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OLD AND NEW PROBLEMS IN THE FIELD OF VAPOR-LIQUID
EQUILIBRIA

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OLD AND NEW PROBLEMS IN THE FIELD
OF VAPOR-LIQUID EQUILIBRIA

Otto Redlich

March 6, 1964

Old and New Problems in the
Field of Vapor-Liquid Equilibria

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(Abstract)

The present survey elaborates some of the topics discussed in an address presented at the 13th Canadian Chemical Engineering Conference in Montreal, October 23, 1963. Such a survey, of course, can mention only few of the important contributions of various authors that have elucidated the field of vapor-liquid equilibria in the last twenty years.

Thermodynamic consistency is only briefly mentioned. Since activity and fugacity coefficients are used for quite different purposes it is better to define them differently without trying to maintain a formal analogy. Activity coefficients of non-associating mixtures are satisfactorily represented by the traditional two-parameter relations. For associated solutions, as a rule, an association function must be superimposed. Further development and testing of association terms is desirable. Progress in the systematic representation of interaction in solution is promising. Calorimetric measurements in recent years have made considerable contributions.

(end of Abstract)

It has always seemed to me that chemical thermodynamics is a new Helen of Troy, who says of herself in Goethe's Faust (2nd Part, 3rd Act) "Admired much, and much reviled". Admiration, indeed, goes so far that we are expected to pull answers out of our sleeves even without first having put in some experimental data. And reviling has not been lacking, for instance, when in reviewing a manuscript we mention the inconsistency of the results with the equation of Gibbs and Duhem, and the author proudly points out that experimental observations should be given preference over mere theoretical speculations.

Consistency of experimental data and convenient tests were a real problem 17 years ago, when Kister and I¹ proposed the area condition

$$\int_0^1 \log (r_1/r_2) dx_1 = 0 \quad (1)$$

as the result of a simple transformation of the relation of Gibbs and Duhem. At the same time Herington² derived essentially the same relation. The area condition was extended to multicomponent mixtures by Prausnitz³ and a comprehensive survey of all consistency criteria was presented by Lu.⁴ These investigations round off the problem quite well so that no further discussion appears to be required.

How Should We Define Activity and Fugacity Coefficients?

Ibl and Dodge⁵ discussed quite extensively variations of temperature and pressure in relation to the equation of Gibbs and Duhem. Rowlinson⁶ thought that the area condition (1) was restricted to isothermal data at low pressure. Actually, however, our discussion¹ covered explicitly the variation of the temperature, and the influence of high pressure was taken into account by our clearly indicated definition of the activity coefficient.

It was a natural consequence of the state of development in 1923 that Lewis and Randall discussed in considerable detail activity coefficients and their standard states for electrolyte solutions but left some leeway in the definitions for non-electrolyte mixtures. It cannot surprise anybody that various authors proposed, within the frame given by Lewis and Randall, different definitions of the activity coefficient and also of the fugacity coefficient. A detailed discussion of these definitions would be unprofitable since the question is only one of greater or lesser convenience. It may be advisable, however, to justify briefly the definitions which we have found most useful in the course of years.

Conceptual economy is an important principle in the definition of useful terms. One should introduce only those terms which are really needed and restrict them to the field in which there is a need. Thus we define activity coefficients strictly for liquid (or solid) mixtures at low pressures ($P = 0$, though in general we may just as well say $P = 1$ atm.). As a consequence of the restriction to liquids (or solids), the variation of the partial molal free energy with pressure is small. But it must be taken into account (as Poynting correction) in the computation of activity coefficients. In general, this can be done by an easily computed correction term (Poynting correction). In the vicinity of the critical state, however, and also for dissolved gases the pressure influence is large and not easily estimated. As soon as the pressure influence on the liquid is taken care of, once and forever, in the numerical computation of activity coefficients, we relieve both general discussions and numerical applications of the bothersome cloud of correction terms.

For gases, the fugacity coefficient represents the deviation from the perfect gas as well as the deviation of a mixture from the perfect solution. The fugacity coefficient ϕ_j of species j , defined by the fugacity f_j and the mole fraction y_j according to

$$f_j = P y_j \phi_j, \quad (2)$$

depends on the pressure and the composition (and of course on the temperature). Its values are practically always derived from an equation of state. For a mixture we define the mean fugacity coefficient ϕ by

$$\ln \phi = \sum_a y_a \ln \phi_a \quad (3)$$

and obtain its value from the compressibility factor

$$Z = PV/RT \quad (4)$$

by

$$\ln \phi = \int_0^P (Z-1) dP/P. \quad (5)$$

Individual fugacity coefficients are obtained by means of

$$\ln \phi_j = \ln \phi + \partial \ln \phi / \partial y_j - \sum_a y_a \partial \ln \phi / \partial y_a. \quad (6)$$

In the differentiations pressure, temperature and all mole fractions except the one indicated are kept constant.

When we presented⁷ a relation of the type of (6) we assumed that this quite basic equation was generally known. This appears to have been an error. A brief discussion may be in order even if it comes very late.

