CONFIGURATIONS OF CLOSED RING MOLECULES

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Introduction

1. An assembly which contains a number of species can be specified by the numbers of molecules of each species and its total interaction energy. If the molecules of the assembly are considered to be arranged to form a lattice, and interactions other than those between closest neighbours can be neglected, the interaction energy is determined by the number of closest neighbour pairs of each possible kind. In this case, the assembly can be specified by the number N_i of molecules of each species i and by the quantities X_{ij}, where zX_{ij} is the number of closest neighbour pairs of sites of which one is occupied by a molecule of species i and the other by a molecule of species j. A quantity X_{ii} can also be introduced and defined by the fact that zX_{ii} is the number of closest neighbour pairs of sites each of which is occupied by a molecule of species i, but excluding those cases in which the pair of sites is occupied by adjacent groups of the same molecule.

The partition function for such an assembly includes a term which is usually, and conveniently, called the combinatory factor and which specifies the number of ways in which the given numbers of molecules of the various species can be arranged. In the general case, this is the number of ways of arranging N_i molecules of the species i (for all i) so that there are zX_{ij} closest neighbour i-j pairs; this factor can be denoted by $g(N_i, X_{ij})$. For the particular case in which all the energies of mixing are zero it is sufficient to determine the number of arrangements of N_i molecules of species i (for all i) since all of these arrangements have the same interaction energy irrespective of the numbers of closest neighbour pairs of the various possible kinds. This factor can be denoted by $g(N_i)$, and, in fact, we have

$$g(N_i) = \sum_{X_{ij}} g(N_i, X_{ij}). \tag{1}$$

It is possible that a number (say N_v) of sites on the lattice may be vacant and, corresponding to these unoccupied sites, there would be zX_{vi} (all i) pairs of closest neighbour sites one of which is occupied by a molecule of species i and the other of which is vacant. It is unnecessary to introduce this possibility explicitly since unoccupied sites contribute the same kind of terms to the combinatory factor as do an equal number of molecules each of which occupies only one site.

For mixtures in which the molecules of each species are spherical in shape and are of roughly the same size, the determination of the appropriate combinatory factor is comparatively easy, and is even trivial in the case of a mixture of any number of species with zero energies of mixing. For mixtures of molecules of different sizes and shapes, however, detailed analysis is required to determine the combinatory factor. By using the Bethe technique to determine the equilibrium conditions for the case in which each

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molecule of one kind occupied two closest neighbour sites and of the other occupied only one site, Chang (1) obtained a differential equation which could be solved to give $g(N_1, N_2)$ in this case. The same method of approach, which has been described in detail elsewhere (2), was used by the author (3) to consider mixtures in which each molecule of one kind occupied three sites, adjacent groups of such a trimer molecule occupying closest neighbour sites, while each molecule of the other kind occupied only one site. From the expressions which were obtained in these cases it was possible to write down a formula (4) for the combinatory factor for a mixture of simple chain molecules and simple molecules in which each chain molecule contained r groups and occupied r sites in such a way that adjacent groups occupied closest neighbour sites. This expression was simply a general formula to which the particular formulae, which had been obtained in the simple cases already studied, adhered. Subsequently, Guggenheim (5) derived this formula by kinetic arguments using the principle of detailed balancing and also generalized the expression to mixtures of any number of species which consisted of simple, simple chain or branched chain molecules, but closed ring molecules were specifically excluded. For mixtures with non-zero energies of mixing, Orr (6) gave an expression for the appropriate combinatory factor for mixtures containing simple chain molecules. The generalization of this to mixtures containing any number of species and to include branched chain molecules was given by Guggenheim (7). Again, closed ring molecules are excluded from the formula which he gave for $g(N_i, X_{ij})$.

The purpose of the present paper is to determine expressions for these combinatory factors when one or more of the species contained in the mixture consist of closed ring molecules.

Physical significance of the parameters q

2. In the formulae which have been obtained previously there occurs a parameter q; the value of this parameter as it occurs in the formulae applicable to simple or branched chain molecules will be denoted by q', where q' is given explicitly by the equation

$$(r-q')z = 2(r-1). \tag{2}$$

Originally, for mixtures of trimer and simple molecules, the author defined this parameter by the fact that z times it is the number of sites which are closest neighbours to those sites which are occupied by a trimer molecule when it is constrained to lie along a straight line. It is true that this quantity is equal to zq' as defined by equation (2), but it appears that such a definition obscures the physical significance of the parameters q.

