_j the relative surface area of molecule j . Guggenheim used one lattice number for all molecules and put the relative surface area of one of the molecule types to unity. We do not use this simplification, so that we can interchange the indices A and B in equations later on.

As we mentioned above, the volume fraction can be defined using the lattice approach (Flory-Huggins), as well as the fluid approach (Hildebrand). The same can be done for the surface fraction. In a fluid, the external surface area of the molecules can be used to define the probability that the molecules make contact, therefore

$$\theta_A = \frac{N_A a_A}{N_A a_A + N_B a_B} \quad \text{and} \quad \theta_B = \frac{N_B a_B}{N_A a_A + N_B a_B}. \quad (6)$$

In here, a_j is the external contact area of molecule j .

It is worthwhile to mention that the volume and surface area fractions are related to each other by the expressions

$$\theta_A = \frac{\phi_A}{\phi_A + f\phi_B} \quad \text{and} \quad \theta_B = \frac{f\phi_B}{\phi_A + f\phi_B}, \quad (7)$$

where the factor f can be calculated from

$$f_{\text{lat}} = \frac{z_B q_B r_A}{z_A q_A r_B} \quad \text{and} \quad f_{\text{fluid}} = \frac{a_B V_A}{a_A V_B}, \quad (8)$$

for the lattice and the fluid approach, respectively. These relations enable us to simplify the expressions above, which will be used later on. Further, we mention that in the original lattice model of Guggenheim $r_A = q_A = 1$, $r_B = r$, $q_B = q$, or $z_A = z_B = z$, which makes $f_{\text{lat}} = q/r$.

2.2. Generalized Gibbs energy of mixing expression: lattice-based derivation

We follow the work of Guggenheim [3] and Tompa [6] to derive an expression for the Gibbs energy of mixing of an athermal system. Suppose that a lattice cell is occupied by a segment of molecule B, then the ratio of the probability that a given neighboring cell is occupied by a segment of another molecule B', $p_{BB'}$, or by a segment of molecule A, p_{BA} , is equal to the ratio in number of nearest neighbors, $z_B q_B N_B$ and $z_A q_A N_A$

$$\frac{p_{BB'}}{p_{BA}} = \frac{N_B z_B q_B}{N_A z_A q_A} = \frac{\theta_B}{\theta_A}. \quad (9)$$

Since the total number of nearest neighbors of molecule B is $z_B q_B$ and not $z_B r_B$ due to the connectivity of the segments, the sum of

these probabilities, i.e. $p_{BB'} + p_{BA}$, is equal to the rescaled value of the volume fraction of molecule B:

$$p_{BB'} + p_{BA} = \phi_B \frac{z_B q_B}{z_B r_B} = \phi_B \frac{q_B}{r_B}. \quad (10)$$

Combining the two equations leads to

$$p_{BB'} = \phi_B \frac{q_B}{r_B} \theta_B \quad \text{and} \quad p_{BA} = \phi_B \frac{q_B}{r_B} \theta_A. \quad (11)$$

We note that the probability that the neighboring cell is occupied by the same B molecule is calculated by

$$p_{BB} = \phi_B - p_{BB'} - p_{BA} = \phi_B \left(1 - \frac{q_B}{r_B}\right). \quad (12)$$

Likewise, when a lattice cell is occupied by a segment of molecule A, the probability that a given neighboring site is occupied by molecule B or by another molecule A is

$$p_{AB} = \phi_A \frac{q_A}{r_A} \theta_B \quad \text{and} \quad p_{AA'} = \phi_A \frac{q_A}{r_A} \theta_A. \quad (13)$$

This procedure can be extended to the situation that a lattice cell is surrounded by more neighboring sites. For the probability that segment A has $x - 1$ neighboring sites of type A, we obtain

$$p_{AxA} = \phi_A \frac{q_A}{r_A} (\theta_A)^{x-1}. \quad (14)$$

In the same way, the probability that segment B has $y - 1$ adjacent sites of type B we have

$$p_{ByB} = \phi_B \frac{q_B}{r_B} (\theta_B)^{y-1}. \quad (15)$$

We mention that Guggenheim derived Eqs. (14) and (15) by the concept of exchange rate, where a segment of a molecule having r segments, here molecule B, is replaced by the mono-segmented molecule A. In the above equation, this implies that $r_A = q_A = x = 1$, $r_B = r$, $q_B = q$. We continue with Guggenheim's derivation, but use the term probability, instead of the term exchange rate, and we take a small volume element in the liquid, which has the size of the least common multiple of the number of segments of the molecules in the mixture. Suppose, for instance, a mixture of trimers and tetramers. This requires a partial liquid volume element equivalent to 12 lattice cells, in which 4 trimers or 3 tetramers fit. In general, this volume element is equivalent to $r_A \cdot r_B$ adjacent lattice cells. The ratio of the probability that this liquid volume contains a cell of type A and $r_B - 1$ adjacent cells of type A and the probability that the cell is of type B and has $r_A - 1$ adjacent cells of type B is