The relation follows from the definition of a partial molal quantity

$$\bar{G}_j = \partial(nG)/\partial n_j \quad (7)$$

expressed by the corresponding molal quantity G of the solution, and the number n_j of moles of species j with

$$n = \sum_a n_a \quad (8)$$

Since both \bar{G}_j and G are intensive quantities, one wishes for actual computations a relation free of the (extensive) numbers of moles. Introducing the mole fractions

$$x_k = n_k/n \quad (9)$$

we have

$$\partial x_j / \partial n_j = (1-x_j)/n; \quad \partial x_k / \partial n_j = -x_k/n \quad (k \neq j) \quad (10)$$

Therefore,

$$\bar{G}_j = G + n(\partial G / \partial n_j) = G + n \sum_a (\partial G / \partial x_a) \cdot (\partial x_a / \partial n_j) \quad (11)$$

where the subscript a stands for all components. Introducing (10) we obtain

$$\bar{G}_j = G + \partial G / \partial x_j - \sum_a x_a (\partial G / \partial x_a) \quad (12)$$

This derivation neither requires nor contradicts the condition

$$\sum_a x_a = 1 \quad (13)$$

One may, but need not, eliminate one of the mole fractions before applying (12). The derivatives $\partial G / \partial x_a$, however, have no physical meaning. Only differences of two such derivatives are meaningful.

In algebraic calculations as well as in automatic computing, Eqn. (12) presents practical advantages over equivalent relations⁸ that contain only independent mole fractions.

For binary mixtures we always replace x_2 by $1-x_1$ and obtain from (12) the well-known relations

$$\bar{G}_1 = G + x_2(dG/dx_1) \quad (14)$$

$$\bar{G}_2 = G - x_1(dG/dx_1). \quad (15)$$

It is useful to keep in mind that the z relations (12) for z components are exhaustively represented by

$$G = \sum_a x_a \bar{G}_a \quad (16)$$

and $z-1$ relations of the type

$$\bar{G}_j - \bar{G}_k = \partial G / \partial x_j - \partial G / \partial x_k. \quad (17)$$

For binary mixtures one derives from (14) and (15)

$$G = x_1 \bar{G}_1 + x_2 \bar{G}_2 \quad (18)$$

$$\bar{G}_1 - \bar{G}_2 = dG/dx_1. \quad (19)$$

These relations are helpful in checking algebraic and numerical calculations.

Moreover, recently we found them useful in debugging a computer program.

The concept of the standard or reference state unquestionably has been essential and a major achievement in the system developed by Lewis. But we have always considered it as a halfway station from which we proceed right away to relations containing only realizable quantities. If we express the

partial molal free energies \bar{F}_j and \bar{F}_j' of the species j in the liquid and the gaseous phases by

$$\bar{F}_j = F_j^\circ + RT \ln x_j \gamma_j + \int_0^P \bar{V}_j dP \quad (13)$$

$$\bar{F}_j' = F_j^{\circ'} + RT \ln P y_j \phi_j, \quad (14)$$

the equilibrium condition becomes

$$RT \ln(P y_j \phi_j / x_j \gamma_j) - \int_0^P \bar{V}_j dP = F_j^\circ - F_j^{\circ'}. \quad (15)$$

The constant at the right hand side is eliminated by means of the vapor pressure p_j° of the pure component at which

$$x_j = 1; \gamma_j = 1; y_j = 1; \phi_j = \phi_j^\circ; \bar{V}_j = V_j^\circ \quad (16)$$

so that finally

$$RT \ln(P y_j \phi_j / x_j \gamma_j P_j^\circ \phi_j^\circ) - \int_0^P \bar{V}_j dP + \int_0^{P_j^\circ} V_j^\circ dP = 0. \quad (17)$$

The frequently permissible simplifications are well known.

In this presentation all ideas of symmetry or analogy between activity coefficient and fugacity coefficient are abandoned. The gain in economy, simplicity and easy understanding is believed to outweigh any loss.

There is an important difference in the roles of γ and ϕ in (17). As a rule, the activity coefficient is the unknown. This means immediately that the fugacity coefficients must be known in the application of the equilibrium condition (17). If we cannot assume that the vapor is a perfect gaseous mixture, we have to derive the fugacity coefficients from a suitable equation of state.

The computation of the activity in the liquid from data for vapor-liquid equilibria is therefore entirely independent of any assumptions regarding the molecular state of the solution (the activity coefficients depend on the assumed molecular size in a trivial manner because the mole fractions do). The situation is quite different for fugacity coefficients. If we did base fugacities in the vapor on direct measurements, the molecular state again would be irrelevant. But we use practically always either the perfect gas equation or some other general equation of state for the derivation of the fugacity coefficients. These equations apply to definite molecules. Acetic acid vapor, for instance, deviates greatly from the perfect gas equation. But the relations for a perfect gaseous mixture are approximately valid for an equilibrium mixture of monomeric and dimeric acid. The fugacity coefficients therefore must be derived from relations taking into account the molecular states. A pertinent example has been recently discussed in some detail by Campbell, Kartzmark and Gieskes.⁹

The objectives in our attempts at representing data for activity and fugacity coefficients are somewhat different, too. Since dimerization or other molecular changes in the gaseous state are rare, we leave the consideration of such changes to the discussion of individual cases and are satisfied with general equations of state disregarding them. In the liquid state, however, association is quite frequent and important for some classes of substances. While activity coefficients are computed from observed data without any concern of the molecular state in the liquid, their magnitude and concentration dependence are greatly influenced by association. Therefore they furnish quite definite information on the

molecular state. Conversely, accounting for association greatly increases the efficiency of the representation of activity coefficients.

