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DE91 004168

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- H. "Vapor-Liquid and Liquid-Liquid Equilibria
and Critical States of Water + n-Decane Mixtures".
Fluid Phase Equilibria, submitted,
by Q. Wang and K.C. Chao

- I. "Equilibrium Vaporization of Oils by the Chain-of-Rotators
Group Contribution Equation of State".
Chemical Engineering J., submitted.
by Z.X. Wang, J.D. Pults, R.A. Greenkorn and K.C. Chao

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Final Report

DE-FG02-84ER13288

9/1/87 - 11/30/90

Gas-Liquid-Liquid Equilibria in
Mixtures of Water, Light Gases, and Hydrocarbons

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ABSTRACT

Phase equilibrium in mixtures of water + light gases and water + heavy hydrocarbons has been investigated with the development of new local composition theory, new equations of state, and new experimental data.

The preferential segregation and orientation of molecules due to different energies of molecular interaction has been simulated with square well molecules. Extensive simulation has been made for pure square well fluids and mixtures to find the local composition at wide ranges of states. A theory of local composition has been developed and an equation of state has been obtained for square well fluids. The new local composition theory has been embedded in several equations of state.

The pressure of water is decoupled into a polar pressure and a non-polar pressure according to the molecular model of water of Jorgensen *et al.* The polar pressure of water is combined with the BACK equation for the general description of polar fluids and their mixtures. Being derived from the steam table, the Augmented BACK equation is particularly suited for mixtures of water + non-polar substances such as the hydrocarbons. The hydrophobic character of the hydrocarbons had made their mixtures with water a special challenge.

The augmented BACK equation, containing 107 terms, is exceedingly complex. The complexity discourages use of the equation. We have developed simplified forms of the equation to retain the quantitative character of the original equation and be convenient to use.

The fluid phased equilibria of water + n-decane have been experimentally studied. A rich variety of phenomena are observed at elevated temperatures and pressures. Vapor-liquid equilibria are found to exist where the components have become highly miscible. Liquid-liquid equilibria persists at higher pressures apparently without bound. The new experimental observations confirm predictions of the augmented BACK equation of state.

A new group contribution equation of state is developed to describe phase equilibrium and volumetric behavior of fluids while requiring only to know the molecular structure of the components.

Introduction

Water has attracted the attention of scientists and engineers since the beginning of scientific inquiry due to its wide occurrence and life supporting role. Phase equilibria in mixtures of water + light gases, and water + heavy hydrocarbons are of interest in chemical processes, petroleum and natural gas production, and environment systems. In chemical and petroleum processes water is commonly used as a solvent or a reactant. New conditions of elevated temperature and pressure are encountered in processing refractory fossil fuels and new chemicals, requiring new phase equilibrium information. Petroleum and natural gas reservoirs often coexist with aquifers, making the mutual solubilities of interest in the production processes. Solubility of hydrocarbons in water can markedly affect the quality of water in the environment.

Technological applications and scientific interest require quantitative description of the phase equilibrium and solubility phenomena of these water mixtures. The hydrophobic character of the hydrocarbons and the light gases had presented a challenge to a general quantitative theory.

In this investigation, we have:

- Obtained equations to describe the preferential molecular segregation in fluid mixtures, thus expressing the local composition which is the cause of the highly non-ideal solution behavior of many fluids. We have embedded the local composition expression in commonly used equations of state for improved description of polar fluid mixtures.
- Developed equations of state for the general description of water + light gases and water + hydrocarbons to include their fluid phase equilibria and thermodynamics.
- Extended the equations to polar fluids for the general description of their phase equilibria.
- Experimentally studied mixtures of water + n-decane to observe the exceptionally rich variety of phase behavior, and to verify predictions of the new equations.
- Obtained a group contribution equation of state for non-polar fluids for a general description of their phase and volumetric behavior while requiring only to know the molecular structure of the components.

Local Compositions

Strongly non-ideal polar fluid mixtures are of common occurrence and are encountered in numerous chemical processes. Aqueous mixtures are prominent examples of such mixtures. The electric poles in these molecules contribute to the intermolecular energy in addition to the dispersion energy, giving rise to large total inter-molecular energy, and to large variation in the energy among various molecules. The molecules can preferentially segregate in response to the energy differences. The local composition (LC) at the microscopic neighborhood of a molecule can be much altered from the bulk fluid composition. Debye and Hueckel (1) developed their ionic solution theory by recognizing the LC of ions. Wilson (2) obtained his activity coefficient equation of postulating the dependence of partial entropy on LC. Whiting and Prausnitz (3) derived thermodynamics of mixtures based on LC and showed improved equation of state calculations. The phenomenon of LC must be addressed in modeling the thermodynamics and phase equilibrium of mixtures of water and of other polar substances.

