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Group Interaction. I. A Model for Interaction in Solutions

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A simple model of interaction between two non-electrolyte molecules is derived from the assumption that the interaction energy can be represented as the sum of contributions of pairs of interacting groups (CH_3, CH_2, CO and so on). The contribution of each pair of groups is assumed to be independent of the nature of the molecules involved and dependent on the group concentrations and on group parameters ("cross section" and "interaction coefficient").

The questions related to the dependence of the energy and free energy of non-electrolyte solutions on the concentration have found fairly satisfactory answers by now. For "normal" binary solutions, one of the well-known two-constant equations furnishes a good approximation. For associated substances the addition of an appropriate function[2] gives in general a fair representation. Such a function can be very crudely approximated[2a] by adding to the molal free energy of mixing a fourth-order term in the mole fractions x_1 and x_2, namely, a term proportional to $x_1x_2(x_1 - x_2)^2$.

For the two coefficients appearing in the simplest case of a normal binary solution, we depend on experimental observations. Scatchard's cohesive energy densities or Hildebrand's solubility parameters give only the order of magnitude. Numerous theoretical attempts have produced interesting results but hardly much promise of a general, moderately accurate relation between energy and free energy of mixing and properties of the components. A semi-theoretical generalization of empirical results for the free energy of mixing,[3] on the other hand, proved to be quite satisfactory and showed that useful general rules can be found.

An intermediate method, using a crude theoretical model but also some experimental information, has been believed to promise wide applicability as well as practical usefulness. The simple theory of the heat of mixing developed in this and following investigations is based on the short-range character of intermolecular forces. Going to extremes, we may assume that the energy of interaction of two molecules is the sum of terms contributed by the contacts between parts (characteristic groups or radicals) of the two molecules. We assume, of course, that the contact between a CH_2 group and a CO group contributes to the energy of interaction more than the contact between a CH_2 group and a CH_2 group. But we assume that the contribution of each contact depends only on the two groups and neither on the other parts nor the concentration of the two molecules involved nor on any other molecules present. Thus we consider only interaction of pairs, and even this interaction only in a crude way.

Such a model is not essentially new. When this manuscript was finished, we learned that Langmuir[4] had outlined a similar model more than thirty years ago in a paper on the distribution and orientation of molecules. When we started the present work about ten years ago, similar ideas appeared in some manner in investigations of several authors, particularly Tompa,[5] Scatchard[2b] and Barker.[6] But a general development and check of the method is still missing.

A systematic check has been difficult because of the lack of adequate data. Sufficient information has been available in recent years for free energies of mixing but data on heats of mixing in homologous

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[1] Paper presented at the Symposium "Recent Advances in the Chemical Thermodynamics of Hydrocarbons and Related Substances," Division of Petroleum Chemistry, American Chemical Society, Chicago, September, 1958.

[2] (a) O. Redlich and A. T. Kister, *J. Chem. Phys.*, **15**, 849 (1947). (b) G. Scatchard, *Chem. Revs.*, **44**, 7 (1949).

[3] G. J. Pierotti, C. H. Deal and E. L. Derr, *Ind. Eng. Chem.* **51**, 95 (1959).

[4] I. Langmuir, *Colloid Symposium Monograph*, **3**, 48 (1925).

[5] H. Tompa, *Trans. Faraday Soc.*, **45**, 101 (1949).

[6] J. A. Barker, *J. Chem. Phys.*, **20**, 794, 1526 (1952).

series, as required, are rare. For some time we thought that the small values for the excess entropy of mixing, calculated from the relation of Flory and Huggins, may give the correct order of magnitude also for mixtures of non-linear molecules. This attempt, caused by the lack of adequate data, did not give satisfactory results.[7] It is only now that we are beginning to find barely sufficient data for initial tests. Further experimental information of heats of mixing will be indispensable for a thorough test and application of group interaction relations. We hope that systematic investigations in this field will stimulate the development of the theory of entropy of mixing.

It is obvious that a model of the nature of the present one cannot comprise the formation of complexes or association. But there is no obstacle to combining group interaction results and relations obtained from a theory of association.

The Model.—We split a molecule of the species i into characteristic groups, distinguished by a superscript u. There may be m_i^u groups u in the molecule i. Such groups may be aliphatic CH(u = 1), CH_2(u = 2), CH_3(u = 3) or CO or others. Another molecule j may contain m_j^v groups v.