Fugacity Coefficients

The very fact that many more than a hundred equations of state have been proposed suggests caution. We should consider only practically necessary requirements and let molecular theory helpfully guide rather than dictate our steps.

An algebraic formulation appears to be indispensable. Compressibility factors, of course, can never be better represented by an equation with two individual parameters than by the usual generalized charts. Likewise, an equation with three parameters cannot give better values of Z than the tables of Pitzer and his coworkers¹⁰ or of Riedel.¹¹ The practical interest in an equation of state however does not lie in the compressibility factors but in the fugacity coefficients. Here the algebraic equation has the advantage of retaining its definiteness in the necessary steps of integration and differentiation, which lead to loss of accuracy in numerical operations. Since individual fugacity coefficients in mixtures are the real objective, a definite combination rule for the parameters, independent of specific data for the mixtures, is desirable.

An equation of state, or at least its main term, must imply an equation of third degree in Z . This conclusion can be drawn from Wegscheider's discussion¹² of the equation of A. Wohl.

Good performance at high pressures is closely connected with the approach of the experimentally well established limiting condition for the reduced volume V_r

$$\lim_{P \rightarrow \infty} V_r = 0.26. \quad (18)$$

For mixtures, Neusser's long forgotten condition¹³ of additivity of the volume at high pressure should be satisfied. It is obvious to interpret this condition as the additivity of the proper volume of the molecule. The condition is important particularly since the volume in general is far from being additive at moderate pressures.

Approach of the perfect gas equation at low pressure and high temperature is an obvious condition.

An equation proposed 13 years ago¹⁴ satisfies these conditions. It is very similar to van der Waals' equation but represents the compressibility factor of gases much better. Except for the vicinity of the critical point, it gives results fairly close to the data of the generalized charts (Figure 1). However, since it contains only two individual parameters, we did not expect too much of it in view of the well-known invalidity of the theorem of corresponding states.

One would hesitate, of course, to compare a two-parameter equation such as our old one with the eight-parameter equation of Benedict, Webb and Rubin.¹⁵ It goes without saying, that their equation is much superior in the representation of data in a limited range. But it is the great adaptability and flexibility of this equation that impairs its power of extrapolation and prediction. Two independent investigations of mixtures, namely, of heat contents¹⁷ and of the critical properties¹⁸, led to the conclusion that the crude two-parameter equation is not inferior to the eight-parameter equation.

The remarkable success of the tables of Pitzer or Riedel for compressibility factors justifies the expectation that a three-parameter equation of state will furnish, by means of a convenient computer program,

satisfactory values for fugacity coefficients and other thermodynamic quantities of technical interest.

Naturally we tried to modify our old equation by introducing one or even more individual parameters. One can proceed quite systematically. Since the main defect of the old equation occurs in the vicinity of the critical point, we started from the general equation of the third degree, introduced the required conditions and examined the resulting family of equations. Strangely enough, these attempts were a complete failure.

Finally we decided to keep the old equation as a main term and to superimpose a correction term, which has to satisfy, of course, certain conditions to be useful. The improved equation¹⁹ contains, in addition to the critical temperature and pressure, Pitzer's "acentric factor" as a third parameter. Further improvement has been achieved in current work by Mr. F. J. Ackerman, Mr. R. Gunn and Mr. M. Jacobson. We hope to present soon a computer program which will furnish compressibility factors, heat contents, entropies and individual fugacity coefficients of mixtures, based only on the same three parameters.

As usually, other problems will arise as soon as the more immediate ones are settled. The use of a better equation of state in the general thermodynamic relations²⁰ for the critical state of mixtures is only one of them. Another one may be the use of a general equation of state for liquids, perhaps only for hydrocarbons. A recent discussion by Wilson²¹ shows that the derivation of vapor-liquid equilibria from an equation of state may change from a theoretical possibility to a practically useful method.

The Representation of Activity Coefficients

For well-known reasons the experimental information available for vapor-liquid equilibria is efficiently stored in the form of activity coefficients. The questions of computing, representing and using activity coefficients are related.

We prefer algebraic representation not only for reasons of trivial economy but also because of the suitability for computer use and, most of all, because interaction coefficients in algebraic relations provide the best basis for interpolations, extrapolations and generalizations.

The results of numerous discussions may perhaps be summarized in the following manner. The activity coefficients of mixtures of "normal" substances are always satisfactorily represented by van Laar's equation or by the equation of Margules (Figure 2). On the basis of wide experience, Black finds that van Laar's equation is superior. The difference, however, is not great.

As a historical aside it may be mentioned that the names of these two equations, chosen apparently by Carlson and Colburn²² in an early pioneering discussion, are not entirely justified. According to van Laar, the ratio A_1/A_2 of the two coefficients should be the ratio b_1/b_2 of the van der Waals coefficients. This restriction was omitted by Carlson and Colburn. On the other hand, Margules suggested a power series rather than a two-parameter relation. When we expressed this power series by writing for a binary mixture

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 = x_1 x_2 [B + C(x_1 - x_2) + D(x_1 - x_2)^2 + \dots] \quad (19)$$

we were unaware that Guggenheim²³ as well as Scatchard and his coworkers²⁴ had used similar relations.

