# THERMODYNAMIC ASPECTS OF THE THEORY OF NON-ELECTROLYTIC SOLUTIONS

JOEL H. HILDEBRAND

*Department of Chemistry, University of California, Berkeley, California*

*Received October 21, 1935*

I wish to discuss several of the important steps in the development of the theory of solutions of non-electrolytes with special reference to their thermodynamic corollaries. We will begin, of course, with the mention of Raoult's law. This rests historically upon an experimental foundation; however, its theoretical basis is now clear and so simple that anyone should be able to understand it and to see the conditions under which actual systems should approximate thereto (6, 15, 23). Its thermodynamic implications have, for the most part, been thoroughly set forth. There is only one minor, but nevertheless interesting, addition I wish to make here. If the partial vapor pressure of a component of a binary mixture is expressed as proportional to its volume concentration instead of its mole fraction, as in Raoult's law, the application of the Gibbs equation[1] connecting the partial molal free energies of the two components of a mixture shows that the molal volumes of the two components must be equal, in which case the volume concentration reduces to the mole fraction of Raoult's law. This means that volume concentration can satisfy the Gibbs equation only in the special case that it is identical with mole fraction, whereas the latter is always consistent therewith.

Earlier attempts to treat concentrated solutions on the basis of osmotic pressure formulae have been abandoned (1, 8, 14, 19) by all who have taken the trouble to inform themselves regarding the more adequate methods now available.

The majority of systems do not satisfy the condition of equal molecular fields required for obedience to Raoult's law and a more general treatment is necessary. The success of van der Waals in setting up an approximate equation of state naturally invited its extension to mixtures. The energy of a mixture of $n_1 + n_2$ moles according to this theory should be given by the expression $(n_1^2a_1 + 2n_1n_2a_{12} + n_2^2a_2)/(n_1b_1 + n_2b_2)$, where $a$ and $b$ are

---

[1] This equation is usually known as the Duhem-Margules Equation, but should be credited to Gibbs, unless special forms of it are regarded as worthy to bear another name.

the usual "constants" of the van der Waals equation, the subscripts referring to the pure components and the mixture, respectively. This was applied by van Laar (19, 20, 21) to yield the following expression for the partial vapor pressure of a component of a binary solution.

$$RT \ln (p_1/p_1^0 \mathrm{N}_1) = \alpha \mathrm{N}_2^2/(1 + r\mathrm{N}_2)^2$$

where

$$\alpha = (a_1 b_2^2 - 2a_{12} b_1 b_2 + a_2 b_1^2)/\mathrm{b}_1^3$$

and

$$r = (b_2 - b_1)/b_1$$

Sometimes $\mathrm{v}_1$ and $\mathrm{v}_2$ were substituted for $b_1$ and $b_2$, respectively. (Actually v is often 25 per cent greater than $b$.) The "derivation" of this equation is not easy to follow; some of the steps seem to be assumed rather than derived, and the molal volume is interchanged *ad libitum* with the "constant" $b$; the notation is not always clearly defined and moles and mole fractions are not clearly distinguished. The derivation was patched up and presumably improved, however, each of the many times it was repeated in the series of papers. Experimental tests were fragmentary and usually confined to citing systems which show qualitative agreement with the theory. It was concluded that equality of critical pressures was the criterion for ideal behavior of a solution. This is not only comparatively useless but often untrue. Anyone familiar with the shortcomings of the van der Waals equation for a pure substance could hardly feel great confidence in the validity of this treatment by van Laar in which good thermodynamics was scrambled intimately with an inadequate equation of state. The result turned out far better than could be expected, as we shall show later.

Dolezalek (3) and many others have attributed all deviations from Raoult's law to "chemical" changes alone—association and solvation—but although such equilibria often exist it is just as naïve to attribute all deviations to this cause as it would be to attribute all deviations from the perfect gas laws to chemical equilibria to the neglect of non-valence intermolecular forces and the effects of molecular volumes.

The above equation of van Laar simplifies to

$$RT \ln \gamma_1 = \alpha \mathrm{N}_2^2$$

in the special case that $b_1 = b_2$ (or $\mathrm{v}_1 = \mathrm{v}_2$). We have substituted the activity coefficient, $\gamma_1$, for $p^1/p_1^0\mathrm{N}_1$. This equation was also derived by Heitler (5) without the aid of an equation of state, by assuming the structure of the liquid to be a simple cubic lattice in which the two molecular species are interchangeable. The term $\mathrm{N}_2^2$ arises from a consideration of the frequency with which adjacent molecules are made up of the respective combinations, 1–1, 1–2, and 2–2. This derivation is not as convincing as it would be if it did not depend upon a model so highly artificial and did not involve the assumption that the volumes of the two molecular species are equal.

