Combinatorial Entropy of Mixing for Molecules Differing in Size and Shape

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In reducing experimental vapor–liquid equilibrium data it is common to calculate the Gibbs energy of mixing in excess of that for a solution whose entropy of mixing is given by one of two expressions: ideal entropy or Flory–Huggins entropy. The first of these is proper for a mixture of small molecules of similar size and the second one is proper for a mixture of monomer and chain polymer. This paper considers intermediate cases where there are significant differences in molecular shape as well as size. An expression is derived for the combinatorial entropy of mixing; this expression has Flory's result as the leading term but also contains corrections for molecular bulkiness. The combinatorial entropy of mixing depends on characteristic parameters reflecting both molecular size and shape. Methods are given for simple evaluation of these parameters and illustrations for representative mixtures are presented. In some case, the corrections for bulkiness can be very large.

En réduisant les données sur l'équilibre expérimental vapeur liquide, il est commun de calculer l'énergie de mélange de Gibbs en excès de celle d'une solution dont l'entropie de mélange est donnée par l'une des deux expressions: entropie idéale ou entropie Flory–Huggins. La première est propre au mélange de petites molécules aux dimensions semblables et la seconde est relative à un mélange de monomère ou polymère en chaine. Cette note traite des cas intermédiaires où il n'existe pas de différences significatives aussi bien dans la forme que dans la taille de la molécule. Une expression a été déduite pour l'entropie combinatoire de mélange cette expression contient le résultat de Flory comme terme dominant et aussi des termes correctifs pour l'encombrement moléculaire. L'entropie combinatoire de mélange dépend des paramètres caractéristiques reflétant à la fois la forme et la dimension de la molécule. Des méthodes simples d'évaluation de ces paramètres et des illustrations par des mélanges représentatifs ont été présentées. Dans certains cas les corrections apportées à l'encombrement peuvent être très élevées.

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In recent years much effort has been devoted toward developing the statistical thermodynamics of liquid mixtures (1). While most of this effort has been directed at mixtures of simple fluids containing small, spherical molecules, considerable progress has also been achieved in mixtures containing both large and small molecules as in polymer solutions (2); this progress follows primarily from work by Flory (3) and by Patterson and Delmas (4) based on a partition function proposed by Prigogine (5). These recent developments, however, are concerned with residual thermodynamic properties, determined by differences in free volumes and in intermolecular forces. In the last twenty years very little attention has been given to the configurational properties of solutions as determined by the combinatorial factor. In this work we reconsider the problem of calculating the combinatorial entropy of mixing fluids whose molecules differ in size and shape. We have derived an expression similar to that of Tompa (6) using arguments different from those used previously. Our main concern, however, is directed at application of Tompa's result which appears to have been forgotten by contemporary workers in solution thermodynamics. We make some specific suggestions toward quantitative calculations of the combinatorial entropy of mixing which, in turn, are useful for reduction and subsequent interpretation of experimental data for real solutions.

We consider a binary mixture of two fluids indicated by subscripts 1 and 2. The entropy of mixing is defined as the change in entropy when N_1 molecules of 1 and N_2 molecules of 2 are mixed at constant temperature and pressure to form a homogeneous solution. It is convenient to write this entropy of mixing as the sum of two parts:

$$[1] \qquad \Delta S = \Delta S^C + \Delta S^R$$

where superscript C stands for combinatorial and superscript R stands for residual. While the recent work of Flory, Patterson and others has been directed at ΔS^R, we are here concerned only with ΔS^C. The mixing process considered here is one where the molecules of fluids 1 and 2 have finite size but no forces of attraction and where the isothermal, isobaric mixing process occurs also at constant volume.

Let molecule 1 consist of one segment and molecule 2 of r segments. As discussed in numerous textbooks, two expressions are commonly used for ΔS^C:

[2] $$\frac{\Delta S^C}{k} = -[N_1 \ln x_1 + N_2 \ln x_2]$$

[3] $$\frac{\Delta S^C}{k} = -[N_1 \ln \Phi_1 + N_2 \ln \Phi_2]$$

where x is the mole fraction

$$[x_1 = N_1/(N_1 + N_2) \quad x_2 = N_2/(N_1 + N_2)]$$

and Φ is the segment fraction

$$[\Phi_1 = N_1/(N_1 + rN_2) \quad \Phi_2 = rN_2/(N_1 + rN_2)].$$

Equation 2 gives the ideal entropy of mixing as used in the theory of regular solutions (7) and eq. 3, due to Flory, is used, almost without exception, in the polymer-solution literature. Equation 3 follows from well-defined assumptions (8) including the assumption that molecule 2 (the polymer) is a long, flexible chain; eq. 3, then, was not intended to apply to large bulky molecules. Using an approach different from Flory's, eq. 3 has also been derived by Longuet–Higgins (9) and by Silberberg (10).

