APPLICATION OF MOLECULAR CONCEPTS OF PREDICTING PROPERTIES NEEDED FOR DESIGN*

JOHN P. O'CONNELL and KEITH GUBBINS
University of Florida
Gainesville, Florida
and
JOHN PRAUSNITZ
University of California
Berkeley, California

JOHN PRAUSNITZ' OPENING remarks for the Workshop on Applications of Molecular Concepts at the ASEE Summer School gave the historical development of chemical engineering thermodynamics teaching and the basis of its particular emphasis on fluids and their mixtures. Presently due to the increased abstractness of physical chemistry courses and the increased sophistication of industrial design computation, "we must assume the burden of teaching some classical physical chemistry and we must also teach students how to apply physical chemistry, through the computer, to chemical engineering design". Although much of what we talked on may have been familiar to the audience, we hoped that some new aspects emerged from the discussions. The workshop aim was "breadth not depth, to present ideas and techniques which are suitable for course work . . . perhaps some of them will strike you as interesting and useful for your own particular educational objectives". We tried to have "novel ways of looking at old ideas" result from reviewing together our collective experience, because, as John Prausnitz reminded us what St. Augustine said, "the essence of good preaching is *Non Nova Sed Nove*".

SESSIONS WITH PRAUSNITZ

THE INITIAL SESSION was a review by John O'Connell of the fundamentals and terminology of classical thermodynamics so that everyone would begin at the same level. Of most interest was setting out expressions for thermodynamic properties, in terms of equations of state and for fugacities of condensed phases, which are vital for calculating phase equilibria involving liquids and/or solids. Discussion was made of the importance of vapor-phase nonidealities, activity coefficient conventions for subcritical components and for supercritical components, and liquid phase reference fugacities for both situations. Much of this material is found in Prausnitz' book "Molecular Thermodynamics of Fluid-Phase Equilibria"[1].

The second session by Prausnitz covered "phenomenological theories" for fluids. While examples of empirical equations of state were given (see ref. 2, for example), it was emphasized that all of these have essentially arbitrary rules to combine pure component parameters to obtain properties of mixtures. Since fugacity coefficients significant in mixtures are often quite sensitive to the rules, errors often occur. This is even more of a problem for vapor-liquid equilibria calculations when a single equation of state is used for both phases since liquid properties are particularly sensitive to the rules. As a result, different approaches are taken for the two phases: equation of state for the vapor and activity for the liquid. For liquid phase activity coefficients, the distinction was made between enthalpy-dominated models, such as the Wohl generalization of the Scatchard-Hildebrand theory (solubility parameter) and the NRTL equation, and entropy-dominated models such as the Flory-Huggins and Wilson equations. Illustration of a practical multicomponent example was made through the NH_3-H_2-N_2-CH_4-Ar system where only binary information is used[3] Both the value and the limitations of empirical theories were discussed, leading toward molecular-based analyses and correlations to allow greater generalization.

---

* Report on the Thermodynamics Workshop at the ASEE Summer School in Boulder, Colorado, prepared by J. P. O'Connell.

DESCRIPTIONS BY GUBBINS AND O'CONNELL

Keith Gubbins then outlined the formalisms of statistical thermodynamics, describing the relations between partition functions and macroscopic properties although he emphasized the more recently developed radial distribution-function theories for fluids. This material can be found in the new book by T. M. Reed and K. E. Gubbins "Applied Statistical Mechanics"[4]. John O'Connell followed this with a description and classification of intermolecular forces and their effects on physical properties, particularly liquid phase mixing functions (see ref. 4, chap. 4). Division of forces was made into those of repulsion, dispersion (nonpolar attraction), polarity, induction, and nonclassical attraction (e.g., hydrogen-bonding). Dispersion and repulsion always contribute significantly except when nonclassical effects are very large as in carboxylic acids. Analytic potential models, with parameters for the nonpolar forces, the use of angle averaging for polar molecules to obtain effective parameters, and mixing rules for unlike interactions were shown. Due to the sensitivity of properties to mixing rules 5[5,6] it appears that at least one state independent binary parameter is necessary to describe unlike interactions accurately.

