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## The Entropy of Mixing of Binary Liquid Mixtures\*

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Three factors which may contribute to the excess entropy of mixing of binary solutions have been explored. These are the relative volumes of the molecules, the spatial distribution of the molecules about a given reference molecule, and the lack of randomness of the orientational distribution of the molecules about a reference molecule. Of these, the spatial distribution, which depends upon the energy of mixing, is the smallest. It yields a negative value for the excess entropy and becomes zero at infinite dilution. The effect of differences in the volumes of the molecules of the components is positive and may be appreciable. The greatest effect is obtained from the orientational distribution. An estimation of the lack of randomness in this distribution for the pure components is obtained from the differences of the entropies of evaporation of the components and that of argon compared

under corresponding conditions. This difference is positive and is comparable, at least in order of magnitude, to the observed partial molal excess entropy of mixing at constant pressure and at infinite dilution for the six binary mixtures composed of benzene, carbon tetrachloride, cyclohexane, and methanol. The contribution of the change in the orientational distribution of the components to the partial molal excess entropy at infinite dilution is then considered to be caused by two effects, one in which the orientational distribution of the solute becomes completely random when dissolved in a solvent at infinite dilution and the other in which the orientational distribution of the solvent is changed by the substitution of a solute molecule for a solvent molecule. The individual behavior of each solvent is very evident and is consistent with its molecular structure.

NUMEROUS determinations of the thermodynamic functions of binary liquid mixtures indicate that the change of the entropy on mixing non-polar components either at constant volume or constant pressure is greater than that of an ideal solution over the entire range of composition. Further, the excess change of entropy on mixing a polar and a non-polar component may have all positive values, positive and negative values, or all negative values. It is the purpose of this paper to consider, semi-quantitatively, three effects which may enter in an explanation of this excess entropy change on mixing.

The formal distribution function of molecules about a given reference molecule, based on statistical mechanics, is a function of the position coordinates of the molecules and of the angular coordinates required to describe the relative orientation of the molecules. Because of the complexity and consequent lack of knowledge of the liquid state, it is necessary to consider in this paper that the distribution function may be factored into three terms, the first of which involves the repulsive forces of the molecules, the second of which depends primarily on the

attractive forces expressed in terms of the position coordinates alone, and the third of which involves the angular coordinates. Thus the excess change of the entropy on mixing, resulting from the difference of the entropy of the solution and that of the pure components, is discussed in terms of the relative volumes of the molecules, the spatial distribution, and the orientational distribution of the molecules about a reference molecule. It is evident that these three effects are not necessarily independent but yet it is unavoidable to consider them so. It appears that the smallest effect is that caused by the spatial distribution, the next is that caused by the differences in the volume of the molecules, and the largest is that caused by the orientational distribution. However, a generalization of the effect of the orientational distribution is not possible and indeed the partial molal excess entropy of mixing of a given solute at infinite dilution in various solvents depends upon the characteristic molecular structure of each solvent as well as on the properties of the solute.

### THE VOLUME EFFECT

The effect of differences in the sizes of the molecules on the behavior of solutions has been the subject of several investigations. Guggen-

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heim<sup>1</sup> has shown that there is no basis for believing that solutions formed of molecules differing greatly in size should obey Raoult's law. Fowler and Guggenheim<sup>2</sup> obtained the thermodynamic functions for a mixture of double and single molecules, and Miller<sup>3</sup> has treated the similar problem of a mixture of two molecules, one occupying three sites on a lattice structure and the other occupying only one site. Further, Flory,<sup>4</sup> Huggins,<sup>5</sup> and Guggenheim<sup>6</sup> have obtained expressions for the thermodynamic functions for mixtures of two kinds of molecules, one of which occupies  $r$  sites of a lattice structure and the other only one site. In these treatments the energy of mixing is taken as zero. The results of all of these treatments are similar in that the change of the entropy on mixing at constant volume may be expressed as

$$S_V^M = -n_1 R \ln z_1 - n_2 R \ln z_2 + \text{higher terms} \quad (1)$$

where  $z_1$  and  $z_2$  are the volume fractions of the components. In order to obtain at least an approximate value of this volume effect on the entropy of mixing, one is led, as Huggins has already suggested, to assume that the change of the entropy on mixing molecules of ordinary size is given by Eq. (1) with the neglect of the higher terms, thus ignoring also the conditions under which this equation was derived. With these assumptions, the molal excess entropy of mixing is given by

$$S_X^E = x_1 R \ln(x_1/z_1) + x_2 R \ln(x_2/z_2) \quad (2)$$

where  $x_1$  and  $x_2$  represent the mole fractions of the components. The values of the excess entropy have been calculated according to this equation at 30° for the six possible binary mixtures formed from the four substances, benzene, carbon tetrachloride, cyclohexane, and methanol. The molal volumes in cc used for these calculations at 30° are: benzene 89.939, cyclohexane, 109.427, carbon tetrachloride, 97.673, and methanol 40.983. The partial molal excess entropies of

TABLE I. Partial molal excess entropies of mixing at infinite dilution at 30°.