$$\alpha_{\text{liq}} = C \frac{\phi_B \frac{q_B}{r_B} (\theta_B)^{r_A-1}}{\phi_A \frac{q_A}{r_A} (\theta_A)^{r_B-1}} = K_{\text{liq}} \frac{\phi_B (\theta_B)^{r_A-1}}{\phi_A (\theta_A)^{r_B-1}}, \quad (16)$$

where C is a proportionality constant, that is independent of concentration, and K_{liq} is a constant that includes the size parameters r_j and q_j of the components. Guggenheim's formula is recovered when $r_A = 1$ and $r_B = r$. In order to connect this probability to the Gibbs energy, Guggenheim used the thermodynamic constraint that at equilibrium the Gibbs energy of the liquid and the ideal gas are equal. We now consider an ideal gas volume element. The probability to fill this volume element by A or B molecules is proportional to

the partial pressures, P_A and P_B . Therefore, the ratio of the probability to fill this gas volume element with r_A molecules of type B and the probability to fill it with r_B molecules of type A is

$$\alpha_{\text{gas}} = K_{\text{gas}} \frac{P_B^{r_A}}{P_A^{r_B}}, \quad (17)$$

with K_{gas} a constant that is concentration independent.

The chemical potential of compound j in the ideal gas state can be written as:

$$\mu_j(P, T) = \mu_j^0(P_0, T) + RT \ln \left(\frac{P}{P_0} \right), \quad (18)$$

where P_0 is the reference pressure at which the reference chemical potential $\mu_j^0(P_0, T)$ of compound j is known. Substitution of Eq. (18) into the logarithmic expression of Eq. (17), and using the reduced chemical potentials $\tilde{\mu} = \mu(P, T)/RT$ and $\tilde{\mu}^0 = \mu(P_0, T)/RT$, leads to

$$\begin{aligned} \ln \alpha &= \ln K_{\text{gas}} + r_A \ln P_B - r_B \ln P_A \\ &= \ln K_{\text{gas}} + r_A (\tilde{\mu}_B - \tilde{\mu}_B^0 + \ln(P_0)) \\ &\quad - r_B (\tilde{\mu}_A - \tilde{\mu}_A^0 + \ln(P_0)). \end{aligned} \quad (19)$$

Because K_{gas} , $\tilde{\mu}_j^0$ and $\ln(P_0)$ are constants, differentiation yields

$$d \ln \alpha = r_A d\tilde{\mu}_B - r_B d\tilde{\mu}_A. \quad (20)$$

By using the Gibbs-Duhem equation

$$\sum_j N_j d\tilde{\mu}_j = 0, \quad (21)$$

the reduced chemical potential of compound B can be eliminated and we obtain

$$d\tilde{\mu}_A = -\frac{N_B}{(N_A r_A + N_B r_B)} d \ln \alpha = -\frac{\phi_B}{r_B} d \ln \alpha = -\frac{\phi_B}{r_B \alpha} d\alpha. \quad (22)$$

Integration of Eq. (22) from the pure state of compound A, $\phi_B = 0$, to a final concentration ϕ_B provides the change in Gibbs energy upon mixing of compound A with B to concentration ϕ_A

$$\int_{\text{pure A}}^{\text{mixture}} d\tilde{\mu}_A = \Delta\tilde{\mu}_A = -\frac{1}{r_B} \int_0^{\phi_B} \frac{\phi_B}{\alpha} \left(\frac{\partial \alpha}{\partial \phi_B} \right) d\phi_B. \quad (23)$$

Substitution of Eq. (16) into Eq. (23) gives for the chemical potential difference of compound A in the pure liquid state and the mixture

$$\Delta\tilde{\mu}_A = -\frac{1}{r_B} \int_0^{\phi_B} \frac{1}{\phi_A} + (r_A - 1) \frac{\phi_B}{\theta_B} \left(\frac{\partial \theta_B}{\partial \phi_B} \right) - (r_B - 1) \frac{\phi_B}{\theta_A} \left(\frac{\partial \theta_A}{\partial \phi_B} \right) d\phi_B. \quad (24)$$

After evaluating the partial derivatives the integral reduces to

$$\Delta\tilde{\mu}_A = -\frac{1}{r_B} \int_0^{\phi_B} \frac{r_A \theta_A + r_B \theta_B}{\phi_A} d\phi_B. \quad (25)$$