The model of characteristic group interaction requires that each contact between a group u and a group v contributes always the same amount C^{uv} to the energy of interaction between molecules i and j. For the frequency of these contacts we introduce the simplest assumption, namely, that it is proportional to the numbers of groups u and v present. With the aid of the numbers of moles n_i and n_j of components i and j present, the numbers of groups u and v present are $n_i m_i^u$ and $n_j m_j^v$.

Since the groups are of different size, we assign to each a characteristic "cross section" s^u and assume that the contact frequency is proportional to $s^u s^v$. The frequency of a uv contact between two molecules i and j is therefore proportional to $m_i^u m_j^v n_i n_j s^u s^v$. Multiplication by C^{uv} furnishes a contribution to the energy of interaction. In the present approximation, energy and heat content need not be distinguished from each other.

The coefficients C^{uv} should determine the cohesive energy in the theory of Scatchard and Hildebrand. As will be shown in the Appendix, the relative heat content of a solution, which is of interest at present, is determined by the interaction coefficients

$$k^{uv} = C^{uv} - 0.5(C^{uu} + C^{vv}) \qquad (1)$$

These coefficients and the cross sections s^u are the quantities used in the group interaction model.

The relative molal heat content of one mole of a mixture is found in the Appendix to depend on the mole fractions x_i according to

$$L = 0.5\sum_{ij} A_{ij}x_i x_j s_i s_j / \sum_{h} x_h s_h \qquad (2)$$

Here, the "molecular cross sections"

$$s_i = \Sigma m_i^u s^u \qquad (3)$$

and the "molecular interaction coefficients"

$$A_{ij} = -\sum_{uv} k^{uv}(m_i^u/s_i - m_j^u/s_j)(m_i^v/s_i - m_j^v/s_j)s^u s^v \qquad (4)$$

are introduced for abbreviation.

The partial relative molal heat content can be derived from (2) by means of equations 14 or 15 of Redlich and Kister.[8] Since L is homogeneous of the first degree in the mole fractions, we have

$$\bar{L}_r = \partial L/\partial x_r$$
$$= (s_r/\sum_h x_h s_h)(\sum_j A_{rj}x_j s_j - 0.5\sum_{ij} A_{ij}x_i x_j s_i s_i/\sum_h x_h s_h) \qquad (5)$$

For a binary mixture we find

$$L = A_{12}x_1 x_2 s_1 s_2/(x_1 s_1 + x_2 s_2) \qquad (6)$$

$$\bar{L}_1 = A_{12}x_2^2 s_1 s_2^2/(x_1 s_1 + x_2 s_2)^2 \qquad (7)$$

$$\bar{L}_2 = A_{12}x_1^2 s_1^2 s_2/(x_1 s_1 + x_2 s_2)^2 \qquad (8)$$

For dilute solutions of component 1 in component 2 and conversely one has

$$\bar{L}_1^0 = A_{12}s_1;\ \bar{L}_2^0 = A_{12}s_2 \qquad (9)$$

These relations are of the type of what is usually called van Laar's equation.[9] Thus the group interaction model furnishes the correct concentration dependence since van Laar's equation is quite generally experimentally confirmed for non-associated solutions. But the model goes beyond van Laar's equation by resolving the molecular interaction coefficients A_{ij} into group interaction coefficients k^{uv} (equation 4) and by recognizing the quantities s^u as group cross sections.

The coefficients introduced, by the way, are redundant. The experimental quantities $\bar{L}_1^0$ and $\bar{L}_2^0$ can be represented by $A_{12}s_1$ and s_1/s_2. Similarly, in equation 5 one needs only the coefficients $A_{ir}s_r$ and the ratios s_h/s_i, not the values of s_h separately. The redundancy is removed by the arbitrary convention $s^{(2)} = 1$ for the CH_2-group.

A practical advantage of these relations is the separability of cross sections and interaction coefficients. If the ratios

$$\bar{L}_1^0/\bar{L}_2^0 = s_1/s_2 \qquad (10)$$

are experimentally given, one can establish a set of cross sections before attacking the more complicated problem of finding a set of interaction coefficients.

The group interaction model leads to relations of the type (6) to (8) for the solution of a compound in a multicomponent mixture. Group interaction data are directly applicable to this case.

The opportunities for testing the model will be discussed in following investigations of this series.

Acknowledgments.—The authors are greatly obliged to Mr. D. R. Douslin, who contributed to the early development of the model, and to Mr. R. C. Hurlbert, who participated in later work.

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(7) Langmuir (ref. 4) neglected the excess entropy of mixing and undoubtedly could not get a good check of the model. A detailed discussion, announced in his paper (ref. 4, p. 52, footnote) was never published.