LC cannot be determined conveniently by experiments in the laboratory, but can be simulated by computer calculations. Nakanishi and co-workers (4-7) and Hoheisel and Kohler (8) obtained LC in mixtures of Lennard-Jones molecules by molecular dynamics simulation. Lee, Sandler and Patel (9) determined local composition of square-well mixtures.

In this investigation we have determined LC of square-well fluids by means of Monte Carlo simulation. Square-well molecules were chosen for the clearly defined neighborhood in which local composition occurs. LC is found to be dependent on density, temperature and energy difference. A wide range of states of temperature, density, interaction energies, and molecular diameters are observed. Appendices A and B present the results and the models of LC that have been developed for both the total LC and the relative LC.

An equation of state for square-well fluids is obtained from the total LC model. The equation is presented in Appendix C.

The LC model has been embedded (10) in three equations of state: Soave, Patel-Teja, and Cubic Chain-of-Rotators. Improvement in representation of vapor-liquid equilibrium is generally obtained with the use of LC mixing rules. Figure 1 shows the vapor-liquid equilibrium of methanol + benzene mixtures at 100°C. The cubic chain-of-rotators equation with embedded local composition mixing rules represents the data to about the uncertainty of the experiments. The other two equations of state are also substantially improved when using LC relative to classical quadratic mixing rules.

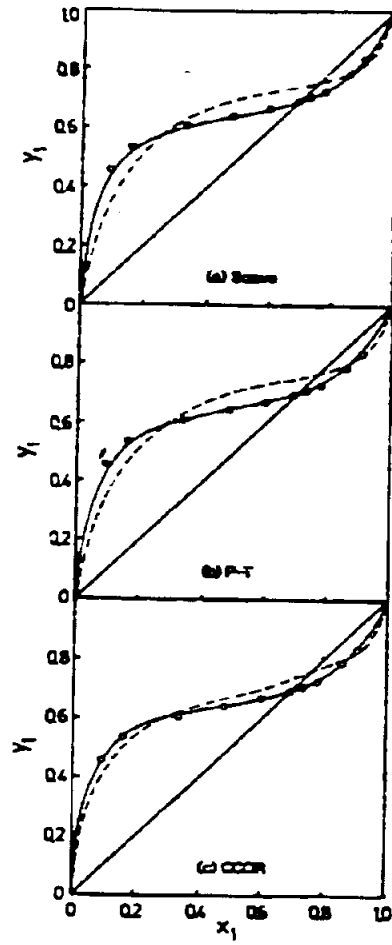


Figure 1. Vapor-liquid equilibrium of methanol + benzene mixtures at 100°C. (○) Data of Butcher and Medani (1968). (—) LC mixing rules; (---) quadratic mixing rules.

Systems with like components, such as methanol + ethanol are well described by either quadratic or LC mixing rules. However, systems containing non-polar + polar species are highly non-ideal due to large differences in the molecular interactions, and their behavior is not well described by the quadratic mixing rules. Substantial improvement is obtained for these systems by employing density dependent LC mixing rules. LC embedded equations of state are of particular interest at high pressure states because the activity coefficient method becomes unsuitable.

Augmented BACK Equation of State

The pressure of a polar fluid like water is made up of contributions due to interactions of the electric poles of the molecules and other modes of interaction that also occur in non-polar fluids. It is the interaction of the poles that imparts the characteristic complexity to the thermodynamics of polar substances. We have determined the polar pressure of water by decoupling the total pressure into a polar pressure and a non-polar pressure according to the molecular model of water proposed by Jorgensen and coworkers (11). The augmented Boublick-Alder-Chen-Kreglewski (BACK) equation is obtained by combining this polar pressure with the BACK equation.

Appendix D presents the derivation of the augmented BACK (ABACK) equation for polar fluids. For molecules of zero polarity the equation simplifies to the BACK equation (12) which, as a very accurate equation for non-polar fluids, has been used for preparing standard thermodynamic property tables. For water the ABACK equation reduces to the Keenan Steam Table equation (13). For mixtures of water and for polar substances in general, the equation in effect interpolates between the BACK and Keenan equations. The interpolation is, however, not a simple algebraic procedure but is based on a corresponding states conversion.

