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tween the mass susceptibilities of the vapor and liquid would appear to require inter-molecular forces in the liquid state sufficient to produce a substantial alteration of electronic orbits. Certainly, for liquids composed of symmetrical molecules such as benzene and carbon tetrachloride it would be difficult to account for inter-molecular forces of a type to effect importantly the susceptibility. It is noteworthy that neither Oxley¹⁷ nor Cabrera and Fahlenbrach¹⁸ found any detectible difference in the magnetic susceptibilities of benzene in the crystalline and liquid states, though small differences were found for other organic substances. Cabrera

¹⁷ A. E. Oxley, Phil. Trans. **214A**, 109 (1914).

¹⁸ B. Cabrera and H. Fahlenbrach, Zeits. f. Physik **85**, 568 (1933); **89**, 682 (1934).

and Fahlenbrach found that in general the change in susceptibility in passing from the crystalline to the liquid state was smaller the smaller the electric dipole moment of the molecules. Further evidence that inter-molecular forces do not have much effect on the susceptibility of non-polar liquids is given by measurements on non-polar liquid mixtures¹⁸⁻¹⁹ which have shown that the additivity principle of susceptibility holds to within 0.5 percent. The results of the present investigation are consistent with the hypotheses that for benzene and carbon tetrachloride there is negligible difference between the mass susceptibilities in the vapor and liquid states.

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Statistical Mechanics of Binary Mixtures

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The possibility of specifying both the enumeration of the complexions of an assembly and the evaluation of its configurational energy in terms of the numbers of closest neighbor pairs of sites of various kinds, without introducing parameters explicitly to specify the occupation of individual sites, is considered. The formula obtained on such a basis by Alfrey and Mark is examined. Their work depends on an assumption which at first sight appears plausible. Furthermore, if this assumption could be justified, it would imply that the quasi-chemical equation, which has been introduced in the theory of regular assemblies as an *ad hoc* assumption, could be derived from the Boltzmann equilibrium law and the elementary formulas

of algebraic combinations. If a pair of closest neighbor sites of which one is occupied by a molecule of species i and the other by a molecule of species j is called an $i-j$ pair, then it is shown that the assumption made by Alfrey and Mark is equivalent to neglecting the restrictions on the free allocation (amongst the $\frac{1}{2}zN$ pairs available in all) of pairs of different kinds which are inherent in the interconnections of an assembly of interacting particles. It is concluded, therefore, that the assumption in question is unjustified and leads to an incorrect result, and that consequently the quasi-chemical equation is correctly introduced as an *ad hoc* assumption.

1. INTRODUCTION

THE basic problem in the determination of the equilibrium properties of an assembly of interacting particles is the evaluation of the appropriate combinatorial factor which is necessary in order to set up the partition function for the assembly. Much work has been devoted to this question. A detailed discussion of it can be dispensed with here as reviews^{1,2} have appeared

¹ F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938).

² G. H. Wannier, Rev. Mod. Phys. **17**, 50 (1945).

elsewhere. We consider a simple binary mixture containing N_i molecules of a species i and N_j molecules of a species j on an array of N ($=N_i+N_j$) sites formed by the points of a regular lattice. It is assumed further that the molecules of each species are of about the same size and roughly spherical in shape, and that the interaction energy of the assembly can be expressed as the sum of closest neighbor contributions. If X_{ii} , X_{ij} , and X_{jj} , respectively, are the numbers of $i-i$, $i-j$, and $j-j$ closest

neighbor pairs, then the interaction energy is given by

$$E = X_{ii}V_{ii} + X_{ij}V_{ij} + X_{jj}V_{jj}$$

where V_{ii} , V_{ij} , and V_{jj} , respectively, are the interaction energies of a pair of particles of the kind denoted by the suffixes. With suitable choice of the energy zero this can be written as

$$E = X_{ij}w_{ij} \quad (1)$$

where w_{ij} is the energy of mixing. The partition function can then be written as

$$Z = \sum_{X_{ij}} g(N_i, N_j, X_{ij}) \exp(-X_{ij}w_{ij}/kT) b_i^{N_i} b_j^{N_j} \quad (2)$$

where b_i , b_j are terms which include factors to take account of the partition functions corresponding to the internal degrees of freedom of the molecules and of their effective free volumes. In this expression $g(N_i, N_j, X_{ij})$ is the number of distinct configurations of the given numbers of molecules of each kind in which there are X_{ij} closest neighbor pairs of the kind $i-j$. Certain simple relations exist between the various parameters N and X ; we have, in fact, made use of these relations in obtaining an expression for the energy which depends only on X_{ij} . These relations are