Work has proceeded in our laboratory over a period of years to amass experimental data involving non-polar, symmetrical molecules having molecular fields of widely different strength, as indicated by various criteria. It was soon evident that, in the absence of specific valence or polar forces, differences in the field strengths or "internal pressures" give rise to corresponding positive deviations from ideal solubility relations. Moreover, there was an unmistakable regularity of behavior as shown by the temperature coefficients of the solubility curves for many of these highly imperfect or non-ideal solutions. The explanation suggested itself that in these solutions the thermal agitation is sufficient to overcome the segregating effect of unequal molecular fields and give, at least approximately, the same randomness of mixing as would exist in an ideal solution, where the molecular fields are equal. The interpretation of randomness in terms of entropy suggested that the above statement might be formally expressed as $\bar{\mathrm{s}}_1^r = \bar{\mathrm{s}}_1^i$ when $\mathrm{N}_1^r = \mathrm{N}_1^i$, that is, the partial molal entropy of a component of a regular solution is the same as it would be in an ideal solution of the same composition. The latter is known, being given by

$$\bar{\mathrm{s}}_1^i = -R \ln \mathrm{N}_1$$

There are a number of interesting thermodynamic consequences of this definition which have been set forth elsewhere (7).

Scatchard (18) utilized this concept, together with a certain formulation of the "cohesive energy" of a mole of mixture, to arrive at a formula without involving the van der Waals equation. He says, "For non-ideal solutions also we shall neglect the change in volume and we shall consider only the case in which the interaction between any pair of molecules is independent of the composition. We may then split the cohesive energy of a mole of the mixture in the following way

$$u_x = (\mathrm{a}_{11}\mathrm{v}_1^2 x_1^2 + 2_{12}\mathrm{a}\mathrm{v}_1\mathrm{v}_2 x_1 x_2 + \mathrm{a}_{22}\mathrm{v}_2^2 x_2^2)/(\mathrm{v}_1 x_1 + \mathrm{v}_2 x_2)$$

where the a's are constants" (and the $x$'s mole fractions). "For the pure components $u_1 = \mathrm{a}_{11}\mathrm{v}_1$ and $u_2 = \mathrm{a}_{22}\mathrm{v}_2$, so that $\mathrm{a}_{11}$ and $\mathrm{a}_{22}$ are the cohesive energy densities of the components." The a's in this formulation are not, of course, constant over a range of temperature, but merely characteristic functions of each liquid at a given temperature. They are not the van der

Waals *a*'s, which are, theoretically at least, given by the relation $u = a/\mathrm{v}$, so that $\mathrm{a} = a/\mathrm{v}^2$. If we make this substitution in the above equation, we arrive at the same formula used by van Laar.

Meanwhile, we have been endeavoring to make a more rigorous study of the problem on a statistical basis. The method of Heitler was extended to cover any lattice arrangement in connection with a problem involving molten salt solutions (10). The "probability function," *W*, used by Prins (17), Zernike (24), and Debye and Menke (2, 16; see also 13) to express the structure of a liquid in terms of radial distribution then supplied the means for extending the proof to liquids, yielding the equation (11)

$$\Delta E' = \frac{2\pi N^2}{\mathrm{v}}\left[n_1^2 \int W_{11}\epsilon_{11}r^2\mathrm{d}r + n_2^2 \int W_{22}\epsilon_{22}r^2\mathrm{d}r + 2n_1 n_2 \int W_{12}\epsilon_{12}r^2\mathrm{d}r\right]$$

where $N$ is the Avogadro number and the $\epsilon$'s are the intermolecular potentials. In the absence of more exact knowledge of some of its terms certain assumptions had to be made in order to subject it to certain experimental verification, the results of which, however, have turned out to be remarkably satisfactory (9). The simplified approximation formula is