Solute	Solvent	Volume effect	Orientalional effect	Observed
C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>12</sub>	+0.04	+1.09	+1.29
	CCl <sub>4</sub>	+0.01		+0.14
	CH <sub>3</sub> OH	+0.81		-1.85
C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>	+0.04	+0.89	+1.81
	CCl <sub>4</sub>	+0.01		+0.25
	CH <sub>3</sub> OH	+1.37		-2.41 <sup>b</sup>
CCl <sub>4</sub>	C <sub>6</sub> H <sub>12</sub>	+0.01	+0.14	+0.22
	C <sub>6</sub> H <sub>6</sub>	+0.01		+0.14
	CH <sub>3</sub> OH	+1.02		-1.98
CH <sub>3</sub> OH	C <sub>6</sub> H <sub>12</sub>	+0.69	+7.47 <sup>a</sup>	+8.10 <sup>b</sup>
	C <sub>6</sub> H <sub>6</sub>	+0.48		+1.99
	CCl <sub>4</sub>	+0.57		-1.46

(a) The value given is at 35°.

(b) The value given is at 31°.

mixing at infinite dilution of one component in each of the other components are given in the third column of Table I. These values do not change markedly with temperature. It will be observed that for mixtures of benzene, carbon tetrachloride, and cyclohexane these values are very small and in fact almost negligible. However, for solutions containing methanol the values are much larger since the molal volume of methanol is less than one-half that of the other three substances. It should be noted, however, that the excess entropy of mixing because of differences in the relative volumes of the molecules is always positive according to Eq. (2).

### THE SPATIAL DISTRIBUTION

In the previous section the results were obtained assuming that the energy of mixing was zero. The effect of a non-zero energy of mixing has been considered by Orr<sup>7</sup> and Guggenheim,<sup>8</sup> who have obtained expressions for the thermodynamic functions of a mixture of non-polar molecules occupying different numbers of sites of a lattice. The results for the free energy are expressible in two parts, one independent of the energy of mixing and identical to that obtained when the energy of mixing is zero, and the other a function of the energy of mixing. Similar studies have been made by Rushbrooke<sup>9</sup> and Kirkwood<sup>10</sup> for mixtures consisting of rigid, spherical mole-

<sup>1</sup> E. A. Guggenheim, Trans. Faraday Soc. **33**, 151 (1937).

<sup>2</sup> Fowler and Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), p. 366.

<sup>3</sup> A. R. Miller, Proc. Camb. Phil. Soc. **38**, 109 (1942); *ibid.* **39**, 54 (1943).

<sup>4</sup> P. J. Flory, J. Chem. Phys. **10**, 51 (1942); **12**, 452 (1944); **13**, 453 (1945).

<sup>5</sup> M. L. Huggins, Ann. N. Y. Acad. Sci. **43**, 1 (1942).

<sup>6</sup> E. A. Guggenheim, Proc. Roy. Soc. London **A183**, 203 (1944).

<sup>7</sup> W. J. C. Orr, Trans. Faraday Soc. **40**, 320 (1944).

<sup>8</sup> E. A. Guggenheim, Proc. Roy. Soc. London **A183**, 213 (1944).

<sup>9</sup> G. S. Rushbrooke, Proc. Roy. Soc. London **A166**, 296 (1938).

<sup>10</sup> J. G. Kirkwood, J. Phys. Chem. **43**, 97 (1939).

cules of equal size. The qualitative results of all these studies are similar in that the contribution to the excess entropy of mixing at constant volume is always negative, independent of the sign of the energy of mixing. This contribution is also very small as shown in the results of Scatchard, Wood, and Mochel<sup>11-13</sup> for the three systems: benzene—carbon tetrachloride, carbon tetrachloride—cyclohexane, and cyclohexane—benzene. Orr estimates that this ordering of the spatial distribution of the molecules about a reference molecule is about 20 percent of the volume effect. If the mixtures contained polar molecules, the magnitude of this effect might be larger but it would presumably still be negative.

Since, in the following sections, emphasis will be placed on the partial molal excess entropy of mixing at infinite dilution, it should be pointed out here that the contribution of this ordering in the spatial distribution to the partial molal excess entropy becomes zero at infinite dilution.