(8) O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 375 (1948). In the differentiation with respect to x_r *all* other mole fractions are kept constant. The derivation of these equations from the definition of a partial molal quantity does not require any assumption regarding independence or interrelation of the mole fractions. The relation $\Sigma x_j = 1$ may be introduced therefore before or after application of (14) or not at all.

(9) As a matter of fact, we believe that this equation has hardly ever been derived from clearly stated assumptions. The derivations of van Laar himself lead invariably to the relation of Scatchard and Hildebrand.

Appendix

We derive at first equations 4 and 6 for a binary solution.

The frequency of contacts between two groups u and v in a given binary mixture is, according to the model discussed before, equal to

$$Z^{\mathrm{uv}} = 0.5N[n_1^2 m_1^{\mathrm{u}} m_1^{\mathrm{v}} s^{\mathrm{u}} s^{\mathrm{v}} + n_1 n_2 (m_1^{\mathrm{u}} m_2^{\mathrm{v}} + m_1^{\mathrm{v}} m_2^{\mathrm{u}}) s^{\mathrm{u}} s^{\mathrm{v}} + n_2^2 m_2^{\mathrm{u}} m_2^{\mathrm{v}} s^{\mathrm{u}} s^{\mathrm{v}}]$$

$$= 0.5N(n_1 m_1^{\mathrm{u}} + n_2 m_2^{\mathrm{u}})(n_1 m_1^{\mathrm{v}} + n_2 m_2^{\mathrm{v}}) s^{\mathrm{u}} s^{\mathrm{v}} \qquad (11)$$

where N is a proportionality factor. The total frequency of contacts

$$Z = \sum_{\mathrm{uv}} Z^{\mathrm{uv}} = 0.5N[\sum_{\mathrm{u}} s^{\mathrm{u}}(n_1 m_1^{\mathrm{u}} + n_2 m_2^{\mathrm{u}})]^2 \qquad (12)$$

is an extensive quantity, *i.e.*, homogeneous of first degree in n_1 and n_2. From the model one concludes that Z is changed by doubling n_1 in the same way as by doubling m_1^{u} or the cross sections of all groups in component 1. Moreover, the frequency of contacts is not changed if one molecule is replaced by another with the same molecular cross section (eq. 3). For these reasons, Z can contain n_1 and n_2 only as the sum of $n_1 m_1^{\mathrm{u}} s^{\mathrm{u}}$ and $n_2 m_2^{\mathrm{u}} s^{\mathrm{u}}$. Thus

$$Z = n_1 \sum_{\mathrm{u}} m_1^{\mathrm{u}} s^{\mathrm{u}} + n_2 \sum_{\mathrm{u}} m_2^{\mathrm{u}} s^{\mathrm{u}} \qquad (13)$$

except for an irrelevant constant factor, and

$$N = 1/\sum_{\mathrm{v}} s^{\mathrm{v}}(n_1 m_1^{\mathrm{v}} + n_2 m_2^{\mathrm{v}}) \qquad (14)$$

The contribution of all uv contacts to the heat content is, according to (11) and (14), if we specialize for one mole of the solution

$$H^{\mathrm{uv}} = 0.5C^{\mathrm{uv}} s^{\mathrm{u}} s^{\mathrm{v}} (x_1 m_1^{\mathrm{u}} + x_2 m_2^{\mathrm{u}})(x_1 m_1^{\mathrm{v}} + x_2 m_2^{\mathrm{v}}) / \sum_{\mathrm{w}} s^{\mathrm{w}}(x_1 m_1^{\mathrm{w}} + x_2 m_2^{\mathrm{w}}) \qquad (15)$$

For one mole of the pure component 1 we obtain

$$H_1^{\mathrm{uv}} = 0.5C^{\mathrm{uv}} s^{\mathrm{u}} s^{\mathrm{v}} m_1^{\mathrm{u}} m_1^{\mathrm{v}} / \sum_{\mathrm{w}} s^{\mathrm{w}} m_1^{\mathrm{w}} \qquad (16)$$

The corresponding contribution to the relative molal heat content is given by

$$L^{\mathrm{uv}} = H^{\mathrm{uv}} - x_1 H_1^{\mathrm{uv}} - x_2 H_2^{\mathrm{uv}} \qquad (17)$$

We abbreviate

$$s_1 = \sum_{\mathrm{w}} s^{\mathrm{w}} m_1^{\mathrm{w}};\ s_2 = \sum_{\mathrm{w}} s^{\mathrm{w}} m_2^{\mathrm{w}} \qquad (18)$$