$$RT \ln \gamma_1 = \mathrm{v}_1\left\{\frac{\mathrm{N}_2\mathrm{v}_2}{\mathrm{N}_1\mathrm{v}_1 + \mathrm{N}_2\mathrm{v}_2}\right\}^2\left\{\left(\frac{\Delta\mathrm{E}_1}{\mathrm{v}_1}\right)^{\frac{1}{2}} - \left(\frac{\Delta\mathrm{E}_2}{\mathrm{v}_2}\right)^{\frac{1}{2}}\right\}^2$$

which, surprisingly enough, turned out to be identical with the formula of van Laar, provided v's are used in place of *b*'s and $\Delta\mathrm{E} = a/\mathrm{v}$. The term, $\Delta\mathrm{E}$, denotes energy of vaporization, N is mole fraction, and $\gamma$ the activity coefficient referred to the pure liquid as the standard state.

Guggenheim (4) has recently published an interesting paper on the subject of the statistical mechanics of regular solutions. He defines a regular solution as follows: "For the sake of simplicity we shall consider a mixture of two species 'A' and 'B'. The extension to mixtures of more than two species will be obvious. In our model of a regular solution we postulate first the absence of long-range (electrostatic) forces between the molecules. Our second assumption is that the 'A' and 'B' molecules may be treated as spheres of at least approximately the same size. Thirdly, we assume that each molecule whether of 'A' or 'B' is directly surrounded by the same number *r* of other molecules. If the molecules are closely packed, *r* will have the value 12, but for our present purpose, there is no need to assign any specified value to *r*, provided its value is the same for the 'A' molecules as for the 'B' molecules. Fourthly, we assume that the liquids 'A' and 'B' mix in all proportions without volume change. Our fifth assumption is that, for varying configurations (all of the same volume) of the system, the total potential energy may be regarded as the sum of contributions of each pair of molecules in direct contact. This assumption is slightly less drastic than assuming that the field of a given molecule does not extend beyond the further side of the next molecule. It is equivalent to ignoring differences between the field of an 'A' molecule and that of a 'B' molecule at distances exceeding one molecular diameter. Obviously our first assumption is included in our fifth."

I should like to utter a good-natured complaint, first of all that he should adopt a term which I invented and defined in a certain way but should give it a different and restricted definition. He practically rules out all solutions whose components have significantly different molecular radii. It is, of course, easy to see why a "statistical mechanic" or "mechanical statistician," whichever one should be called, should wish to confine his attention to molecules of equal size. The problems of statistical distribution of checkers on an ordinary checker-board are very simple, but suppose that the two sets of checkers were not only of unequal size but required the squares on the board to change size to accommodate them as they move; the statistics of such a checker-board would be rather baffling. It would be still worse if one of the players would use sausages, corresponding to paraffin molecules, in place of checkers.

Using the simple model he sets up it is, perhaps, not surprising that he should state that the volume fraction in the formula used by Scatchard and by myself "must be regarded as purely empirical." Even if the derivation is not convincing, the experimental evidence is all in favor of the volume fraction occurring in the formula. Many examples of this will be given in the second edition of my monograph on "Solubility" now in press and I need give here only one sample. The molal volumes of liquid cadmium and lead at 432°C. are 14.2 cc. and 19.1 cc., respectively. The values of the excess partial molal free energy of cadmium in the actual over the ideal solution should give a constant, according to our equation, when divided by the square of the volume fraction, $v_2^2$, rather than the mole fraction, $N_2^2$, of the lead. The following brief table for widely different compositions shows that this is the case.

| $N_1$ | $\frac{\bar{F}_1 - \bar{F}_1^i}{v_2^2}$ | $\frac{\bar{F}_1 - \bar{F}_1^i}{N_2^2}$ |
|---|---|---|
| 0.696 | 1800 | 2790 |
| 0.401 | 1760 | 2180 |
| 0.123 | 1820 | 1960 |

A much more important criticism by Guggenheim is to the effect that in the presence of unequal molecular fields the completely random distribution postulated in my definition of a regular solution cannot persist, but will give rise to some approach to the eventual segregation into two liquid phases as the temperature is lowered and the thermal agitation falls off. To take this tendency into account he defines and evaluates a certain quantity, $\bar{x}$, expressing departure from randomness. He then sets up a semi-empirical expression,

$$\bar{x}^2 = (N_1 - \bar{x})(N_2 - \bar{x})e^{-2\lambda/rkT}$$

which cleverly introduces the exponential, which is undoubtedly a step in the right direction. Here $2\lambda/r$ is the "work required to change a 1–1 pair and a 2–2 pair into two 1–2 pairs, and $N_1$ and $N_2$ denote the numbers of molecules. This takes account of the fact that there will be departures from random mixing favoring contact between molecules with low mutual potential energy."