$$2X_{ii} + X_{ij} = zN_i, \quad (3)$$

$$2X_{ij} + X_{jj} = zN_j. \quad (4)$$

These relations also imply that of the five quantities which have been introduced to specify the system, only three of them are independent. It therefore follows that the partition function could be written in terms of X_{ii} , X_{ij} , and X_{jj} equally well as in terms of N_i , N_j , and X_{ij} . It was pointed out by Alfrey and Mark³ that the difficulty of evaluating the combinatory factor lies in the fact that ordinarily different variables are used for enumerating the complexions of the assembly and for determining its configurational energy. Whereas the distinguishable configurations of the assembly are specified by the occupation of individual lattice sites, the configurational energy arises from closest neighbor (or more distant) interactions and has to be determined by the specification of closest

neighbor (or more distant) pairs of sites. It therefore follows that if a means could be found by which both the evaluation of the configurational energy and the enumeration of the complexions of the assembly could be carried out in terms of one and the same kind of variable (that is, by the specification either of pairs of sites or of the occupation of individual sites, but not both) one could hope greatly to simplify this task. It is clear that the configurational energy can be expressed only in terms of the specification of pairs of sites; can, then, the distinguishable complexions of the assembly also be expressed in terms of these variables? This was attempted by Alfrey and Mark³ with the help of an assumption, which is described in Section 2 below (Eq. (7)), concerning the occurrence of closest neighbor pairs of different kinds. The purpose of the present note is to discuss this assumption and the reasons that the specification of pairs of sites fails to provide an alternative method, far less a simpler one, than those already proposed⁴⁻⁸ for evaluating the combinatory factors appropriate in the study of cooperative phenomena and of mixtures which contain polymer molecules.

2. STATISTICAL FORMULAS

We first examine the procedure adopted by Alfrey and Mark. They consider a set of $N/2$ numbered pairs of closest neighbor lattice sites which are chosen in such a way that each site of the lattice belongs to one and to only one pair. If among the selected set of $N/2$ closest neighbor pairs there are X $i-j$ pairs, then the number of $i-i$ and $j-j$ pairs are $\frac{1}{2}(N_i - X)$ and $\frac{1}{2}(N_j - X)$, respectively. The number of configurations is then calculated by considering (i) the number of ways of arranging X indistinguishable elements of one kind, $\frac{1}{2}(N_i - X)$ indistinguishable elements of a second type, and $\frac{1}{2}(N_j - X)$ indistinguishable elements of a third type among the $\frac{1}{2}N$ available places, and (ii) by allowing for the fact that each $i-j$ pair can be arranged in two distinct ways within its reference position. On this basis, they give, for the combinatory factor,

⁴ T. S. Chang, Proc. Camb. Phil. Soc. **35**, 265 (1939).

⁵ A. R. Miller, Proc. Camb. Phil. Soc. **39**, 54 (1943).

⁶ P. J. Flory, J. Chem. Phys. **10**, 51 (1942).

⁷ M. L. Huggins, J. Phys. Chem. **46**, 151 (1942).

⁸ E. A. Guggenheim, Proc. Roy. Soc. **A183**, 203 (1944).

³ T. Alfrey and H. Mark, J. Chem. Phys. **10**, 303 (1942).

an expression

$$\phi(X) = \frac{(N/2)! 2^X}{X! \{\frac{1}{2}(N_i - X)\}! \{\frac{1}{2}(N_j - X)\}!}, \quad (5)$$

and, correspondingly, for the partition function

$$Z = \sum_X \phi(X) \exp(-zXw_{ij}/kT), \quad (6)$$

apart from factors allowing for the internal motions of the molecules.

This treatment involves the assumption that if in the selected group of $\frac{1}{2}N$ closest neighbor pairs there are X pairs of the kind $i-j$, then in the complete assembly the total number of $i-j$ pairs is exactly zX . This also implies that the total numbers of $i-i$ and $j-j$ pairs are $\frac{1}{2}z(N_i - X)$ and $\frac{1}{2}z(N_j - X)$, respectively. In fact, in terms of our notation, it is assumed that

$$\left. \begin{aligned} zX &= X_{ij} \\ \frac{1}{2}z(N_i - X) &= X_{ii} = \frac{1}{2}(zN_i - X_{ij}) \\ \frac{1}{2}z(N_j - X) &= X_{jj} = \frac{1}{2}(zN_j - X_{ij}) \end{aligned} \right\}. \quad (7)$$