Appreciable deviations from the two-parameter relations indicate a chemical change. Such a change may be the formation of a compound between two components (chloroform-acetone). This case occurs infrequently and is best discussed individually. Polymers, too, require a special treatment. Association by hydrogen bonds, however, is a frequent and technically important chemical change. It must be taken into account in the general methods of representation. Dimerization of aliphatic acids in liquid solutions is well known. Its effects are similar to those of association.

Qualitatively the influence of association on activity coefficients is well established.²⁵ The contrast between a normal binary (Figure 2) and an associating binary (Figure 3) is striking. The third term (D-term) in equation 19 gives a crude approximation of the additional function required by association. The association effect is greatest in mixtures of a strongly associating and a non-associating substance (methanol-carbon tetrachloride, ethanol-iso octane). It is reduced or suppressed by "interassociation", i.e., hydrogen bonding between the molecules of two associating components.

The quantitative representations proposed by Redlich and Kister²⁵, Scatchard²⁶, and Prigogine, Mathot and Desmyter²⁷, furnish better approximations than the third term in (19). One has to take into account the direct effect of the "true" activity coefficient of the associating substance and its effect on the association equilibrium. Starting from the relation of Scatchard and Hildebrand one arrives consistently at the association function proposed by us.²⁵ The relation of Flory and Huggins leads to the different function derived by Scatchard.²⁶ Prigogine, Mathot

and Desmyter²⁷ derive the same result for the association and simply superimpose it on the relations for activity coefficients of non-associating solutions. The question of intrinsic consistency has been discussed by us²⁵ and in some detail by Lacmann.²⁸

So far these association functions have not been thoroughly investigated. A serious discrepancy, though, has been noticed by us and by Kretschmer and Wiebe.²⁹ The association function contains only a single parameter, which, in addition, should be characteristic (at a given temperature) of the associating component, independent of the non-associating component. This requirement is not confirmed by the experimental data. Slight inter-association with the solvent has been suggested²⁹ for an explanation. A study of this question with the aid of a suitable computer procedure has been long on our program.

The clean separation of the various association effects from ordinary interaction is expected to give a much improved basis for attempts to describe systematically the relation between interaction and chemical constitution of the components.

Group Interaction, Heat Content, Volume

The systematic interpolation and extrapolation of coefficients characterizing the interaction of a substance with members of a homologous series (normal paraffins) has been repeatedly suggested. The consistent development of this idea by Pierotti, Deal and their coworkers³⁰ has resulted in an efficient and useful system of estimating interaction parameters.

Langmuir³¹ enthusiastically described and quickly abandoned a model that in a similar way systematically resolves interaction between two molecules into interactions between their constituent groups. The reason of Langmuir's

sudden loss of interest was clear to us on the basis of our own experience. Unaware of Langmuir's work, we tried to develop a similar model in 1950 (At about the same time, other authors^{32,33} had proposed similar ideas). But we found that tests were inconclusive since the model applied to heat contents rather than free energies and data for heat contents were entirely insufficient. Experimental information³³⁻³⁷ in this field became available at an increasing rate later at the time of our discussion of the group interaction model.³⁸ Lundberg's determinations³⁹ of the heats of mixing of 27 hydrocarbon binaries have been undertaken as a first step in the further systematic development of the model.

For several different reasons further experimental work as well as examination of the model appear to be promising problems. Undoubtedly the best technique requires heats of mixing for determining the temperature dependence of the activity coefficients while the direct measurement of activity coefficients may be restricted to a single temperature. In this way one obtains not only a more precise basis for covering a sufficient temperature range. The measurement is also quicker as soon as a good and convenient calorimeter has been set up. Vaporization in calorimetric work deserves special attention. In addition to the usually corrected vaporization due to the change in temperature of the calorimeter, one has to take into account also the "isothermal vaporization". It is due to the change in partial vapor pressures of the components brought about by the mixing. According to our experience it may be much larger than the other contribution to vaporization. The use of carbon tetrachloride-benzene for testing calorimeters has been discussed by Peña and McGlashan.⁴⁰

Increasing information of heat contents will also furnish a basis for the discussion of the excess entropy. Hildebrand's "regular solution"⁴¹ was an early and very useful model. Further development will require experimental data as a starting point.

The volume change V^M on mixing has been studied not very frequently. Early in this century Biron suggested the relation

$$V^M = Bx_1x_2 \quad (20)$$

The natural development of this equation is a relation similar to (19).

Theoretically significant results have been derived from volume changes of mixtures of normal paraffins by van der Waals and his coworkers.¹² The relation of their results to Brönsted's principle of congruence has been discussed by McGlashan.⁴³ The volume change on mixing may very well turn out to furnish interesting results in other problems.

Computation

In view of the development of computers the question is hardly whether but only how we should apply automatic computation. This is not purely a question of computer technique.