#### THE ORIENTATIONAL DISTRIBUTION

Scatchard, Wood, and Mochel<sup>11</sup> explained the positive excess entropy of mixing in the benzene-cyclohexane system as being caused by a lack of complete randomness in orientation in the pure liquids which became complete in the mixtures. This explanation became untenable when the excess entropy of mixing of the benzene-carbon tetrachloride<sup>13</sup> and cyclohexane-carbon tetrachloride<sup>12</sup> systems had been determined, since the sum of the excess entropies of the latter two systems was about one-fourth that of the first system rather than equal to or greater than that of the first system. In the more clear cut cases in which methanol is used as a component<sup>14-16</sup> the positive excess entropy was explained as an increase in the randomness of orientation of the methanol molecules and the negative excess entropy as being caused by a decrease in the randomness of orientation of the non-polar

molecules and an ordering in the spatial distribution. The decrease of randomness of orientation is presumably of greater importance here.

It would seem that any positive excess entropy of mixing must be explained in terms of a lack of random orientation in the pure liquids and some estimation of this must be obtained. Pitzer<sup>17</sup> and Guggenheim<sup>18</sup> have shown that the law of corresponding states should be valid for liquids under certain conditions and that many liquids composed of simple molecules do follow this law. The conditions, in outline, are that (1) classical statistical mechanics are valid for the liquids, (2) the molecules are either spherical or freely rotating, (3) the intramolecular vibrations are the same in both the liquid and vapor phases, (4) the potential energy is a function of the distance only, and (5) the potential energy of a pair of molecules may be written as  $E = A\phi(R/R_0)$  where  $\phi$  is a universal function of the distance  $R$ , and  $A$  and  $R_0$  constants characteristic of each substance. According to this law the entropy of evaporation, the reduced vapor pressure, and the ratio of the molal volume of the gas to that of the liquid should be the same for all substances at the same reduced temperature. Any substance whose properties deviate from the above conditions would be expected to have an entropy of evaporation different from that of a "perfect" liquid whose properties do fit these conditions, when compared under corresponding changes of states. Only the first condition is expected to be satisfied by the four substances compared in this paper. When the second, fourth, and fifth conditions are not satisfied a preferred orientation in the liquid phase would be expected and the difference in the entropies of evaporation of the substance under consideration and that of the "perfect" liquid under corresponding conditions would be positive. Except for the effect of the third condition, which will be mentioned later, this difference should be a measure of the lack of randomness of the orientational distribution in the pure liquid. In an infinitely dilute solution of a solute in a solvent, the orientational distribution between the solute molecules would be expected to be completely random, and thus the partial molal excess entropy of mixing

<sup>11</sup> G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Phys. Chem.* **43**, 119 (1939).

<sup>12</sup> G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.* **61**, 3206 (1939).

<sup>13</sup> G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.* **62**, 712 (1940).

<sup>14</sup> G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.* **68**, 1957 (1946).

<sup>15</sup> G. Scatchard, S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.* **68**, 1960 (1946).

<sup>16</sup> S. E. Wood, *J. Am. Chem. Soc.* **68**, 1963 (1946).

<sup>17</sup> K. S. Pitzer, *J. Chem. Phys.* **7**, 583 (1939).

<sup>18</sup> E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).

might be compared to this difference in the entropies of evaporation, provided that the solvent acted merely as an inert diluent and that no effects other than orientation entered into this difference. However, the solvent is certainly not an inert substance, and further, the orientational distribution in the pure solvent will probably not be random. Consequently, the substitution of a solvent molecule by a solute molecule may change this distribution such that the randomness of orientation of the solvent molecules surrounding the solute molecule may be either increased or decreased. Examples of these effects are evident in the six possible binary systems composed of the four compounds considered here. A qualitative discussion of the properties of several compounds based on the differences in their entropies of evaporation as determined from the Hildebrand rule has already been given by Hildebrand.<sup>19</sup>

In these suggested comparisons the validity of the third condition, that the intramolecular vibrations are the same in both the liquid and vapor phases, must be considered. If there is a difference in these vibrations, then this difference will enter into the entropy of evaporation along with the effect of orientation, and consequently, the entropy differences may not be comparable to the partial molal excess entropy at infinite dilution. This effect should be small for benzene, cyclohexane, and carbon tetrachloride. For methanol, however, it is well known that there is a distinct difference in the vibration of the O-H group in the pure liquid and vapor phases. But there is also a similar shift when methanol is dissolved at low concentrations in benzene and carbon tetrachloride. Thus the entropy change caused by this shift would be present in both the entropy of evaporation and the partial molal excess entropy, although it might not be identical in the two cases. It then seems that this third condition may be ignored at least qualitatively in these comparisons. Moreover, it seems that the influence of the dipolar field of methanol on the orientational distribution is of much greater importance.