With Eqs. (7) and (8), the surface area fractions in the integral can be written in terms of ϕ_A , after which the integration yields

$$\begin{aligned} \Delta\tilde{\mu}_A &= -\frac{1}{r_B} \left[\frac{r_A \ln(\phi_A + f_{\text{lat}} \phi_B)}{f_{\text{lat}} - 1} - r_B \ln(1 - \phi_B) - \frac{r_B \ln(\phi_A + f_{\text{lat}} \phi_B)}{f_{\text{lat}} - 1} \right] \\ &= \ln(\phi_A) + \frac{1 - r_A/r_B}{f_{\text{lat}} - 1} \ln \left(\frac{\phi_A}{\theta_A} \right) \\ &= \ln(\phi_A) - \Gamma_A \ln \left(\frac{\phi_A}{\theta_A} \right). \end{aligned} \quad (26)$$

Interchanging the indices results for component B in

$$\Delta\tilde{\mu}_B = \ln(\phi_B) - \Gamma_B \ln \left(\frac{\phi_B}{\theta_B} \right). \quad (27)$$

In the above equations, we defined the concentration independent factors:

$$\Gamma_A \equiv \frac{z_A q_A r_A - z_A q_A r_B}{z_B q_B r_A - z_A q_A r_B} \quad \text{and} \quad \Gamma_B \equiv \frac{z_B q_B r_B - z_B q_B r_A}{z_A q_A r_B - z_B q_B r_A}. \quad (28)$$

From Eq. (26) and Eq. (27) follows that the total reduced Gibbs energy change upon mixing of compounds A and B is given by

$$\Delta\tilde{G} = N_A \ln(\phi_A) + N_B \ln(\phi_B) - \left[N_A \Gamma_A \ln \left(\frac{\phi_A}{\theta_A} \right) + N_B \Gamma_B \ln \left(\frac{\phi_B}{\theta_B} \right) \right]. \quad (29)$$

Again, Guggenheim's original equation is recovered by setting $r_A = q_A = 1$, $r_B = r$, $q_B = q$, and $z_A = z_B = z$, which yields $\Gamma_A = (r - 1)/(r - q)$ and $\Gamma_B = q\Gamma_A$.

2.3. Generalized Gibbs energy of mixing expression: off-lattice derivation

The above derivation was carried out in terms of lattice parameters, but the same results can be derived without the definition of a lattice. We start by considering a small volume element in the liquid with volume V_{box} . The number of molecules of type j that fit into this volume element, m_j , is determined by the molecular volume of molecule V_j given by

$$m_j = \frac{V_{\text{box}}}{V_j}. \quad (30)$$

The ratio of the probabilities that this volume element is filled with only A or B molecules from the liquid phase, and which are all adjacent to each other, is

$$\alpha_{\text{liq}} = K_{\text{liq}} \frac{\phi_B(\theta_B)^{m_A-1}}{\phi_A(\theta_A)^{m_B-1}}. \quad (31)$$

In the gas phase, the ratio of the probabilities that a volume element is filled with only A or B molecules, is ruled by the partial vapor pressures

$$\alpha_{\text{gas}} = K_{\text{gas}} \frac{P_B^{m_A}}{P_A^{m_B}}. \quad (32)$$

By applying the same procedure as in Section 2.2, we obtain again Eq. (29), but now the factors, Γ_j , are defined by the molecular volume and external surface area of the compounds

$$\Gamma_A = \frac{a_A V_A - a_A V_B}{a_B V_A - a_A V_B} \quad \text{and} \quad \Gamma_B = \frac{a_B V_B - a_B V_A}{a_A V_B - a_B V_A}. \quad (33)$$

Fig. 1. Correction term of Eq. (36) as a function of ratio of volume and surface fraction of compound j .

2.4. Combinatorial activity coefficients

Differentiation of Eq. (29) to N_A yields the combinatorial activity coefficient of component A

$$\ln(\gamma_A) = \left[\ln\left(\frac{\phi_A}{x_A}\right) + 1 - \frac{\phi_A}{x_A} \right] - \Gamma_A \left[\ln\left(\frac{\phi_A}{\theta_A}\right) + 1 - \frac{\phi_A}{\theta_A} \right]. \quad (34)$$

The factor Γ_A can be written in terms of x_A , ϕ_A , and θ_A by substitution Eqs. (3) and (5) into Eq. (28)

$$\Gamma_A = \frac{1 - \frac{r_B}{r_A}}{\frac{z_B q_B}{z_A q_A} - \frac{r_B}{r_A}} = \frac{1 - \frac{\phi_B}{\phi_A} \frac{x_A}{x_B}}{\frac{\theta_B}{\theta_A} \frac{x_A}{x_B} - \frac{\phi_B}{\phi_A} \frac{x_A}{x_B}} = \frac{1 - \frac{\phi_A}{x_A}}{1 - \frac{\phi_A}{\theta_A}}. \quad (35)$$