In 1947 Hildebrand (11) presented a phenomenological, free-volume derivation of the combinatorial entropy of mixing. While that derivation is *ad hoc* and difficult to justify theoretically, it points to an important conclusion (later verified by Tompa (12)), *viz.*, the entropy of combinatorial mixing has a lower bound given by eq. 2 and an upper bound given by eq. 3; the "true" combinatorial entropy of mixing lies between these limits. Just where the "true" combinatorial entropy lies between these limits depends on the size and shape of the molecules. Tompa has shown that for mixtures of bulky molecules, eq. 2 provides a better approximation than eq. 3.

While eqs. 2 and 3 are quoted in all textbooks on liquid-mixture thermodynamics, it will be useful to have an expression which, taking molecular size and shape into consideration, is capable of covering the domain bounded by eqs. 2 and 3. We have derived such an expression here; it is

[4] $$\frac{\Delta S^C}{k} = -[N_1 \ln \Phi_1 + N_2 \ln \Phi_2]$$
$$+ \sum_{t=1}^{z} \frac{\alpha^{(t)}}{\left(1 - \left(\frac{q}{r}\right)^t\right) r} \left\{ \left[N_1 + \left(\frac{q}{r}\right)^t rN_2\right] \right.$$
$$\times \left[\ln\left(N_1 + \left(\frac{q}{r}\right)^t rN_2\right) - \ln(N_1 + N_2)\right]$$
$$\left. - rN_2\left(\frac{q}{r}\right)^t \ln\left(\frac{q}{t}\right)^t \right\}$$

A derivation of eq 4 is given in the Appendix. A similar equation, based on a different derivation, was given by Tompa (6).

In eq. 4, r is the number of segments of molecule 2 divided by that of molecule 1 and q is the surface (contact) area of molecule 2 divided by that of molecule 1. The coordination number z is the number of nearest neighbors of a molecular segment.

The parameters $\alpha^{(t)}$ depend on molecular size and shape. They obey the relations

[5] $$\sum_{t=1}^{z} \alpha^{(t)} = r - 1$$

[6] $$\sum_{t=1}^{z} t\alpha^{(t)} = \frac{z}{2}(r - q)$$

The quantity on the right side of eq. 6 is the number of contacts made by segments of molecule 2 with other segments in the same molecule.

Before discussing particular applications of eq. 4, it is instructive to point out some general properties of that equation.

(a) The first two terms in eq. 4 are identical to eq. 3; in other words, the summation term in eq. 4 is essentially a correction to Flory's equation.

(b) If molecules 1 and 2 are identical in shape and size, then $q = r = 1$. In that event, all $\alpha^{(t)}$'s are zero and eq. 4 reduces to eq. 2.

(c) If the coordination number z becomes very large, $q/r \to 1$ and it can be shown that the summation term in eq. 4 vanishes.

(d) The first two terms in eq. 4 are always positive and for $r > 1$, eq. 3 always gives an entropy of mixing that is larger than that given by eq. 2. Therefore, if eq. 4 is to give a result intermediate between eqs. 2 and 3, it is necessary that the summation term in eq. 4 be negative for $q/r < 1$ ($q/r > 1$ is physically impossible). The

summation term in eq. 4 is essentially always negative and increasingly so as $q/r \rightarrow 0$. For mixtures of bulky molecules of different size ($q/r \ll 1$), eq. 4 approaches eq. 2 as suggested by Monte Carlo studies of mixtures of different-sized spheres (1, 13). For mixtures where q/r is slightly less than unity, eq. 4 gives an entropy of mixing which is very slightly less than that given by eq. 2. In such a case therefore, eq. 4 is, strictly speaking, not valid although the error is negligibly small. For such mixtures and for mixtures where $r \approx 2$ or less, eq. 2 should be used.

(*e*) For mixtures of chain molecules, eq. 4 reduces to the result obtained by Huggins (14) and discussed by Guggenheim (15).

Determination of Parameters

To apply eq. 4, it is necessary to devise a consistent and physically reasonable method for evaluating the parameters r, q, and $\alpha^{(t)}$. We present such a method below.

To evaluate r, we use the van der Waals volumes calculated by Bondi (16). Using the group contributions of Chapt. 14 in Bondi's book it is simple to calculate the van der Waals volume v^* of a large variety of molecules. Then

$$[7] \qquad r = v_2^*/v_1^*$$

For typical mixtures, we find that r is nearly equal to the ratio of molar volumes.

To evaluate q, it is tempting to use Bondi's calculations of van der Waals surface areas. However, the surface areas given by Bondi are too large for our purposes; Bondi calculates the total surface area whereas we require that part of the total surface area which is available for interaction with neighboring molecules. Because of steric requirements, not all of the total surface area is available for interaction with nearest neighbors.