This assumption is essential in the treatment given by Alfrey and Mark for two reasons: (i) In order that the interaction energy, which we have seen is equal to $X_{ij}w_{ij}$, can be expressed in terms of the parameter X which they introduce, namely as zXw_{ij} . This is the specific form in which Alfrey and Mark express this assumption in Eq. (7) of their paper. (ii) It is also necessary because their treatment assumes that the particular arrangement of particles on the lattice in which there are X_{ii} , X_{ij} , and X_{jj} pairs of $i-i$, $i-j$, and $j-j$ closest neighbors, respectively, is equivalent to, and can be described precisely by, the allocation of X , $\frac{1}{2}(N_i - X)$, and $\frac{1}{2}(N_j - X)$, respectively, $i-j$, $i-i$, and $j-j$, pairs among the group of $\frac{1}{2}N$ pairs selected in the way specified. This is considered further in the discussion below (Eqs. (9) and (10)).

In fact, from a lattice of N sites in which no closest neighbors of any site are also closest neighbors of one another, a group of $\frac{1}{2}N$ closest neighbor pairs which are such that every lattice point belongs to one and to only one pair can be chosen in $\{(z-1)^{z-1}/z^{z-2}\}^{\frac{1}{2}N}$ different ways.⁹ While, at first sight, it appears possible that the assumption made by Alfrey and Mark might be

valid (or nearly so) for a sufficient number of these possible selections of the group of pairs to enable the method to give a reasonable estimate of the combinatory factor, they offer no justification of it. Furthermore, it is difficult to see how any formal justification of their assumption could be constructed. When the problem is examined from a somewhat different viewpoint, the nature and implications of the assumption made by Alfrey and Mark become clearer, and it is seen to be far from justified.

3. DISCUSSION

It has been noted above that X_{ii} , X_{ij} , and X_{jj} can be taken as the three independent parameters which are used to specify the assembly. With this specification, the determination of the combinatory factor reduces to the evaluation of the number of ways in which X_{ii} indistinguishable elements of one type, X_{ij} indistinguishable elements of a second type, and X_{jj} indistinguishable elements of a third type can be distributed among $\frac{1}{2}zN$ available pairs, *subject to any restrictions inherent in the interconnections of the assembly*. The closing phrase indicates where the difficulty lies. A little reflection shows that if, from the total number of available pairs, X_{ii} are chosen for the $i-i$ closest neighbors, then not all the remaining $(\frac{1}{2}zN - X_{ii})$ pairs can be utilized to accommodate a $j-j$ pair, for it is inherent in the interconnections of the pairs that a large number of those now remaining can accommodate only an $i-j$ pair. Furthermore, the position is not helped by selecting the pairs for the $i-j$ closest neighbor pairs second, for unless severe restrictions on our freedom of choice of the required number of pairs are accepted, we would be left finally with a large number of pairs which could not accommodate a $j-j$ closest neighbor pair and at the same time an insufficient number of possible pairs to accommodate all the $j-j$ closest neighbors. In passing it should also be noted that the precise specification of these restrictions, if not impossible, is certainly neither simple nor straightforward. It appears likely that it is in this restriction on the free choice of elements to accommodate the closest neighbor pairs of different kinds that the implications of the assumption made by Alfrey and Mark are to be found.

⁹ A. R. Miller, Proc. Camb. Phil. Soc. **38**, 108 (1942), Eq. (16).

We now proceed to show that this is, in fact, the case.

Stirling's theorem for the asymptotic behavior of a factorial ensures that for large values of r and s and a constant α then

$$\alpha \log \left[\frac{(r+s)!}{r!s!} \right] = \log \left[\frac{\{\alpha(r+s)\}!}{(\alpha r)!(\alpha s)!} \right]. \quad (8)$$

If the three Eqs. (7) are valid, that is, if the assumption made by Alfrey and Mark can be justified, it then follows that

$$\left[\frac{(N/2)!}{X! \left\{ \frac{1}{2}(N_i - X) \right\}! \left\{ \frac{1}{2}(N_j - X) \right\}!} \right]^z \\ = \frac{(zN/2)!}{X_{ii}! \left\{ \frac{1}{2}(zN_i - X_{ij}) \right\}! \left\{ \frac{1}{2}(zN_j - X_{ij}) \right\}!} \quad (9)$$

The right-hand member of Eq. (9) reduces to

$$\frac{(zN/2)!}{X_{ii}! X_{ij}! X_{jj}!}, \quad (10)$$

which is precisely the number of ways of arranging X_{ii} elements of one kind, X_{ij} elements of a second kind, and X_{jj} elements of a third kind among $\frac{1}{2}zN$ positions *without any restriction whatsoever*. Thus, the assumption made by Alfrey and Mark amounts to neglecting the restrictions on the allocation of the closest neighbor pairs of different kinds which are inherent in the arrangements of two or more species of molecules on a regular lattice. It will thus give a value for the combinatory factor which is far from the correct value, being, in fact, far too large.