From equations 15 to 18 one obtains in lengthy but elementary calculation

$$L^{\mathrm{uv}} = -0.5C^{\mathrm{uv}} s^{\mathrm{u}} s^{\mathrm{v}} (m_1^{\mathrm{u}}/s_1 - m_2^{\mathrm{u}}/s_2)(m_1^{\mathrm{v}}/s_1 - m_2^{\mathrm{v}}/s_2)\, x_1 x_2 s_1 s_2/(x_1 s_1 + x_2 s_2) \qquad (19)$$

For further simplification we write

$$B^{\mathrm{u}} = s^{\mathrm{u}}(m_1^{\mathrm{u}}/s_1 - m_2^{\mathrm{u}}/s_2) \qquad (20)$$

and note that according to the definition (20)

$$\sum_{\mathrm{u}} B^{\mathrm{u}} = 0 \qquad (21)$$

We indicate by an accent that the summation over u should not be extended to v = u and conclude from (21) that

$$B^{\mathrm{v}} = -\Sigma' B^{\mathrm{u}} \qquad (22)$$

The partial molal heat content is obtained by summation of (19)

$$L = \sum_{\mathrm{uv}} L^{\mathrm{uv}} = -0.5 \sum_{\mathrm{uv}} C^{\mathrm{uv}} B^{\mathrm{u}} B^{\mathrm{v}} x_1 x_2 s_1 s_2/(x_1 s_1 + x_2 s_2) \qquad (23)$$

The sum can be written as

$$\sum_{\mathrm{uv}} C^{\mathrm{uv}} B^{\mathrm{u}} B^{\mathrm{v}} = 2\sum_{\mathrm{uv}}{}' C^{\mathrm{uv}} B^{\mathrm{u}} B^{\mathrm{v}} + \sum_{\mathrm{u}} C^{\mathrm{uu}} (B^{\mathrm{u}})^2 + \sum_{\mathrm{v}} C^{\mathrm{vv}} (B^{\mathrm{v}})^2 \qquad (24)$$

Introducing (22) into the last two terms by writing

$$(\mathrm{B}^{\mathrm{u}})^2 = -B^{\mathrm{u}} \sum_{\mathrm{v}}{}' B^{\mathrm{v}};\ (B^{\mathrm{v}})^2 = -B^{\mathrm{v}} \sum_{\mathrm{u}}{}' B^{\mathrm{u}} \qquad (25)$$

we obtain

$$\sum_{\mathrm{uv}} C^{\mathrm{uv}} B^{\mathrm{u}} B^{\mathrm{v}} = 2\sum_{\mathrm{uv}}{}' (C^{\mathrm{uv}} - 0.5C^{\mathrm{uu}} - 0.5C^{\mathrm{vv}}) B^{\mathrm{u}} B^{\mathrm{v}} \qquad (26)$$

We define the group interaction coefficient by (1) and obtain from (23) and (26) the final result for the molecular interaction coefficient as anticipated in (2) and (4). The accent in the summation symbol in (4) can be omitted in view of (1), but it will be understood that each superscript combination uv is taken only once.

The extension from a binary solution to a multicomponent solution is justified by the fact that the model takes into account only binary contacts so that the heat content can be obtained by simple superposition.

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Group Interaction. II. A Test of the Group Model on Binary Solutions of Hydrocarbons

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The method of group interaction, which furnishes a model for predicting heats of mixing of non-electrolytes, has been tested on available data of binary solutions of hydrocarbons. It was found that for the cases tested, which comprised dilute binary systems exhibiting wide ranges of deviation from ideality, the model correctly predicts the relative partial molal heat contents of components.

According to the group interaction model presented in the preceding paper,[2] the limiting partial molal heat contents $\bar{L}_1^0$ and $\bar{L}_2^0$ of the components of a non-associated binary liquid mixture are described by two sets of quantities, namely, a set of *group cross sections* s^{u} and a set of group *interaction coefficients* k^{uv}. The model furnishes the relations

$$\bar{L}_1^0 = A_{12} s_1,\ \bar{L}_2^0 = A_{12} s_2 \qquad (1)$$

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[1] Paper presented at the Symposium "Recent Advances in the Chemical Thermodynamics of Hydrocarbons and Related Substances," Division of Petroleum Chemistry, American Chemical Society, Chicago, September, 1958.

[2] O. Redlich, E. L. Derr and G. J. Pierotti, THIS JOURNAL, **81**, 2283 (1959).