To establish a consistent method for evaluating both q and $\alpha^{(t)}$, we use a simple lattice model with $z = 6$. We assume that the dimensions of a molecule can be represented by three mutually perpendicular, characteristic lengths (l_x, l_y, l_z), whose product is equal to the van der Waals volume:

$$[8] \qquad v^* = l_x l_y l_z$$

As indicated in the Appendix for this simple lattice $\alpha^{(4)} = \alpha^{(5)} = \alpha^{(6)} = 0$. Therefore the three

parameters $\alpha^{(1)}$, $\alpha^{(2)}$, and $\alpha^{(3)}$ suffice to describe the bulkiness of the molecule. It can then be shown that

$$[9] \qquad r = \frac{(l_x l_y l_z)_2}{(l_x l_y l_z)_1}$$

$$[10] \qquad q = \frac{(l_x l_y + l_x l_z + l_y l_z)_2}{(l_x l_y + l_x l_z + l_y l_z)_1}$$

$$[11] \qquad \alpha^{(1)} = 2(r - 1) - 3(r - q) + \alpha^{(3)}$$

$$[12] \qquad \alpha^{(2)} = 3(r - q) - (r - 1) - 2\alpha^{(3)}$$

$$[13] \qquad \alpha^{(3)} = (r - 1) - 3q + 3\frac{(l_x + l_y + l_z)_2}{(l_x + l_y + l_z)_1}$$

For a given molecule, the parameters l_x, l_y, l_z must be determined by the size and shape of that molecule, subject to the boundary condition given by eq. 8. To find these parameters, we utilize data for bond angles and bond lengths. To illustrate, Table 1 gives parameters for some representative molecules. These parameters were obtained primarily from van der Waals radii given by Bondi. For silicon-containing compounds Bondi's method of calculation was used with bond parameters taken from Handbook of Chemistry and Physics.

Combinatorial Entropies of Mixing for
Some Representative Binary Mixtures

To illustrate the use of eqs. 4 and 9–13, we present calculations for a few typical binary mixtures. These are shown in Figs. 1–4. Parameters used to prepare these figures can easily be calculated with eqs. 9 to 13 using the numbers given in Table 1.

Our main interest is to compare results obtained from eq. 4 with those obtained from Flory's equation (eq. 3). The essential difference between these equations is related to the largest possible number of connections (bonds) which a segment, upon being placed in the lattice, may have with already placed segments of the same molecule. In Flory's equation, suitable for chain molecules, that maximum number is one. We therefore designate results obtained from Flory's equation by the letters SCSM which stand for Single-Connected Segment Model. By contrast, eq. 4 permits a segment of a large molecule to be connected to as many as $z - 1$ other segments of the same molecule which have already been placed on the lattice. Therefore we designate results obtained from eq. 4 by the letters MCSM

TABLE 1. Molecular parameters for combinatorial entropy of mixing

Fluid	l_x	l_y (Å)	l_z	v^* In cm³/mol	In Å³/molecule
n-Alkanes					
CH₄	3.05	3.05	3.05	17.1	28.4
C₂H₆	4.12	3.32	3.32	27.3	45.4
C₃H₈	5.66	3.32	3.32	37.6	62.4
C₄H₁₀	7.20	3.32	3.32	47.8	79.4
C₅H₁₂	8.74	3.32	3.32	58.0	96.3
C₆H₁₄	10.3	3.32	3.32	68.3	114
C₇H₁₆	11.8	3.32	3.32	78.5	130
C₈H₁₈†	13.3	3.32	3.32	88.7	147
n-Alkenes					
C₂H₄	3.60	3.32	3.32	23.9	39.7
C₃H₆	5.13	3.32	3.32	34.1	56.5
C₄H₈	6.68	3.32	3.32	44.3	73.6
C₆H₁₂	9.71	3.32	3.32	64.7	107
C₈H₁₆	12.8	3.32	3.32	85.2	141
n-Alkynes					
C₂H₂	3.48	3.32	3.32	23.1	38.4
C₄H₆	6.55	3.32	3.32	43.5	72.2
C₈H₁₄	12.7	3.32	3.32	84.4	140
Cycloalkanes					
C₅H₁₀	5.31	5.31	2.90	49.2	81.8
C₆H₁₂	5.67	5.67	3.03	58.7	97.4
Aromatics					
C₆H₆	5.81	5.81	2.38	48.4	80.3
Naphthalene	8.88	5.81	2.38	74.0	123
Anthracene	11.9	5.81	2.38	99.6	165
Spherical Molecules					
CF₄	3.57	3.57	3.57	27.3	45.5
CCl₄	4.43	4.43	4.43	52.3	86.9
CBr₄	4.68	4.68	4.68	61.7	103
CI₄	5.20	5.20	5.20	84.7	141
C(CH₃)₄	4.58	4.58	4.58	58.0	96.1
Si(CH₃)₄	4.76	4.76	4.76	65.3	108
(CH₃)₈(SiO)₄	6.52	6.52	6.52	167	277

†For *n*-alkanes $C_{N_c}H_{2N_c}(N_c > 1)$ the following equations are valid: $l_x = 1.54N_c + 1.04$ Å; $l_y = l_z = 3.32$ Å.
$v^* = 10.23N_c + 6.88$ cm³/mol $= 16.98N_c + 11.42$ Å³/molecule.

which stand for Multiple-Connected Segment Model.