For these comparisons it is then necessary to calculate the entropy of evaporation of these

substances and that of a "perfect" liquid under corresponding conditions. Argon, being one of the substances which follow the law of corresponding states, has been chosen as an example of such a liquid. However, when a substance deviates from this law in one property, it deviates in all properties. Hence the question of what are corresponding conditions is presented. Various values of the difference of the entropy of evaporation of the liquid under consideration, and that of argon, are obtained depending upon what conditions are used. For this paper the entropy change has been calculated for the evaporation of benzene, cyclohexane, and carbon tetrachloride at 30° and methanol at 35° and at the vapor pressures of the liquids at these temperatures to an ideal gas at the same temperature and an arbitrary concentration. For argon the change in state is from the liquid at one atmosphere pressure and at a reduced temperature equal to the four reduced temperatures of the other liquids to an ideal gas at this temperature and the same arbitrary concentration. Values about two cal. per degree higher than those obtained with this change of state are obtained for the non-polar liquids if the comparisons are made at the same reduced temperatures and the same reduced vapor pressures. But in this case the concentration of the two substances in the vapor phase is not identical; this results in a difference in the entropies of the vapor phases even in the ideal gas state. Smaller values than those used in this paper, some of which are negative, are obtained if the comparisons are made either at temperatures at which the reduced vapor pressures are identical<sup>18</sup> or at temperatures at which the ratios of the molal volume of the vapor phase to that of the liquid phase are identical.<sup>17</sup> In these two cases the actual temperatures of argon are much lower than those corresponding to the same reduced temperature of the liquids resulting in a greater entropy of evaporation of argon; this entropy change increases about 12 percent for a ten degree decrease in temperature. Moreover, a large extrapolation of the vapor pressure of argon is necessary. It was because of these considerations that the changes of state stated above have been used. They do give the best agreement of the differences of the entropies of evaporation with the observed

<sup>19</sup> J. H. Hildebrand, *J. Chem. Phys.* **7**, 233 (1939).

values of the partial molal excess entropies of mixing, but it is not necessarily true as a consequence that they are the correct conditions. Nevertheless, no matter what conditions are used for comparison, the main conclusions drawn from this study will be the same.

The entropies of evaporation of benzene, cyclohexane, carbon tetrachloride, and methanol have been calculated from the vapor pressure equations of Scatchard, Wood, and Mochel<sup>12,14</sup> and the densities of benzene and cyclohexane given by them, of carbon tetrachloride given by Wood and Brusie,<sup>20</sup> and of methanol obtained from the International Critical Tables. The corrections for the non-ideality of the vapor have been obtained from the second virial coefficient only, using nine-tenths the value calculated by the theory of corresponding states for benzene, cyclohexane, and carbon tetrachloride using the equation of Keyes, Smith, and Gerry<sup>21</sup> and the full value of this quantity for methanol. The entropy of evaporation of argon has been determined from the calorimetric value of its heat of evaporation at the boiling point,<sup>22</sup>  $1557.5 \pm 1.5$  cal. per mole, and the molal heat capacities of the vapor and liquid phases,<sup>23</sup> 5.3 and 10.6 cal. per degree, respectively. The necessary vapor pressures have been obtained from the equation given by Born,<sup>24</sup> and the corrections for the non-ideality of the vapor have been determined from the second virial coefficient given by Holborn and Otto.<sup>25</sup>

The differences of these entropies of evaporation of benzene, carbon tetrachloride, cyclohexane, and methanol from that of argon are given in the fourth column of Table I. In order to show the effect of temperature on these differences they have also been calculated at 70° for the non-polar compounds and at 55° for methanol and are 2.22 for benzene, 2.07 for cyclohexane, 1.84 for carbon tetrachloride, and 8.22 for methanol. The partial molal excess

entropies of the solutes at constant pressure and at infinite dilution, determined from the data of the vapor-liquid equilibria<sup>11-15</sup> for all the systems except the cyclohexane-methanol system and from the liquid-liquid equilibria<sup>16</sup> for that system, are given in the last column of Table I. These observed entropies are independent of the temperature within the accuracy of the experimental data except those of the cyclohexane-methanol system. The values given for this system are at 31°. It should be pointed out here that the uncertainties in the entropies of this system are exceedingly large.