On the basis of this formulation, he sets up the following expression, using our notation, with $n$ denoting number of moles and $N$ the Avogadro number, for the free energy of mixing,

$$\Delta F = \frac{n_1 n_2}{n_1 + n_2} N\lambda \left\{ 1 - \frac{2n_1 n_2}{(n_1 + n_2)^2} \cdot \frac{2N\lambda}{rRT} \right\}$$

(The original contains an error in omitting to square the second $n_1 + n_2$.) He points out the effect of values of $2\lambda/rkT$ approaching unity and states that the "application by Hildebrand and others" of a formula omitting this factor "to two liquids that are incompletely miscible is particularly unwarranted." His final conclusion is that "the semi-empirical formulae proposed by Hildebrand and other authors are inconsistent with the principles of statistical mechanics."

Now no one can deny that any differences in molecular field strength will introduce a tendency towards segregation which must prevent the partial molal entropy being strictly equal to its value in an ideal solution of the same composition. The only question is, are the departures sufficient to vitiate the simple conclusions one can draw from equating free and total energy. I am indebted to Professor Linus Pauling, with whom the matter was discussed, for suggesting a simple but striking test of the matter. We may calculate $\Delta F$ by means of the above equation, assuming it to be correct, and note the magnitude of the correcting term in the bracket. If we set $r = 12$, $T = 300$, and $\lambda = 1800$ cals., we find that $\Delta F$ is 394 cals., at $n_1 = n_2 = 0.5$, with the bracketed term 0.875 instead of 1.000, i.e., the correction amounts to 12.5 per cent, although the deviation from Raoult's law is large; the activity would be nearly 100 per cent greater than the ideal in the 50 mole per cent solution having this value of $\Delta F$. Moreover, the correction is greatest at this composition, falling off rapidly in either direction, e.g., it is but 4.5 per cent in a 10 mole per cent solution. The discrepancy for most systems in the range of interest would thus be at least as small as the other sources of uncertainty. The greatest effect would occur in the neighborhood of the critical solution temperature; an experimental measure of its magnitude will be possible by comparing the shape of the actual solubility curve in this region with its course elsewhere. This point was briefly discussed in the paper by myself and Wood.

The analogous case of the critical behavior of a pure substance is enlightening. If a gas is compressed at a temperature well below its critical temperature there is very little departure from the behavior of a perfect gas as the saturation pressure is reached, and even this can be well accounted for by a simple equation of state without introducing the picture of clustering, i.e., the molecular arrangement is random. The pure condensate also possesses a random molecular arrangement, unaffected by the presence of the gaseous phase. On the other hand, if the gas is compressed at, say, one degree below the critical temperature, the clustering is clearly visible to the naked eye. The size of these clusters changes, however, very rapidly with temperature, in such a way as to indicate their practical disappearance not many degrees away from the critical point in either direction. The behavior of a liquid solution should be similar. If a little of $X_2$ is dissolved in much $X_1$, having a very different internal pressure, the molecules of the former will have a random distribution, in spite of the large difference in intermolecular potentials. If the temperature is well below the critical solution temperature, a second liquid phase will appear as more $X_2$ is added in which $X_1$ is dilute in $X_2$ and likewise randomly distributed. Only if the temperature is such that the system passes near the critical point as the composition is altered should there be much of the segregation due to an approximate balance of thermal energy and unequal molecular potentials.

It seems to me probable, therefore, that the assumption of completely random mixing will be found to hold nearly enough for most solutions of non-polar substances to serve the purpose of usefully approximate calculations. It may be doubted, further, whether statistical mechanics, in its present state of development, can be counted upon to give an answer to the question which is at once reliable and workable. Until so simple a problem as the entropy of vaporization shall receive a satisfactory statistical treatment, I am willing to run the risks of refusing to give up a method of attack which is supported by much experimental evidence simply because it is "inconsistent with the principles of statistical mechanics." I feel constrained, however, to reject this last objection of Professor Guggenheim entirely, because the probability functions in our general equation, expressing the structure of the solution, include the effect of segregation upon this structure whenever it can be adequately expressed, either upon an experimental or a theoretical basis. Even the effects of unsymmetrical fields or departures from spherical shape[2] can be expressed by suitable formulations of $W$.