The same result is obtained when Eqs. (4) and (6) are substituted into Eq. (33). Therefore, regardless of whether a lattice- or fluid-based model is used, and regardless of the shape of the molecules, the general expression for the combinatorial activity coefficient of component j in a multicomponent mixture is given by

$$\ln(\gamma_j) = \ln\left(\frac{\phi_j}{x_j}\right) + \left(1 - \frac{\phi_j}{x_j}\right) \left[\frac{\ln\left(\frac{\phi_j}{\theta_j}\right)}{\frac{\phi_j}{\theta_j} - 1} \right]. \quad (36)$$

Here, the term in the square brackets defines the Guggenheim correction with respect to the Flory-Huggins model. For $\phi_j = \theta_j$, the correction term is unity. Fig. 1 shows the correction term as a function of the ratio ϕ_j/θ_j .

3. Discussion and concluding remarks

We recall that Guggenheim used a simplified form for Γ_j . He imposed $r_A = q_A = 1$, $r_B = r$, $q_B = q$, and $z_A = z_B = z$ and applied the lattice relation: $zq = zr - 2(r - 1)$, which is valid for linear and branched molecules. As a result, Guggenheim obtained $\Gamma_A = \frac{z}{2}$ and $\Gamma_B = q \frac{z}{2}$ for Eq. (29). Later, Vera et al. [7] used this equation to derive the following restricted form of the combinatorial activity coefficient

$$\ln(\gamma_j) = \ln\left(\frac{\phi_j}{x_j}\right) - \frac{zq_j}{2} \ln\left(\frac{\phi_j}{\theta_j}\right), \quad (37)$$

but this form was seldom applied in activity coefficient models. Instead, lattice activity coefficient models still contained the combinatorial term of the original UNIQUAC model [8]; Eq. (34) with $\Gamma_A = zq_A/2$. See, for instance, the development of the UNIFAC [9], the COSMOSPACE [10], the MOQUAC [11] and the COSMOSAC [12] model. Our result of Eq. (36) shows that there is no need to define a lattice and molecular sizes in terms of lattice number (z), segment number (r_j) and relative surface (q_j). Therefore, the original and restricted form of the combinatorial activity coefficient could be replaced by Eq. (36), and supplemented with an activity coefficient model that accounts for the dispersive interaction between non-polar molecules. Such an approach has been applied in the MOSCED model [13], which is used to calculate the activity coefficients at infinite solution of binary mixtures. In here the dispersion is based on

Fig. 2. Comparison of models to predict the combinatorial activity coefficient of hexane in n -alkanes at infinite dilution as function of the carbon number. Right graph is a detail of the left graph to emphasize differences.

the Hansen solubility model [14], while the combinatorial activity coefficient at infinite dilution of solute *A* in solvent *B* is computed by

$$\ln(\gamma_A^\infty) = \ln\left(\frac{V_A}{V_B}\right)^{0.953} + 1 - \left(\frac{V_A}{V_B}\right)^{0.953}. \quad (38)$$

This is a modified form of the combinatorial activity coefficient of the Flory-Huggins model. The use of an exponent was proposed by Donahue and Prausnitz [15] to tweak the Flory-Huggins model, where the exponent is 1, towards the ideal solution model, where the exponent is zero. This modification, however, has no physical basis. Fig. 2 shows that this correction of the combinatorial term is larger than the Stavermann-Guggenheim correction used in the UNIQUAC model and also larger than the correction given by Eq. (36). Since Eq. (36) is a generalized form of the UNIQUAC model and has a physical meaningful basis rather than being an ad-hoc modification, it could replace the combinatorial term in the MOSCED model. However, this implies that the dispersion contribution needs to be made more repulsive in order to bring the MOSCED model in agreement with the experimental activity coefficients of alkane mixtures.

The essence of the derivation, which leads to the generalized expression for the combinatorial activity coefficient, is the introduction of a reference volume, in which only a limited number of molecules fit due to their size and shape. The probability to fill this volume with one type of molecules is the second essential step in the derivation. Because of the existence of a gas-liquid equilibrium, it is permitted to relate these probabilities to the probabilities to fill a reference volume in the vapor phase. This relation in combination with the Gibbs-Duhem law leads to a general expression of the Gibbs energy of mixing and subsequently a general expression for the combinatorial activity coefficient.

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