3. In examining discrepancies between the values of the thermodynamical functions of rubber-benzene mixtures determined by experiment and from the theory of liquid mixtures, the author considered a mixture of spherical molecules and of flat disk-shaped molecules. The formula which was obtained for the appropriate combinatory factor (8) conformed with the general formula which had been obtained previously for chain molecules, although it was quite clear that in the case of disk-shaped molecules zq was not the number of sites which were closest neighbours to those sites occupied by a disk-shaped molecule. The analysis which was used in examining this case was inadequate to distinguish between a disk-shaped molecule and a four-branched

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molecule. Further consideration showed that the *verbal* definition which had previously been given for q was inadequate not only, as had already been noted, for flexible simple chain molecules, but also for any branched chain molecule. The importance of this lay in the physical significance of the parameter q, for once this had been determined satisfactorily it was possible immediately to extend the earlier analysis to cover mixtures containing closed ring molecules.

4. It can easily be verified that zq' defined by equation (2) is the number of closest neighbour *pairs* which can be formed by the sites which are occupied by a simple chain or by a branched chain molecule with the remainder of the sites. In physical terms zq' can be described as the number of closest neighbour interactions into which a simple chain or a branched chain molecule enters. For a simple chain molecule which consists of r groups in all, there are $z-2$ closest neighbour interactions for each internal group and $z-1$ for each of the end-groups; thus, there are $(r-2)(z-2)+2(z-1) = rz-2r+2$ closest neighbour interactions in all. For a branched chain molecule there is one less interaction at the junction of each branch, but each branch introduces an additional 'end' group and so an additional interaction. Thus the total number of interactions for a branched chain molecule is the same as for a simple chain molecule and has the value given by equation (2). For a closed ring molecule, however, this no longer holds; and it is due to this fact that the formulae obtained by Guggenheim are inapplicable, as they stand, to mixtures which contain such molecules. The essential fact can be expressed by saying that a closed ring molecule has no 'end-groups'. Each group in a closed ring molecule gives rise to $z-2$ closest neighbour interactions; thus, the total number of closest neighbour interactions for a closed ring molecule is zq'', where q'' is given by

$$zq'' = r(z-2). \tag{3}$$

STATISTICAL RELATIONS

5. The way is now clear to remove the restriction which excludes closed ring molecules from the jurisdiction of Guggenheim's formulae for the combinatory factor. We consider a mixture which contains N_i molecules of species i (all i); each molecule of species i contains r_i groups and occupies r_i sites so that adjacent groups in the molecule occupy closest neighbour sites. We introduce a parameter q_i for each species; the physical significance of q_i is that a molecule of species i has zq_i closest neighbour interactions. We first obtain some results which are valid for all kinds of mixtures. It should be noted that for the present the precise numerical values of the parameters q_i are unimportant and play no part in the deduction of the results which follow.

The interactions formed by each molecule of species i must either be with another molecule of the same species (forming an i-i interaction) or with a molecule of another species (of which an i-j interaction is typical). In totalling all the interactions in which all the molecules of species i take part each of the former kind must be included twice and each of the latter kind must be included once. It therefore follows that the relations

$$2X_{ii} + \sum_k{}' X_{ik} = q_i N_i \quad (\text{all } i) \tag{4}$$

must hold. In addition, there are some pairs of closest neighbour sites which are occupied by adjacent groups of the *same* molecule; let zx_{ii} be the number of pairs of

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sites which are occupied by two adjacent groups of a molecule of the species i. We consider the r_i sites which are occupied by a molecule of species i. Each site has z closest neighbour sites. The quantity zr_i will include all the interactions of this molecule with other molecules once or twice according as the other molecule is not or is of the same species i, and it will also include twice the number of pairs of sites occupied by adjacent groups in the given molecule of species i. Thus the relations

$$2x_{ii} + 2X_{ii} + \sum_k{}' X_{ik} = r_i N_i \quad (\text{all } i) \tag{5}$$

must also hold. It must be emphasized that equations (4) and (5) are valid for mixtures of all kinds of molecules whether they consist of simple or branched chains or of closed rings. From equations (4) and (5) it follows that

$$2x_{ii} = (r_i - q_i) N_i \quad (\text{all } i) \tag{6}$$

for all types of molecules. The quantities x_{ii} could easily be expressed in terms of the r_i alone, but these expressions would have different forms according to the kind of molecule; the virtue of equation (6) is that it gives a value for x_{ii} which is valid for all the kinds of molecule under consideration.