Figures 1–4 give excess combinatorial entropies per mole of sites. The excess entropy is defined, as usual, as the entropy of mixing in excess of that found for an ideal system (eq. 2). While eqs. 2, 3, and 4 give entropies per mole of mixture, we can easily convert to entropies per mole of sites by writing

[14] $\dfrac{S^E(\text{per mole of sites})}{S^E(\text{per mole of mixture})} = 1 - \left(1 - \dfrac{1}{r}\right)\Phi_2$

where Φ_2 is the site fraction of polymer.

Figure 1 gives results for the system *n*-hexane–*n*-hexadecane. Since both components are chain molecules, results from eq. 3 are essentially identical to those from eq. 4.

Figure 2 gives results for the system methane–*n*-hexadecane. Because of the larger size difference, entropies shown in Fig. 2 are appreciably larger than those shown in Fig. 1. Again, there is not much difference between SCSM and MCSM results. However, the relative difference in Fig. 2 is larger than that shown in Fig. 1 because the width of methane is smaller than that of hexadecane while the width of hexane is the same as that of hexadecane. The lower entropy for MCSM is in agreement with computer calculations reported by Bellemans (17).
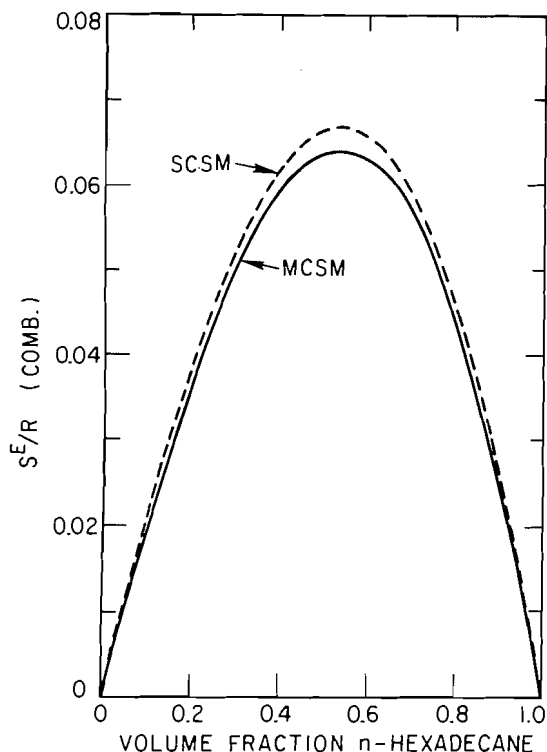
FIG. 1. Excess combinatorial entropy per mole of sites for n-hexane–n-hexadecane.

Figure 3 gives results for the system carbon tetrachloride – octamethylcyclotetrasiloxane (OMCTS). Both components consist of spherical molecules and therefore we expect a significant difference between SCSM and MCSM results. While the magnitude of the excess entropy is small, Fig. 3 shows that Flory's equation gives an excess entropy nearly twice as large as that found from eq. 4.

Figure 4 gives results for mixtures of benzene and polyethylene of carbon number 8022. All calculations shown are obtained from eq. 4 with parameters given in Table 1. The purpose of Fig. 4 is to show how the degree of bulkiness of the polyethylene affects the excess combinatorial entropy. Curve A refers to linear (straight-chain) polyethylene with $l_x = 12354$ and $l_y = l_z = 3.32$ (See Table 1 where all distances are given in Angstroms.) Curve B refers to a flat ribbon, i.e. to a double-strand linear polyethylene with $l_x = 6177$, $l_y = 6.64$, and $l_z = 3.32$. Curve C is also for a flat ribbon, but now the polyethylene is a quadruple-strand chain with $l_x = 3089$, $l_y = 13.28$, and $l_z = 3.32$. Curve D is for polyethylene

in a rod-like shape with $l_x = 3089$, $l_y = l_z = 6.64$. Curve E is for a similar rod-shaped polyethylene but with shorter axis and larger cross-section; in this case $l_x = 154$, $l_y = 66.4$, and $l_z = 13.28$. Finally curve F is for polyethylene in the shape of a cube with $l_x = l_y = l_z = 51.4$.

Figure 4 clearly shows that the entropy is strongly affected by the bulkiness of the large molecule, i.e. by the extent to which the segments in the large molecule are multiple-connected rather than single-connected when placed onto the lattice. Flory's formula (eq. 3) cannot distinguish between the six cases shown in Fig. 4. Since Flory's formula depends only on the volume ratio, it gives results which are the same for all six cases, independent of molecular shape. Excess combinatorial entropies from eq. 3 are essentially identical to those shown by curve A.