All old methods depended heavily on the judgment of the calculating experts. Activity coefficients were computed from each measurement, and either checked for consistency, smoothed and represented graphically or in a table, or smoothed with the aid of a suitable algebraic relation.

The subjective smoothing now must be replaced by a least squares operation. Here the problem is the assignment of weights. The whole calculation is meaningless if incorrect weights are chosen. Although not a high accuracy is required, weighting of activity coefficients is neither easy nor very reliable. The worst assumption is of course that of equal weight for the activity coefficients since the error of y_1/x_1 increases beyond any limit on approach of $x_1 = 0$.

The second problem is the consistency test, provided the vapor composition is determined (so that the data are redundant) and provided that consistency is not automatically enforced by the use of a correct algebraic relation.

Techo⁴⁴ attempted to develop an unbiased method. He represents the total pressure P and the mole fraction y_1 in the vapor by means of orthogonal polynomials. He introduces the equation of Gibbs and Duhem and uses essentially the quantity $RT \, d \ln P / dy_1$ as a smoothing variable. For this variable he derives values at 99 points, uniformly distributed in x_1 . These values are implicitly assumed to have equal weights. Such an assumption is as a rule quite reasonable but not necessarily the best possible one. Moreover, it is hardly transparent. The reasonableness depends on the uniformity of the distribution of the measurements and on practically equal accuracy in $\ln P$ and y_1 over the whole range. The influence of non-uniformity of distribution or accuracy would be difficult to estimate.

Even though Techo's method cannot be called unbiased in a strict sense, it is attractive as an attempt to eliminate arbitrariness. But the practical disadvantages are considerable. It furnishes only intermediate results, which in addition are expressed by an inconvenient set of numbers. For any desired application one depends again inevitably on a high speed computer. The number of coefficients required is so large that there is little hope for an ordering system of the kind of the group interaction model.

Conclusions

On the whole, a technique of direct representation of properly weighted observations by means of an equation of the van Laar or Margules type, with an association function superimposed where necessary, still appears to be preferable. It lacks formal rigidity and depends more on experience and judgment. The development and testing of a suitable association function will be helpful.

For a systematic exploration of the field of vapor-equilibria isothermal measurements are far more valuable than isobaric determinations. It is an old experience that a small number of precise measurements carries more information than any number of less accurate ones. In general, the analysis of the vapor is desirable. But pressure determinations alone are sufficient for some purposes, particularly if the deviations from the perfect solution are not large. As a rule, phase equilibrium determinations should be supplemented by calorimetric work.

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References

1. Redlich, O., and A. T. Kister, Ind. Eng. Chem. 40, 341 (1948).
2. Herington, E. F. G., Nature 160, 610 (1947).
3. Prausnitz, J. M., and G. D. Snider, A. I. Ch. E. Journ. 5, 7 (1959).
4. Lu, B. C.-Y., Chem. Eng. 67, No. 20, 105 (1960).
5. Ibl, N. V., and B. F. Dodge, Chem. Eng. Sci. 2, 120 (1953).
6. Rowlinson, J. S., "Liquids and Liquid Mixtures", Butterworth, London (1959).
7. Redlich, O., and A. T. Kister, Ind. Eng. Chem. 40, 345 (1948).
8. For instance, Dodge, B. F., "Chemical Engineering Thermodynamics", McGraw-Hill Book Co., New York 1944, Eqn. IV-17.
9. Campbell, A. N., E. M. Kartzmark and J. M. T. M. Gieskes, Can. J. Chem. 41, 407 (1963).
10. Pitzer, K. S., D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins and D. E. Peterson, J. Amer. Chem. Soc. 77, 3433 (1955).
11. Riedel, L., Chemie-Ing.-Techn. 26, 83, 259, 679 (1954); 27, 209, 475 (1955).
12. Wegscheider, R., Z. physik. Chem. 135, 362 (1928).
13. Neusser, E., Physik. Z. 35, 738 (1934).
14. Redlich, O., and J. N. S. Kwong, Chem. Revs. 44, 233 (1949).
15. Benedict, M., G. B. Webb and L. C. Rubin, J. Chem. Phys. 8, 334 (1940).
10, 747 (1942). Chem Eng. Progr. 47, 419 (1951).
16. Edmister, W. C., R. E. Thompson and L. Yarborough, A. I. Ch. E. Journal 9, 116 (1963).
17. Edmister, W. C., and L. Yarborough, A. I. Ch. E. Journal 9, 240 (1963).
18. Ackerman, F. J., and O. Redlich, J. Chem. Phys. 38, 2740 (1963).