Random distribution

6. For mixtures in which all the energies of mixing are zero there is a random distribution of molecules on the lattice. The total number of closest neighbour interactions in which molecules of species i are partners depends on both the number of molecules of this species and on the number of closest neighbour interactions which each molecule of this species yields. Thus the relative frequency of i-j interactions, for all values of i and j, is $q_i q_j N_i N_j$. The relative frequencies of various typical modes of occupation of a given pair of closest neighbour sites (conveniently referred to as A and B) is given in Table 1. The definitions of X_{ii} and X_{ij} imply that the frequency of occupation of the

Table 1. *Relative frequencies of typical modes of occupation of a given pair of sites*

	Mode of occupation	Relative frequency
α	Both by i (excluding adjacent groups of the same i)	$q_i^2 N_i^2$
β	A by i, B by j	$q_i q_j N_i N_j$
γ	A by j, B by i	$q_i q_j N_i N_j$
δ	By adjacent groups of the same molecule i	$(r_i - q_i) N_i \sum_k q_k N_k$

given pair of sites in the mode α is proportional to X_{ii} and that the sum of the frequencies of occupation in the modes β and γ is proportional to X_{ij}. X_{ij} is proportional to the sum of the frequencies of occupation in the modes β and γ because these are the two possible ways in which the given pair of sites can yield an i-j pair. It therefore follows from the equations (4) and Table 1 that

$$X_{ii} = \frac{q_i^2 N_i^2}{2\sum_k q_k N_k} \quad (\text{all } i), \qquad X_{ij} = \frac{q_i q_j N_i N_j}{\sum_k q_k N_k} \quad (\text{all } i \text{ and } j \text{ with } i \neq j). \tag{7}$$

It will be noticed that the last line of Table 1, referring to the mode of occupation δ, follows immediately from equations (6) and (7).

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7. The probability that a given site, say A, is occupied by a molecule of species i is $r_i N_i / \sum_k r_k N_k$. All the ways in which site A can be occupied by a molecule of species i are included in the modes of occupation indicated by α, β and δ in Table 1. In this connexion the mode of occupation β is regarded as typical of all modes in which site A is occupied by a molecule of species i and site B is occupied by a molecule of any species other than i. Thus when we are considering all the ways in which site A can be occupied by a molecule of species i we have to consider the mode β for all values of j not equal to i. It follows therefore that the probabilities of the occupation of a given pair of sites in the various modes indicated are λ times the relative frequencies given in Table 1 where the constant λ is given by the equation

$$\lambda(\sum_k q_k N_k)(\sum_k r_k N_k) = 1.$$

Without further elaboration it is therefore clear that the probabilities of occupation of a pair of sites in various typical ways for a mixture containing any number of species consisting of simple, simple chain, branched chain or closed ring molecules are given in Table 2. It will be recalled that in these formulae the parameters q_i are defined

Table 2. *Probabilities of occupation of a given pair of sites in various ways*

	Mode of occupation	Probability
α	Both by i (excluding adjacent groups of the same molecule i)	$\dfrac{q_i^2 N_i^2}{\sum_k q_k N_k \sum_k r_k N_k}$
β	A by i, B by j	$\dfrac{q_i q_j N_i N_j}{\sum_k q_k N_k \sum_k r_k N_k}$
γ	A by j, B by i	$\dfrac{q_i q_j N_i N_j}{\sum_k q_k N_k \sum_k r_k N_k}$
δ	By adjacent groups of the same molecule i	$\dfrac{(r_i - q_i) N_i}{\sum_k r_k N_k}$

by the fact that zq_i is the number of closest neighbour interactions of a molecule of the species i, and that its value has to be determined according to the type of molecule. It should be emphasized again that these results follow from the physical meanings of the various parameters which have been introduced and do not depend upon the particular values which any of these parameters assume for any particular kind of molecule. We have already seen that for simple chain or branched chain molecules the parameters q_i have the values q_i' given by equation (2) while for closed ring molecules they have the values q_i'' given by equation (3).