CORRESPONDING-STATES' THEORY DISCUSSION

Corresponding-states' theory was discussed by Prausnitz, referring to the review article by Leland and Chappelear[7] for a general description, to Vera and Prausnitz[8] for application to a mixture of simple substances, to Bondis book[9] for glasses and amorphous polymers, and to Patterson[10] for the Prigogine-Flory corresponding states theory for polymers and mixtures. The most important effect to account for in fluids is the effect of density on molecular rotation, so the inclusion of a properly chosen third parameter allows correlation of thermodynamic properties of a wide variety of substances. For mixtures, conformal solution theory has been recently applied by Ellis and Chao[11] and the van der Waals mixing rules for one-fluid aproaches to mixtures are referenced by Leland, et al[12].

The virial equation of state, which is useful for low to moderately-dense gases was outlined by John O'Connell showing both microscopic and mahroscopic considerations. The series in pressure and in density are essentially equivalent in accuracy when only the second coefficient is used, but if the third coefficient is also used, the density series is much better. The order of magnitude of the second coefficient for various systems, particularly for cross coefficients, was outlined, followed by calculational methods from intermolecular potentials and generalized correlations (see ref. 4, chap. 7). Also shown were the effects of vapor-phase nonideality on relative voltatilities and on the solubility of solids and liquids in compressed gases. It was concluded that the virial equation is a valuable tool because of its considerable range of application and its exact mixing rules.

A LOOK AT PERTURBATION THEORY

A newer development in formal statistical thermodynamics is perturbation theory within the radial distribution function framework. Keith Gubbins showed how hard-sphere fluids are used as a basis (see ref. 4, chap. 8, 9) as well as the usefulness of a simple approximation to predict solubilities of gases and of polymers in liquids,[13,14] and for properties of gases in electrolyte solutions. Impressive results[15,16] were also shown for simple systems using more complete expressions. It was pointed out that perturbation theory shows that anisotropies of intermolecular forces primarly affect heat capacities and pressures (at a given temperature and density) but not energies.

Closely following this was John Prausnitz' discussion of a generalized van der Waals model which leads to similar expressions as perturbation theory but is derived from the partition function. Various recent equations of state for liquids can be derived with different approximations not only unifying the development, but suggesting new ideas for better equations.

Group contribution methods were covered by John O'Connell, illustrating both pure-component and mixture properties. For pure components there are methods to calculate thermodynamic functions of formation[17], ideal gas heat capacities[18] and intermolecular potential parameters[19]. For mixtures, the Pierotti correlations[20] and the solution of groups method[21] for activity coefficients were discussed.

Two diverse topics were discussed in one session by John Prausnitz: polymer solutions and systems with strong interactions. Polymer solution theory is reviewed by Flory[22] and by Patterson[23] and a pedagogical introduction is given by Patterson[10]. Data for polymer systems can be found in the Polymer Handbook[24] and for polymer solutions in an article by Sheehan and Bisio[25]. The "chemical theory" of fluids includes gases[26, 27] (see also ref. 1, p. 134H, where eq. 5.10-11 should have the ½ on the LHS not the RHS), and liquids, where both Prigogine and Defay[28] and Prausnitz (ref. 1, p. 314H) show how the concepts of considering new species to be formed by strong bonding can describe nonidealities in mixtures.

A final topic on thermodynamic properties was electrolyte solutions a topic usually ignored in chemical engineering courses, but one of great relevance not only in inorganic chemical industries, but also organic processes where water contacts gases like ammonia and carbon dioxide. The macroscopic phenomena, and the complex formulations for describing them were discussed by John O'Connell, based on the book by Robinson and Stokes[29]. A brief derivation of the Debye-Huckel expression[30] and its modifications were shown. Since these are accurate only for very low concentrations, various empirical theories for concentrated electrolytes were illustrated, as were those for mixed electrolytes[29]. Finally, a remarkably simple but accurate corresponding-states' treatment for molten salts was described[31].