Residual Excess Gibbs Energy

To interpret and correlate experimental data for liquid mixtures, it is desirable to calculate residual thermodynamic functions which, in turn, can be related to a suitable partition function. Following Flory (18), ΔG^R, the residual
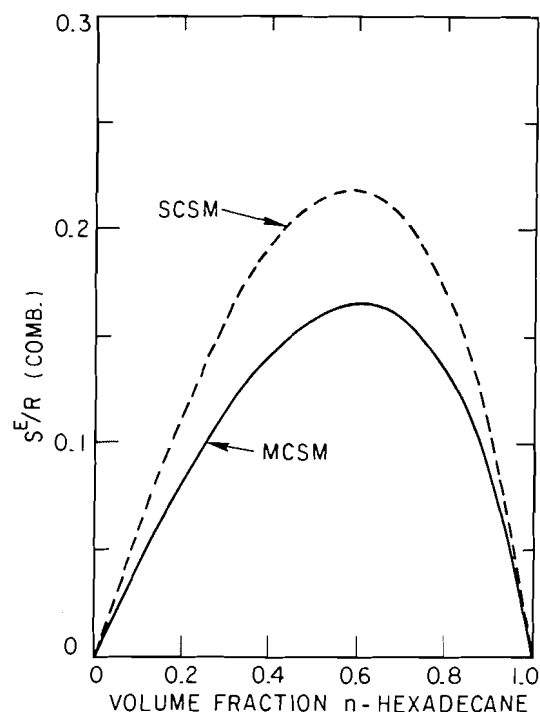

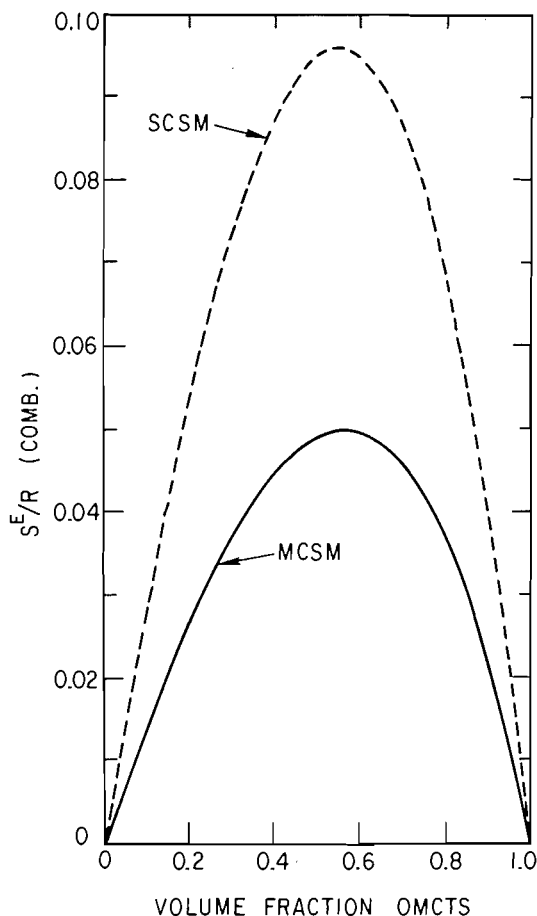FIG. 2. Excess combinatorial entropy per mole of sites for methane–n-hexadecane.

FIG. 3. Excess combinatorial entropy per mole of sites for carbon tetrachloride – OMCTS.

entropy was calculated twice, once with eq. 3 and once with eq. 4. Since OMCTS is a large spherical molecule, many of its segments are multiple rather than single connected when placed onto the lattice. The excess combinatorial entropy calculated from Flory's equation is, therefore, too large and in both binary systems the residual Gibbs energy of mixing based on SCSM is more than twice that calculated from MCSM.