(references continued)

19. Redlich, O., and A. K. Dunlop, Chem. Eng. Progr. Symposium Series, 59, 95 (1963).
20. Redlich, O., and A. T. Kister, J. Chem. Phys. 36, 2002 (1962).
21. Wilson, G. M., Paper presented at the Cryogenic Engineering Conference, Boulder, Colorado, August 19-21 (1963).
22. Carlson, H. C., and A. P. Colburn, Ind. Eng. Chem. 34, 581 (1942).
23. Guggenheim, E. A., Trans. Faraday Soc. 33, 151 (1937).
24. Scatchard, G., and W. J. Hamer, J. Amer. Chem. Soc. 57, 1805 (1935).
Scatchard, G., S. E. Wood and J. M. Mochel, *ibid.* 62, 712 (1940).
25. Redlich, O., and A. T. Kister, J. Chem. Phys. 15, 849 (1947).
26. Scatchard, G., Chem. Revs. 44, 7 (1949).
27. Prigogine, I., V. Mathot and A. Desmyter, Bull. Soc. Chim. Belges, 58, 547 (1949).
28. Lacmann, R., Z. physik. Chem., N. F., 23, 313, 324 (1960); 35, 86 (1962).
29. Kretschmer, C., and R. Wiebe, J. Chem. Phys. 22, 1697 (1954).
30. Pierotti, G. J., C. H. Deal and E. L. Derr, Ind. Eng. Chem. 51, 95 (1959). Wilson, G. M., and C. H. Deal, Ind. Eng. Chem. Fundamentals 1, 20 (1962).
31. Langmuir, I., Colloid Symposium Monograph, 3, 48 (1925).
32. Tompa, H., Trans. Faraday Soc. 45, 101 (1949).
33. Barker, J. A., J. Chem. Phys. 20, 794, 1526 (1952).
34. Brown, I., and W. Fock, Aust. J. Chem. 8, 361 (1955); 9, 180 (1956); 10, 417 (1957); 14, 387 (1961).

(references continued)

35. Jeun, S. K., and B. C-Y. Lu, *Can. J. Chem.* 38, 742 (1960).
36. Prausnitz, J. M., and R. F. Blanks, *J. Phys. Chem.* 67, 1154 (1963).
37. McGlashan, M. L., K. W. Morcom, and A. G. Williamson, *Trans. Faraday Soc.* 57, 581, 588, 601, 907 (1961).
38. Redlich, O., E. L. Derr and G. J. Pierotti, *J. Amer. Chem. Soc.* 81, 2283 (1959).
39. Lundberg, G. W., *J. Chem. Eng. Data*, April 1964.
40. Peña, M. D. and M. L. McGlashan, *Trans. Faraday Soc.* 57, 1511 (1961).
Larkin, J. A., and M. L. McGlashan, *J. Chem. Soc.* 1961, 3425.
41. Hildebrand, J. H., and R. L. Scott, "Regular Solutions", Prentice-Hall (1962).
42. van der Waals, J. H., and J. J. Hermans, *Rec. Trav. Chim.* 68, 161 (1949); 69, 949, 971 (1950). van der Waals, J. H., *Rec. Trav. Chim.* 70, 101 (1951). Desmyter, A., and J. H. van der Waals, *Rec. Trav. Chim.* 77, 53 (1958).
43. McGlashan, M. L., *Molecular Phys.* 4, 87 (1961); *Nature* 198, 683 (1963).
44. Techo, R., *Chem. Eng. Sci.* 18, 27 (1963).
45. Harrison, J. M., and L. Berg, *Ind. Eng. Chem.* 38, 117 (1946).
46. Sieg, L., *Chemie-Ing.-Technik* 1950, 322.
47. Niini, A., *Ann. Acad. Sci. Fennicae, A* 55, No. 8, p. 1 (1940).
48. Scatchard, G., S. E. Wood, and J. M. Mochel, *J. Amer. Chem. Soc.* 68, 1960 (1946).

Figure Captions

Figure 1. Reduced equation of state (Broken lines: generalized charts. Full Line: equation of Redlich and Kwong¹⁴).

Figure 2. Function $\log(\gamma_1/\gamma_2)$ for benzene-trimethylbutane. References: Harrison⁴⁵, Jost and Sieg⁴⁶ (Example for non-associating components).

Figure 3. Function $\log(\gamma_1/\gamma_2)$ for methanol-carbon tetrachloride. References: Niini⁴⁷, Scatchard⁴⁸ (Example for one associating component).