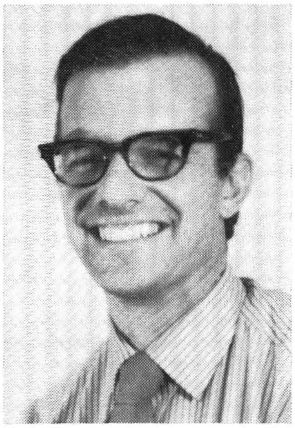
A DAY FOR TRANSPORT PROPERTIES

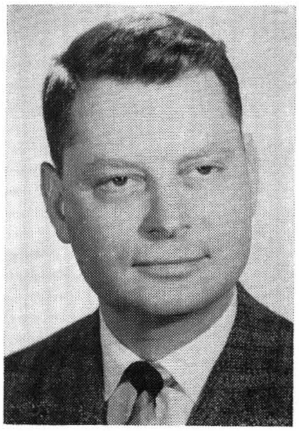
ONE DAY OF THE WORKSHOP was devoted to transport properties, Keith Gubbins describing the macroscopic nonequilibrium thermodynamics development of Fitts[32] and of Reed and Gubbins (ref. 4, chap. 12 and 13). Particular attention was paid to multicomponent diffusion since much confusion and error can arise in the definitions of the coefficients. Statistical mechanics of transport were developed along the time correlation function formalism because of its simplicity and the fact that it leads naturally to corresponding-states' treatments.

Dilute gas theories using intermolecular potential functions were illustrated by John O'Connell, including the use of angle-averaging for polar species[4]. The lack of sensitivity of the data to the details of the potential function was shown clearly by Hanley and Klein[33]. The use of corresponding states was shown for dense fluid transport coefficients, particularly the three parameter form of Tham and Gubins[34] and of Doan and Brunet[35]. These simple methods are impressive in their accuracy and broad application to nonpolar liquids. Finally, Keith Gubbins discussed calculation of dense fluid transport coefficients from statistical mechanical theories. Of particular inteerst was the Enskog hardsphere methods[4, 36].

The variety of course structures for teaching this material showed up in several of the discussions. While most undergraduate Chemical Engineering curricula contain one Physical Chemistry course with the elements of molecular concepts, except for occassional small portions of a chemical engineering thermodynamics, no opportunity is usually available to teach much of the present material. As a result most departments leave this for graduate work or never do it. The leaders felt that this may be some disservice to many of our students who will encounter the need to use methods of design correlation and analysis which will increasingly be based on molecular concepts. Integration of this material into the undergraduate curriculum can be done by a few illustrative examples in usual courses, such as those given above, or more intensive study can be given by thorough use of the books by Prausnitz and Reed and Gubbins as texts in separte Chemical Engineering Course, as is done at the University of Florida.


Keith Gubbins


John P. O'Connell


John Prausnitz

The leaders felt the Workshop group, though small, was enthusiastic and responsive. We learned a great deal in the process of trying to organize what we thought could be "teachable" to undergraduates and graduates. Hopefully this brief guide to some of the topics and the literature sources will help others to bring molecular concepts into greater emphasis in teaching.