The results shown in Figs. 5 and 6 indicate that in some mixtures the residual Gibbs energy of mixing is a strong function of the method used to calculate the combinatorial entropy of mixing. Thus details in the calculation of the combinatorial entropy of mixing may affect interpretation and subsequent correlation of residual excess functions in mixtures.
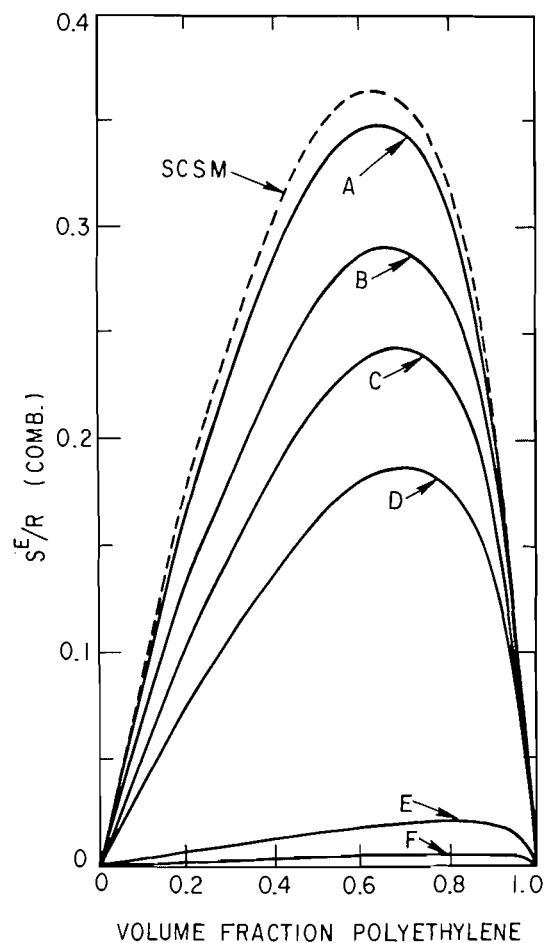
Gibbs energy of mixing is found from the experimental excess Gibbs energy of mixing by

[15] $\Delta G^R = G^E(\text{experimental})$
$$- G^E(\text{combinatorial})$$

Since $H^E(\text{combinatorial})$ is zero, eq. 15 becomes

[16] $\Delta G^R = G^E(\text{experimental})$
$$+ TS^E(\text{combinatorial})$$

In some cases the residual Gibbs energy of mixing is sensitive to the model chosen for calculating $S^E(\text{combinatorial})$. To illustrate, Fig. 5 gives results for the system carbon tetrachloride – OMCTS and Fig. 6 for the system benzene – OMCTS; experimental data are from Marsh (19). For both systems the excess combinatorial

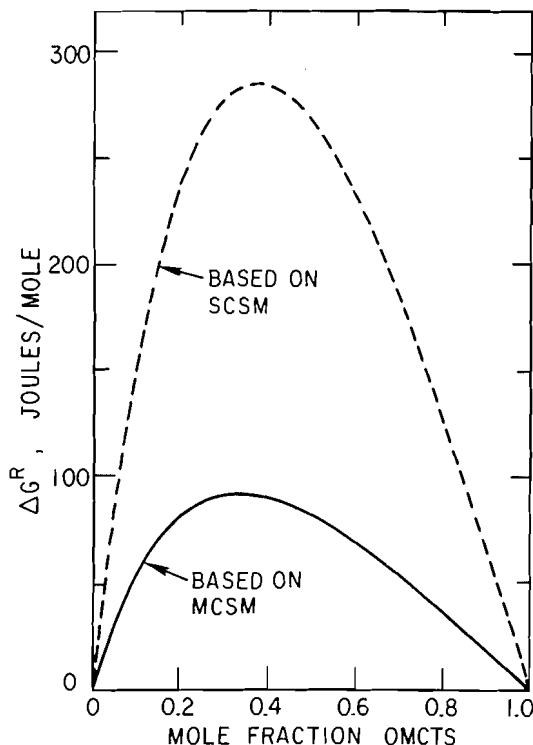FIG. 4. Excess combinatorial entropy per mole of sites for benzene–polyethylene.

FIG. 5. Residual Gibbs energy of mixing for carbon tetrachloride – OMCTS at 25 °C.

Appendix

Derivation of Eq. 4

We consider a three-dimensional lattice with N sites. We want to fill the lattice with N_2 (large) solute molecules and N_1 (small) solvent molecules. Each solute molecule occupies r lattice sites and each solvent molecule occupies one site, such that $N = N_1 + rN_2$. We assume that all configurations have the same energy.

We proceed in the usual way by placing the N_2 solute molecules onto the lattice, one after another. The remaining sites are then filled with solvent molecules. Suppose j solute molecules have already been placed; we now want to compute $\gamma_{j+1,i}$ which is the number of ways we can place the ith segment of the $(j + 1)$th solute molecule.

Consider the first segment of a solute molecule and let Y_1 be the number of ways we can place that segment in the lattice if that lattice were empty. Now for the case where j solute molecules have already been placed previously, $\gamma_{j+1,1}$ is given by

$$[A1] \qquad v_{j+1,1} = \left(\frac{N - rj}{N}\right) Y_1$$

Equation $A1$ says that $\gamma_{j+1,1}$ is smaller than Y_1 by a factor which is the fraction of unoccupied sites.

It is tempting to generalize eq. $A1$ by assuming that the reducing factor, viz. the fraction of unoccupied sites, can also be used to calculate the number of ways of placing the ith segment, that is, to assume

$$[A2] \qquad v_{j+1,i} = \left(\frac{N - rj - (i - 1)}{N}\right) Y_i$$

$$\approx \left(\frac{N - rj}{N}\right) Y_i$$

where Y_i is the number of ways of placing the ith segment of the $(j + 1)$th molecule when the lattice is nearly empty, containing only $i - 1$ segments of the $(j + 1)$th molecule. Since rj is generally much larger than $(i - 1)$, the equation can be simplified as shown.