It is apparent that for the non-polar systems the orientational effect as calculated above is at least of the correct order of magnitude and has the correct sign. This is also true in the case where methanol is dissolved in cyclohexane, although here the comparison is much more uncertain. Thus the partial molal excess entropy of mixing at infinite dilution and constant pressure may be partly explained in terms of a lack of complete randomness in the orientational distribution of the pure solute which becomes complete at infinite dilution. However, with this concept, the observed quantities corrected for the volume effect should be approximately the same in all solutions of a given solute provided that the solvent acted as an inert diluent. But as previously suggested, this is not the case and the effect of substituting a solute molecule for a solvent molecule on the orientational distribution of the surrounding solvent molecules must be considered. These relationships can be discussed only qualitatively at the present time. An explanation of the behavior of the systems containing methanol, which is consistent with the concepts presented here, has already been suggested.<sup>15,16</sup> For the solutions in which benzene or cyclohexane are the solutes, the partial molal excess entropy is much smaller for solutions in which carbon tetrachloride is the solvent than for those in which cyclohexane or benzene, respectively, is the solvent and is larger for those solutions in which methanol is the solvent. Thus in the former solutions the interaction of the benzene or cyclohexane molecule with the surrounding carbon tetrachloride molecules apparently increases the lack of randomness of the orientation distribution of carbon tetrachloride,

<sup>20</sup> S. E. Wood and J. P. Brusie, *J. Am. Chem. Soc.* **65**, 1891 (1943).

<sup>21</sup> F. G. Keyes, L. B. Smith, and H. T. Gerry, *Proc. Am. Acad. Arts and Sci.* **70**, 319 (1936).

<sup>22</sup> A. Frank and K. Clusius, *Zeits. f. physik. Chemie* **B42**, 395 (1937).

<sup>23</sup> Landolt-Bornstein, *Tabellen* (Julius Springer, Berlin, 1923), 5, II, p. 1274, 1278.

<sup>24</sup> F. Born, *Ann. d. Physik*, [4], **69**, 473 (1922).

<sup>25</sup> L. Holborn and J. Otto, *Zeits. f. Physik* **33**, 1 (1925).

this effect being larger for benzene than for cyclohexane. The same relationship between benzene, cyclohexane, and carbon tetrachloride is observed in the three solutions in which methanol is the solute. Thus it would appear that the field of a carbon tetrachloride molecule should not be considered symmetrical, at least at intermolecular distances, and indeed is probably dipolar in nature, an effective dipole operating along each C—Cl bond. A preferred orientation in pure carbon tetrachloride has already been observed by Mencke<sup>26</sup> from x-ray diffraction patterns. The relative behavior of benzene and cyclohexane is evident in the solutions in which either carbon tetrachloride or methanol is the solute and is consistent with the concept of a larger electronic polarization of benzene in comparison to that of cyclohexane<sup>15,16</sup> and a possible closer approach of the neighboring molecules to the benzene molecule. The individual behavior of each solvent is thus very evident but is consistent with that expected from its molecular structure. At infinite dilution then, a qualitative but consistent explanation of the partial molal excess entropy of mixing at constant pressure is possible in terms of the lack of complete randomness in the orientational distribution of both the solute and solvent. However, the individual characteristics of each component are very important.

At finite concentrations the problem becomes exceedingly complex. It has been assumed that at infinite dilution the solute molecules are so far apart that the change in the orientational distribution of the solvent molecules is confined

to those immediately surrounding the solute molecules and does not extend throughout the whole liquid. At finite concentrations, however, these regions of changed orientation will become close enough to have a mutual influence on each other, and further, the orientational distribution of the solute molecules themselves must be taken into account. No quantitative treatment of this problem is available at the present time.

This discussion has been based on the change of entropy on mixing at constant pressure. For the non-polar systems there is an increase in the volume of the mixture which might be expected to accompany an increase in the randomness of the orientational distribution, taking both components into account. Conversely, when there is a decrease in the total randomness of orientation, the volume decreases as is observed in the methanol solutions. Thus there is a correlation between the sign of the excess entropy of mixing and the volume of mixing as pointed out by Lacher.<sup>27</sup> Furthermore, on mixing at constant volume, the volume available for a single molecule in the non-polar systems would be less than on mixing at constant pressure. Thus an increase in the degree of orientation and a decrease in the excess entropy would be expected on mixing at constant volume in comparison to mixing at constant pressure. This is observed. However, since for non-polar molecules the interaction energy between unlike molecules is less than the geometrical mean of that between like molecules, an increase in the randomness of orientation and a positive excess entropy of mixing would be expected and is observed.

<sup>26</sup> H. Mencke, *Physik. Zeits.* **33**, 593 (1932).

<sup>27</sup> J. R. Lacher, *J. Am. Chem. Soc.* **63**, 2422 (1941).