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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

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

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The practical advantage of a systematic representation of vapor-liquid equilibria by means of activity coefficients rests, of course, on the fact that the results are loosened from the restriction to the original experimental conditions and can be extended, more or less reliably, to different conditions to multicomponent mixtures, and even to different substances.

We derive activity coefficients from the equilibrium condition that the chemical potential or partial molal free energy of a substance has the same value in the liquid and the vapor. Notwithstanding formal analogies, we have to treat the two phases differently, for the simple reason that we must assume the chemical potentials of the components in the gas to be known while the potentials in the liquid, or the activity coefficients, are the unknowns in the problem. The most common offense against the requirement of introducing a correct value of the free energy in the vapor phase is, of course, disregard of appreciable deviations from the laws of the perfect gaseous

mixture. Somewhat subtler, though essentially the same mistake, is the disregard of a change of the molecular state, such as the dimerization of formic acid, in the vapor state. The usual approximations for fugacity coefficients cannot correctly represent such chemical changes. Activity coefficients, on the other hand, as the unknowns in the calculation, stand on their own feet without any regard to the molecular state, provided only that the molecular weight in the dilute solution has been correctly introduced.

The phase rule shows that we overdetermine the unknowns of a binary mixture if we measure (for good experimental reasons) the mole fractions $x_1$ and $y_1$ in both phases as functions of temperature and pressure. The ensuing identical relation between the activity coefficients of the two components, essentially the relation of Duhem and Margules, has been a favorite subject of discussion in recent years. I wish to present my apologies because Mr. A. T. Kister and I[1] are in a way guilty of having started this discussion. By way of excuse it may be mentioned that in 1946 consistency criteria were quite useful, in view of the poor state of the available experimental material. Moreover, we said quite briefly (though with rigorous accuracy) what some later authors[2] said in extensive discussions. Perhaps we could have avoided some unjustified criticism[3] regarding supposed restrictions of the area condition if we had expanded our discussion. We thought, however, at that time as we do today, that consistency criteria should be used but not much talked about; the experimenter should use this tool to control and improve his methods.

Automatic computation can be very useful if handled sensibly. The real question is how much one should leave to critical judgment in a problem in which functional relationships are quite complicated and experimental errors have widely varying influence. So far as I can see, the first correct completely mechanized procedure was recently suggested by Techo[4]. He smoothes the immediately observed quantities P and $y_1$, introducing the equation of Duhem and Margules as a condition, and represents the results by orthogonal polynomials. Since he can assign equal weights to the

directly observed values, he avoids the usual pitfall of wrong weighting. Techo's procedure has the intrinsic advantage and disadvantage of a strictly mechanical method: It does not depend on any whim of the calculator and it does not utilize his experience and critical judgment. Moreover, it does not depend on, or utilize, any specific model.

Though often neglected, deviations of the vapor from a perfect gaseous mixture are frequently quite important. A few types of equations of state[6-12] have survived a large number of competitors. Each of these relations has important advantages, which require a special discussion. None is satisfactory in every respect so that it could be used exclusively.

The critical state of gaseous mixtures is of appreciable theoretical and practical interest. The critical lines of a binary mixture (T and P as functions of $y_1$) can be derived from an equation of state but the calculations are extremely involved[13]. The explicit representation of the limiting slopes[14] of the critical lines in their endpoints (i.e., for the pure components) presents some advantage. Further progress will depend on improvements of the equations of state.

The relation between interaction in non-electrolyte solutions and the chemical nature of the components presents an old question. A condition of a satisfactory answer appears to be the further quantitative development of simple models for association, interassociation and compound formation[15]. As soon as these "chemical" influences are accounted for or whenever they are absent, one may expect to represent the remaining "physical" interaction by means of two parameters for any binary. Hildebrand's solubility parameters furnish an approximation for the interaction[16]. A group-interaction model[17] and similar semi-empirical relations[18] are practically useful and promise more elucidation in the future.

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