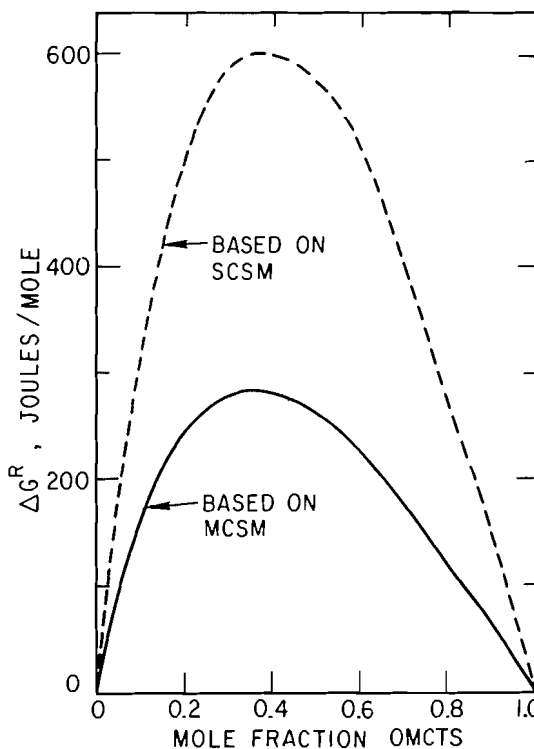Equation $A2$ was used by Flory. We do not use it here, however, because the reducing factor

FIG. 6. Residual Gibbs energy of mixing for benzene–OMCTS at 25 °C.

$(N - rj)/N$, while valid for the first segment, is too low for subsequent segments. Once the first segment of a solute molecule has been placed on a particular site, the probability that an adjacent site is empty, is larger than $(N - rj)/N$. Stated in more general terms, if $i - 1$ sites of a solute molecule have been placed on the lattice, the probability that a fixed site adjacent to the $(i - 1)$th segment is empty, is larger than $(N - rj)/N$. The probability is larger because if we know that $i - 1$ segments have already been placed in the region where we want now to place the ith segment, we know that this region is less concentrated in solute molecules than the lattice as a whole.

To obtain an improved expression for $\gamma_{j+1,i}$, we must first introduce the parameters z and q. The coordination number of the lattice is z; each solvent molecule has z nearest neighbors. Each solute molecule has a number of nearest neighbors equal to qz, which is less than rz, because some of the nearest neighbors of a segment within a solute molecule belong to the same molecule. Whereas the total number of segment–segment contacts for a molecule is rz, only qz contacts are external. For a bulky solute molecule, where many of the segments are internal (*i.e.* completely or primarily surrounded by segments of the same molecule), q/r is well below unity. For a linear chain molecule with no rings, q and r do not differ very much; they are related by

[A3] $qz = rz - 2r + 2$

Equation A3 is valid also for branched chain molecules. However, this equation assumes that a molecule does not bend back on itself, *i.e.* a segment of a molecule is never placed such that one of its immediate neighbors is a segment of that same molecule more than two links removed.

In Flory's equation (eq. A2) the reduction factor $(N - rj)/N$ is too low. If it is known that a given site (arbitrarily labeled A) is the neighbor of one site already occupied by a segment of the $(j + 1)$th molecule, then, the probability that site A is occupied by another segment of that same $(j + 1)$th molecule is $(1 - q/r)$, not zero as assumed in eq. A2. Further, if site A is such that t of its neighbors are occupied by segments of the $(j + 1)$th molecule, then the probability that site A is occupied by another segment of that same $(j + 1)$th molecule is even higher; it is $1 - (q/r)^t$. We therefore replace eq. A2 by writing

[A4] $v_{\substack{j+1,i \\ i>1}} = \left(\dfrac{N - rj}{N} \right)$

$$\times \left[1 - \left(1 - \left(\dfrac{q}{r} \right)^t \right) \dfrac{rj}{N} \right]^{-i} Y_i$$

The factor in parentheses in eq. A4 is always less than unity and since it is in the denominator, the number of ways of placing the ith segment of the $(j + 1)$th molecule as given by eq. A4 is larger than that given by eq. A2.

As the coordination number rises, the difference between r and q falls; when $z \to \infty$, $q/r \to 1$. In that case eq. A4 reduces to eq. A2.