Space does not permit a review of a recent noteworthy formulation by Kirkwood (12) of a comprehensive statistical treatment of fluid mixtures, in which the rather artificial model of Guggenheim is avoided.

Purported evidence for clustering in solutions of benzene with cyclohexane has been given by H. K. Ward (22) on the basis of x-ray scattering. Two distinct diffraction peaks shown by the solution corresponding to the pure liquids were interpreted as indicating a submicroscopic emulsion structure, regarded as the cause of the deviation of these solutions from Raoult's law. This interpretation would be more convincing, first, if a pair of liquids had been chosen whose diffraction peaks are separated by a large enough interval to afford more room for an intermediate peak,—the difference was only 0.41 A.U.; second, if the deviation from Raoult's law were not so small, in this case only 8.5 per cent at 79°C. for an equimolal solution. The study should be repeated using a solution of nonpolar liquids near their critical solution temperature.

The scope of this discussion does not suffice to include other interesting thermodynamic aspects of solubility theory that suggest themselves, such as the effect of volume changes upon the entropy and free energy of mixing; I wish merely to indicate that the subject is by no means exhausted and that there remain various interesting fields for research, both theoretical and experimental.

## REFERENCES

(1) Brönsted, J. N.: Kgl. Danske Videnskab. Selskab Math. fys. Medd. **12**, 7 (1933).
(2) Debye, P., and Menke, H.: Fortschritte der Röntgen-forschung, Chap. I. Akademische Verlagsgesellschaft, Leipzig (1931).
(3) Dolezalek: Z. physik. Chem. **64**, 727 (1908).
(4) Guggenheim, E. A.: Proc. Roy. Soc. London **148A**, 304 (1935).
(5) Heitler, W.: Ann. Physik [4] **80**, 630 (1928).
(6) Hildebrand, J. H.: J. Am. Chem. Soc. **38**, 1453 (1916).
(7) Hildebrand, J. H.: Proc. Nat. Acad. Sci. **13**, 267 (1927); J. Am. Chem. Soc. **51**, 66 (1929).
(8) Hildebrand, J. H.: J. Phys. Chem. **32**, 1086 (1928).
(9) Hildebrand, J. H.: J. Am. Chem. Soc. **57**, 866 (1935).
(10) Hildebrand, J. H., and Salstram, E. J.: J. Am. Chem. Soc. **54**, 4257 (1932).
(11) Hildebrand, J. H., and Wood, S. E.: J. Chem. Physics **1**, 817 (1933).

---

[2] The original address included a brief discussion of some effects of hydrogen bond formation, which is here omitted in view of the fact that it is being written up more extensively for separate presentation (Science **83**, 21 (1936)).

(12) Kirkwood, J. G.: J. Chem. Physics **3**, 300 (1935).

(13) Kratky, O.: Physik. Z. **34**, 482 (1933).

(14) Lewis, G. N.: J. Am. Chem. Soc. **30**, 668 (1908).

(15) Lewis, G. N., and Randall, M.: Thermodynamics, p. 221. The McGraw-Hill Book Co., New York (1923).

(16) Menke, H.: Physik. Z. **33**, 593 (1932).

(17) Prins, J. A.: Physica **6**, 315 (1926); Z. Physik **56**, 617 (1929); Physik. Z. **30**, 525 (1929).

(18) Scatchard, G.: Chem. Rev. **8**, 321 (1931).

(19) van Laar, J. J.: Sechs Vorträge. Vieweg und Sohn, Braunschweig (1906).

(20) van Laar, J. J.: Z. physik. Chem. **72**, 723 (1910); **83**, 599 (1913); **134**, 311 (1928); **137**, 421 (1928).

(21) van Laar, J. J., and Lorenz, R.: Z. anorg. allgem. Chem. **145**, 239 (1925); **146**, 42 (1925); **171**, 41 (1928).

(22) Ward, H. K.: J. Chem. Physics **2**, 153 (1934). Cf. discussion by S. Katzoff: J. Chem. Physics **2**, 841 (1934).

(23) Washburn, E. W.: J. Am. Chem. Soc. **32**, 670 (1910).

(24) Zernike, F., and Prins, J. A.: Z. Physik **41**, 184 (1927).