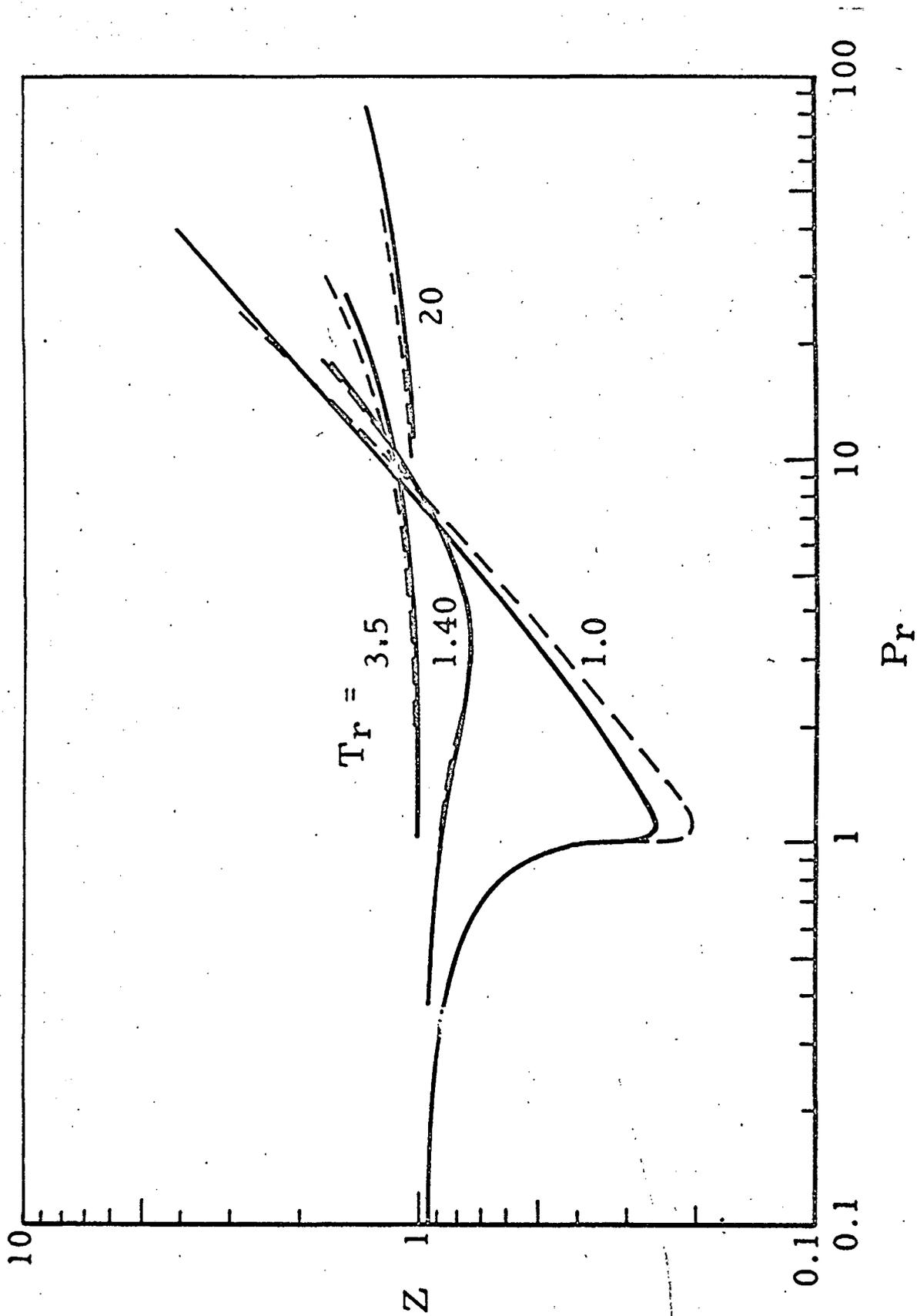


Fig. 1

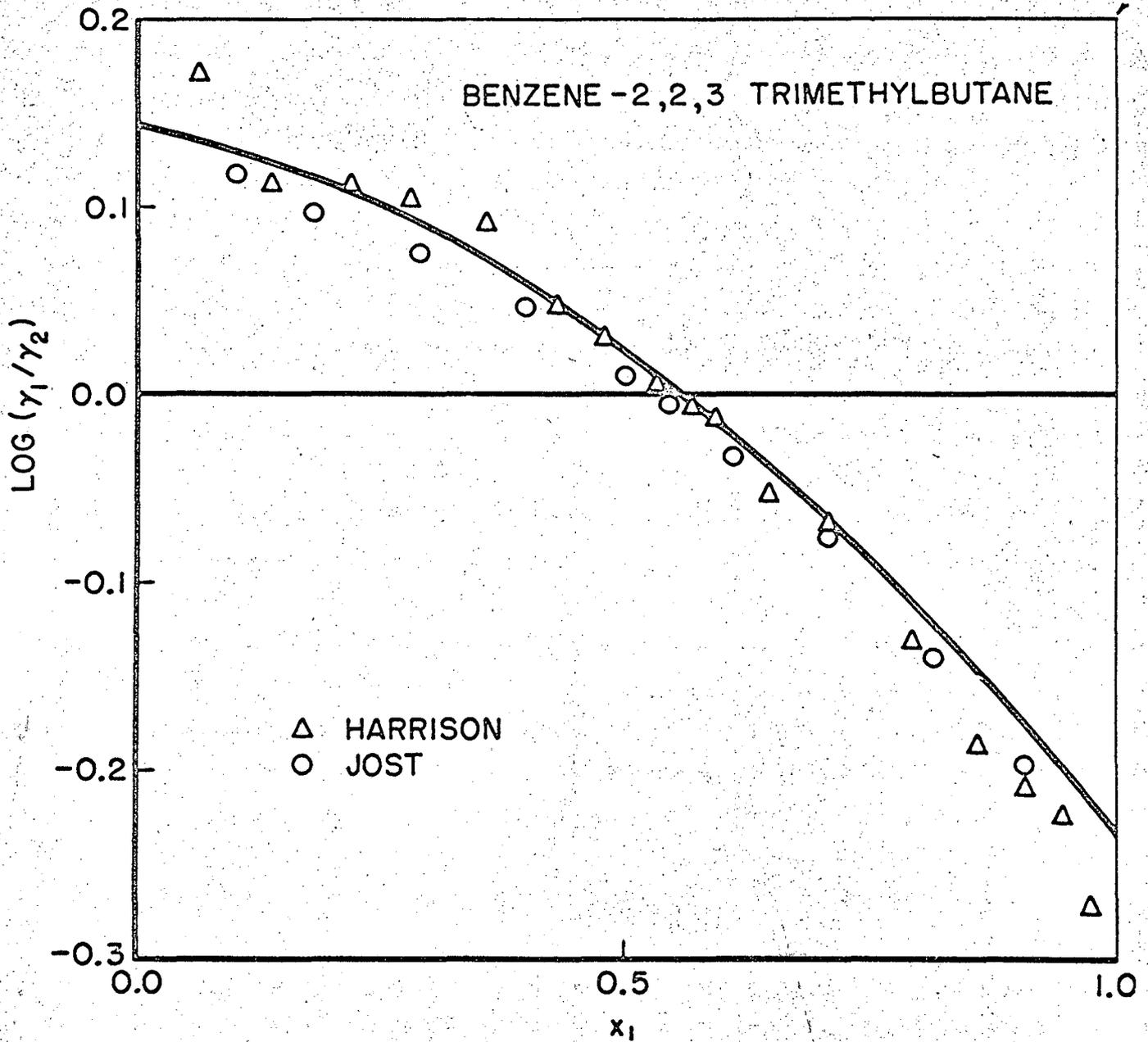


Fig. 2