Allowing for the fact that his expressions are written down for a binary mixture in which each molecule of one of the species occupies only one site so that (say) $r_j = 1 = q_j$, the values given in Table 2 are formally the same as equations (3·1)–(3·5) given by Guggenheim (5) for simple or branched chain molecules, and an equation,

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corresponding to his equation (3·6), and formally identical with it, can be formed from them. The principle of detailed balancing could be applied in a fashion similar to that in which Guggenheim has used it, and it would necessarily lead to equations which are *formally* identical with those which were obtained by Guggenheim ((5), equation (8·2)) for simple or branched chain molecules. Thus it follows that for mixtures containing closed ring as well as simple or branched chain molecules, the number of arrangements of a random distribution of N_i molecules of species i (all i) is given by

$$\log g(N_i) = \frac{r-1}{r-q}\log\left(\sum_i q_i N_i\right)! - \sum_i \log N_i! - \frac{q-1}{r-1}\log\left(\sum_i r_i N_i\right)! + \sum_i N_i \log \rho_i, \tag{8}$$

where zq_i is the number of closest neighbour pairs which can be formed by those sites which are occupied by a molecule of species i with the rest of the sites and ρ_i is the number of distinct configurations of a molecule of species i when one of its groups is fixed on a given site. In every case each parameter q_i must be given the value appropriate to the kind of molecule to which it refers. That is, for each species which consists of simple chain or branched chain molecules the value q_i' given by equation (2) is to be substituted for the corresponding parameter q_i, while for each species which consists of closed ring molecules the value q_i'' given by equation (3) is substituted for the corresponding parameter q_i.

8. It is therefore concluded that the combinatory factor appropriate to a random distribution of molecules is given *formally* by Guggenheim's equation in all cases but that the parameters q_i which occur in this equation have different values according as they refer to closed ring or to simple and branched chain molecules; the appropriate values of these parameters are given in equations (2) and (3) above.

Mixtures with non-zero energies of mixing

9. We now consider mixtures with non-zero energies of mixing. Guggenheim (7) has set down the conditions which the appropriate combinatory factor $g(N_i, X_{ij})$ must satisfy. These conditions are sufficient to enable the correct form of $g(N_i, X_{ij})$ to be deduced unambiguously, in terms of $g(N_i)$, even though its direct determination would be prohibitively difficult. The conditions which have to be satisfied by $g(N_i, X_{ij})$ must be satisfied independently of the kinds of molecules of which the mixture is composed; in particular, these conditions must be satisfied independently of whether the mixture contains simple and branched chain molecules or closed ring molecules. It requires no further elaboration to see that Guggenheim's formulae ((7), equations (5·1) and (5·5)) are still *formally* valid when the mixture contains closed ring molecules provided that in applying the formulae the appropriate values of the parameters q_i are substituted.

10. It is concluded that in the case of mixtures with non-zero energies of mixing the formula given by Guggenheim for $g(N_i, X_{ij})$ is *formally* valid in all cases, provided that for species which consist of simple or branched chain molecules the value q_i' given

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by equation (2) is substituted for the corresponding parameters q_i, while for species which consist of closed ring molecules the value q_i'' given by equation (3) is substituted for the corresponding parameters q_i.

Note added in proof. It should be noted that in his equation (8·2) of (5), Guggenheim has substituted the value of q appropriate to simple or branched chain molecules in the coefficients of the various terms. This is also the case with regard to equation (5·5) of (7). In the reference to Guggenheim's equations in both §§ 7 and 9, the equations in the form they have, before any such substitution has been carried out, are meant. For the case of a random mixture this is given in our equation (8), which is analogous to equation (5·8) of (5).

SUMMARY

The physical significance of the parameters which appear in the combinatory factors $g(N_i)$ and $g(N_i, X_{ij})$ in the statistical mechanics of mixtures is examined. Hitherto, closed ring molecules have been excluded from the jurisdiction of the formulae for these combinatory factors. The means by which this restriction on the validity of the formulae can be removed is indicated. It is concluded that the equations given by Guggenheim are *formally* applicable in all cases provided that appropriate values, which differ according as the molecules are simple and branched chain or closed ring molecules, are substituted for certain parameters which occur in the equations.

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