In the case of polymer molecules, each of which has to be regarded as occupying several sites on the lattice, the restrictions on the distribution of the pairs are even more severe. For each polymer molecule which consists of r units or submolecules there are x pairs of closest neighbor sites which are occupied by adjacent units of the polymer molecule, where¹⁰

$$2x = z(r - q)N_i. \quad (11)$$

In this equation q is determined by the fact that zq is the number of closest neighbor pairs of sites which are formed by the sites which are occupied

by a given polymer molecule and the remaining sites of the lattice. In this case the various kinds of pairs would have to be arranged among the $\frac{1}{2}zN$ available positions so that the x "internal pairs" corresponding to each polymer molecule would be allotted to adjacent closest neighbor pairs, since they define a polymer molecule. Without further elaboration it is clear that in this case one cannot specify the occupation of a group of sites by a polymer molecule without specifying the occupation of each individual lattice site. It therefore follows that the number of configurations of the assembly cannot be determined by the specification of closest neighbor pairs of sites alone.

A value for $g(N_i, N_j, X_{ij})$ in the case of a binary mixture of simple molecules was given by Chang;⁵ his formula is included in the general formula given by Guggenheim.¹¹ For a binary mixture of simple molecules, their result can be written,

$$g(N_i, N_j, X_{ij}) = \frac{\{N_i!N_j!\}^{(z-1)}}{(N!)^{\frac{1}{2}z-1} \{(N_i - X_{ij})!\}^{\frac{1}{2}z} \{X_{ij}!\}^z \{(N_j - X_{ij})!\}^{\frac{1}{2}z}} \quad (12)$$

where zX_{ij} is defined as the total number of $i-j$ interactions. If this formula is compared with the value given by Alfrey and Mark (Eq. (5)) it indicates that their value is too large by a factor of the order of

$$\frac{\{N_i!N_j!\}^{z-1}}{\{N!\}^{\frac{1}{2}z}}. \quad (13)$$

There is one other point to be noted. The most probable value of X can be obtained by maximizing the general term in the partition function. If Stirling's approximation be used and the expression given by Alfrey and Mark for $\phi(X)$ (Eq. (5)) be differentiated with respect to X and the derivative equated to zero, we get

$$\bar{X}^2 = (N_i - \bar{X})(N_j - \bar{X}) \exp(-2w_{ij}/kT). \quad (14)$$

This equation has the familiar form of the equation of quasi-chemical equilibrium. It was originally introduced by Guggenheim¹² as providing a more exact approximation than that

¹¹ E. A. Guggenheim, Proc. Roy. Soc. **A183**, 213 (1944), Eqs. (5.5) and (8.1).

¹² E. A. Guggenheim, Proc. Roy. Soc. **A148**, 304 (1935).

¹⁰ A. R. Miller, Proc. Camb. Phil. Soc. (1947) (to be published) Eq. (6).

which had been used previously in the theory of solutions. It is, however, an *ad hoc* assumption based on analogy with the equation of equilibrium for a chemical reaction. It was the fact that it could be derived from the formula which was given by Alfrey and Mark for $\phi(X)$ which originally led me to look more closely into the nature of the apparently innocent assumption on which their argument is based. For, if it were justified, it would have meant that Eq. (14) followed simply from the Boltzmann equilibrium law and the elementary formulas of algebraic combinations. In view of the way in which this equation of quasi-chemical equilibrium had been introduced in other applications,^{13,14} it hardly seemed possible that this could be so. The foregoing analysis confirms the correctness of this scepticism.

¹³ E. A. Guggenheim, Proc. Roy. Soc. **A169**, 134 (1938).

¹⁴ R. H. Fowler and E. A. Guggenheim, Proc. Roy. Soc. **A174**, 189 (1940).

4. CONCLUSIONS

It is concluded that the assumption made by Alfrey and Mark amounts to neglecting the restrictions on the free allocation of closest neighbor pairs of different kinds, which are inherent in the interconnections of an assembly of interacting particles of different kinds, and leads to an incorrect value for the combinatory factor. It also appears that the combinatory factors, appropriate both for a cooperative assembly and for a mixture containing polymer molecules, cannot be determined by the specification of pairs of sites alone without specifying the occupation of each individual lattice site. It is also shown that the quasi-chemical equation, which would be implied by Boltzmann's distribution law and the elementary formulae of algebraic combinations, if the assumption made by Alfrey and Mark could be justified, is correctly introduced as an *ad hoc* assumption.