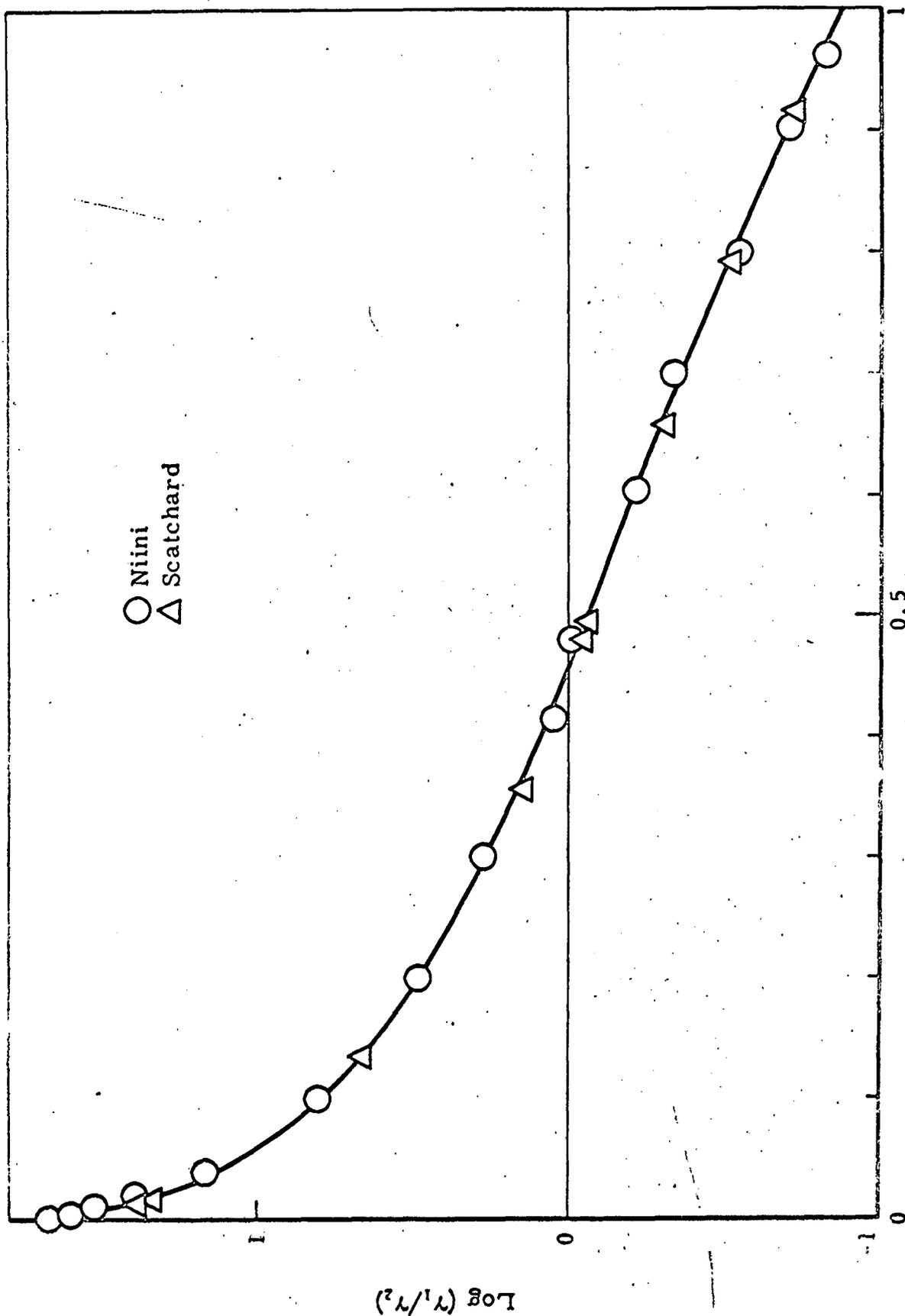


Fig. 3

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