Omitting symmetry numbers, we can now write the number of configurations, *i.e.* the number of ways of arranging N_1 solvent molecules and N_2 solute molecules

[A5] $\Omega(N_1,N_2) = \dfrac{1}{N_2!} \displaystyle\prod_{j=1}^{N_2} \prod_{i=1}^{r} v_{j,i}$

$$= \dfrac{1}{N_2!} \prod_{j=1}^{N_2} \left\{ [N - r(j - 1)] \right.$$

$$\left. \times \dfrac{[N - r(j - 1)]^{r-1}\rho}{\displaystyle\prod_{t=1}^{z} \left[N - \left(1 - \left(\dfrac{q}{r} \right)^t \right) r(j - 1) \right]^{\alpha^{(t)}}} \right\}$$

where ρ is the product of all Y_i values of one solute molecules (for $i > 1$) and $\alpha^{(t)}$ is the number of segments of a solute molecule which, when placed on the lattice, have already t neighbors occupied by segments of that same solute molecule. The sequence of placing segments on the lattice must be such that preference is always given to that segment which, when placed on the lattice, has the largest number of neighbors which are previously-placed segments. Two conservation equations relate the parameters $\alpha^{(t)}$ to the parameters q and t. These are eqs. 5 and 6 in the text.

We can now calculate the combinatorial entropy of mixing from

[A6] $\dfrac{\Delta S^c}{k} = \ln \dfrac{\Omega(N_1,N_2)}{\Omega(0,N_2)\Omega(N_1,0)}$

where k is Boltzmann's constant. To do so we first apply Stirling's approximation for large N to eq. A5 and obtain

$$[A7] \quad \ln \Omega(N_1, N_2) = N_2 \ln \rho - N_2 \ln N_2$$
$$- N_1 \ln N_1 + N \ln N$$
$$+ \sum_{t=1}^{z} \frac{\alpha^{(t)}}{\left(1 - \left(\frac{q}{r}\right)^t\right) r}$$
$$\times \left\{ \left[N - \left(1 - \left(\frac{q}{r}\right)^t\right) r N_2 \right] \right.$$
$$\times \ln \left[N - \left(1 - \left(\frac{q}{r}\right)^t\right) r N_2 \right] - N \ln N \right\}$$

Substitution of $A7$ into eq. $A6$ gives eq. 4 in the text.

The parameter $\alpha^{(t)}$ represents the number of segments of a solute molecule which, upon being placed in the lattice, have t nearest neighbors occupied by other segments of the same molecule. The integer t varies from unity to z.

To illustrate the calculation of $\alpha^{(t)}$, we consider a two-dimensional example. Suppose we have a two-dimensional molecule of 20 sites; the molecule is a rectangle 4 sites wide and 5 sites long, as shown in Fig. 7. We assume that for a two-dimensional lattice $z = 4$; thus, for example, site 8 has four nearest neighbors (3, 7, 9, and 13). The rectangular molecule has $r = 20$ and qz, the number of nearest-neighbor external contacts, is 18 (one external contact each for sites 2, 3, 4, 10, 15, 19, 18, 17, 11, and 6; two external contacts for sites 1, 5, 20, and 16).

We place the segments on the lattice such that each segment placed must have the largest possible number of previously placed segments as neighbors. First we place segment 1. Then we

1	2	3	4	5
6	7	8	9	10
11	12	13	14	15
16	17	18	19	20

FIG. 7. Two dimensional molecule occupying 20 sites.

place segments 2, 3, 4, and 5, and then segment 6. In each of these five placements, the segment placed has one nearest neighbor. Next we could place segment 11 or 10 or 7 or 8 or 9. We must choose segment 7 because it will be placed with two neighbors while the others would be placed with only one neighbor. After 7, comes 8, 9, and 10, each with two neighbors. Next comes 11 (with one neighbor) followed by 12, 13, 14, and 15 (with two neighbors). Finally, we place 16 (one neighbor) followed by 17, 18, 19, and 20 (two neighbors).

All placements (for $i > 1$) have either one or two neighbors. Thus $\alpha^{(3)} = \alpha^{(4)} = 0$. As indicated by the sequence of the previous paragraph

$$\alpha^{(1)} = 7 \quad \text{(Segments 2, 3, 4, 5, 6, 11, and 16)}$$
$$\alpha^{(2)} = 12 \quad \text{(Segments 7, 8, 9, 10, 12, 13, 14, 15, 17, 18, 19, and 20)}$$

It can readily be shown that these values for $\alpha^{(t)}$ satisfy eqs. 5 and 6 in the text:

$$\sum_{t=1}^{z} \alpha^{(t)} = r - 1 = 19$$
$$\sum_{t=1}^{z} t\alpha^{(t)} = \frac{z}{2}(r - q) = 31$$

Extension to Multicomponent Mixtures

Unfortunately there is no unambiguous way to generalize eq. 4 in the text to mixtures containing more than two components. For a mixture of n components the value of $\Omega(N_1, N_2, ... N_n)$ depends upon the sequence 1, 2, ...n used for placing the molecules on the lattice, as pointed out long ago by Miller (20). Generalization can be achieved only in the special case where $\alpha^{(t)} r^{-1} [1 - (q/r)^{(t)}]^{-1}$ is the same for all molecules.

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