REFERENCES

1. Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice-Hall, Englewood Cliffs, (1969).
2. Tsonopoulos, C. and Prausnitz, J. M., Cryogenics, *9*, 315 (1969).
3. Alesandrini, C. G., Lynn, S., and Prausnitz, J. M., Ind. Eng. Chem. Proc. Des. Dev., *11*, 253 (1972).
4. Reed, T. M., and Gubbins, K. E., "Applied Statistical Mechanics", McGraw-Hill, New York, (1972).
5. Singer, K. and Singer, J. V. L., Mol. Phys., *11*, 279 (1970).
6. Eckert, C. A., Renon, H., and Prausnitz, J. M., Ind. Eng. Chem. Fund., *6*, 58 (1967).
7. Leland, T. W., and Chappelear, P. S., Ind. Eng. Chem., *60*, #7, 15 (1968).
8. Vera, J. H., and Prausnitz, J. M., Chem. Eng. Sci., *26*, 1772 (1971).
9. Bondi, A., "Physical Properties of Molecular Crystals, Liquids and Gases", Wiley, New York, (1968).
10. Patterson, D., Macromolecules, *2*, 672 (1969).
11. Ellis, J. A., and Chao, K. C., A.I.Ch.E. Journal, *18*, 70 (1972).
12. Leland, T. W., Sather, G. A., and Rowlinson, J. S., Trans. Farad. Soc., *68*, 320 (1972).
13. Tiepel, E., and Gubbins, K. E., Proc. Internat. Solvent Extraction Conference, (Soc. Chem. Ind., London, 1971).
14. Tiepel, E. W., and Gubbins, K. E., Can. J. Chem. Eng. *50*, 361 (1972).
15. Leonard, P. J., Henderson, D., and Barker, J. A., Tran. Farad. Soc., *66*, 2439 (1970).
16. Rogers, B. L., and Prausnitz, J. M., Tran. Farad. Soc., *67*, 3474 (1971).
17. Benson, S. W., Crookshank, F. R., Golden, P. M., Halgen, G. R., O'Neal, H. E., Rogers, A. S., Shah, R., Walsh, R., Chem. Rev., *69*, 279 (1969).
18. Thinh, T. P., Durran, J. C., and Ramalho, R. S., Ind. Eng. Chem. Proc. Des. Dev., *10*, 576 (1971).
19. Galloway, T. R., A.I.Ch.E. Journal, *18*, 833 (1972).
20. Deal, C. H., and Derr, E. L., Ind. Eng. Chem., *60*, #4, 28 (1968).
21. Deal, C. A. and Derr, E. L., "Distillation", Brighton Soc. Chem. Ind., (1969).
22. Flory, P. J., Disc. Farad. Soc., *44*, 7 (1970).
23. Patterson, D., and Delmas, G., Disc. Farad. Soc., *44*, 98 (1970).
24. Mark, H., and Immergut, E. Ed., "Polymer Handbook", Interscience, New York (1966).
25. Sheehan, D. J., and Bisio, A. L., Rubber Chem. Tech., *39*, 149 (1966).
26. Mason, E. A., and Spurling, T. H., "The Virial Equation of State", Pergamon, New York, (1969).
27. Tsonopoulos, C., and Prausnitz, J. M., Chem. Eng. J., *1*, 273 (1970).
28. Prigogine, I., and Defay, R., "Chemical Thermodynamics", Longmans, London, (1954).
29. Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions", 2nd Ed. Rev., Butterworths, London, (1965).
30. Resibois, P., "Electrolyte Theory", Harper and Row, New York, (1969).
31. Young, R. E. and O'Connell, J. P., Ind. Eng. Chem. Fund., *10*, 418 (1972).
32. Fitts, D. D., "Nonequilibrium Thermodynamics", McGraw-Hill, New York, (1962).
33. Hanley, H. J. M., Klein, M., J. Chem. Phys., *50*, 4765 (1969).
34. Tham, M. J., and Gubbins, K. E., Ind. Eng. Chem. Fund., *4*, 63 (1970).
35. Doan, M., and Brunet, J., Ind. Eng. Chem. Fund., *11*, 356 (1972).
36. Tham, M. K., and Gubbins, K. E., J. Chem. Phys., *55*, 368 (1971).

TECHNOLOGY ASSESSMENT: Hill

(Continued from page 186)

ment and Public Policy. The practice of Technology Assessment, while not a traditional engineering function, has attracted and involved many engineers and scientists and will continue to do so. Chemical Engineers, we believe, will play a key role in this new and exciting area. ☐

REFERENCES

1. *A Study of Technology Assessment,* Report of the Committee on Public Engineering Policy, National Academy of Engineering, July 1969.
2. *Technology: Processes of Assessment and Choice,* Report of the National Academy of Sciences, July 1969.
3. Kasper, R. G. ed., *Technology Assessment,* Praeger, N. Y., 1972.
4. *Technical Information for Congress,* Report to the Subcommittee on Science, Research, and Development of the Committee on Science and Astronautics, U. S. House of Representatives, April 25, 1969.
5. Weisbecker, L. W., *Technology Assessment of Winter Orographic Snowpack Augumentation in the Upper Colorado River Basin,* Stanford Research Institute, May 1972.
6. Jones, M. V., et. al., *A Technology Assessment Methodology,* six volumes, MITRE Corporation, June 1971.
7. Coates, J. F., *Technology Assessment, 1,* 109 (1973).
8. *Technology Assessment,* Official publication of the International Society for Technology Assessment, Gordon and Breach, Publishers.
9. Cetron, M. J. and C. A. Ralph, *Industrial Applications of Technological Forecasting,* Wiley-Interscience, N. Y. 1971.
10. Martino, J. P., *Technological Forecasting for Decision-Making,* American Elsevier, N. Y., 1972.