Five constants are required to be known for a polar fluid to be described by the ABACK equation. These constants are reported in Appendix D for 26 polar fluids, including water, alcohols, acetone, cresol, etc. Appendix D shows that the ABACK equation gives a good account of the vapor pressure and volumetric properties of pure polar fluids. Vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) of water + light gases and water + hydrocarbons are found to be well described by the ABACK equation. Two temperature-independent coefficients are introduced for each unlike pair of molecules in the mixture calculations.

Mixtures of polar + non-polar fluids and of polar + polar fluids are further studied in Appendix E. In addition to VLE, the enthalpy of mixing of liquids and of compressed gases are addressed. A large volume of data has been accumulated in recent years on the heat effects of mixing steam and natural gas. The ABACK equation gives a good account of the observed data.

Simplified Augmented BACK Equations

Although the augmented BACK equation gives a good account of the phase equilibria and thermodynamic properties of polar fluids such as water, alcohols, ketones and their mixtures, the equation is exceedingly complex, and not convenient to use. The 107 terms of the equation can be quite intimidating. The complexity of the equation is compounded when derivation is made for fugacity, enthalpy, and other thermodynamic quantities.

We present in Appendix F a simplified augmented BACK equation. By linear correlation of 1025 points of the polar pressure of water we obtained a simplified function of 57 terms. Experimentally inaccessible states in the condensible range were included in the correlation in order to obtain good fugacity and other derived integral properties for the liquid states. The simplified equation has been tested with fluid phase equilibrium, volumetric, and enthalpy calculations. The quantitative character of the polar pressure of water is retained with a reduction of the equation to about one half its original length.

A further simplification has been made of the augmented BACK equation in view of the still quite lengthy form. In this effort, 42 vapor pressure points of water from 273 to 647 K are taken from the steam tables, together with 126 states of pVT , for the determination of a new expression for the polar pressure of water. A non-linear regression procedure is employed to fit the combined data. Lengthy calculations are involved to fit the saturation pressure of steam, with the benefit of dispensing with the large number of non-experimental states in the condensation range. The new simplified polar pressure of water now contains only 8 terms with 16 fitting constants.

Appendix G presents the simplified augmented BACK (SABACK) equation obtained by non-linear regression. The SABACK equation has been tested with vapor pressure, saturated liquid density for pure fluids, and mixture VLE and LLE calculations. Critical states of mixtures of water + n-decane are found to be well described. Co-existent VLLE three-phase states are calculated for water + paraffins and water + aromatics. Appendix G shows the comparison of the calculation with data.

Fluid Phase Equilibria in Water + n-Decane Mixtures

Mixtures of water + hydrocarbons exhibit a rich variety of fluid phase behavior that is of technological interest because of their common occurrence in chemical processes, in oil reservoirs, and in the environment. Mixtures of water + n-decane are of particular interest as model mixtures for steam stimulated production of heavy residual oils.

The weak interaction between water and hydrocarbon molecules contrasts sharply with the strong interaction between water and water molecules in the same mixtures. The hydrophobic behavior that results from the extreme dissimilarity of the molecular interactions invites unusual attention.

In Appendix H we report experimentally observed vapor-liquid and liquid-liquid equilibria at 573, 593, and 613 K at pressures up to 231 bars. Figure 2 shows that the mixtures behave very differently at high temperature and pressure than at ambient conditions where they are practically immiscible. Water and n-decane become highly miscible at a wide range of states at elevated temperatures and not so high pressures. The homogeneous liquid solution show vaporization equilibrium in about the same way as ordinary miscible solutions. In fact, a vapor-liquid critical state is observed at each temperature studied. High pressure makes liquid-liquid equilibrium to appear. The co-existent liquids are highly asymmetric in composition. Whereas the decane-rich liquid contains a fair amount of water, the water-rich phase is very pure water, containing only a minute amount of decane. The liquid-liquid co-existent states are open ended in the direction of high pressure. It appears that liquid-liquid equilibria persist without limit in the direction of high temperature and high pressure. This is a direct repudiation of the conventional dictum that gases are completely miscible at temperatures above critical.

The observed vapor-liquid critical states of the mixtures are not joined smoothly to the critical states of the two pure components as they do in many other mixtures. Figure 3 shows the observed mixture critical states to run from the critical state of pure decane to the VLLE end point, leaving the critical state of pure water to stand alone by itself. It appears that the critical state of water is in no way connected to the critical states of any mixtures.

The fluid phase equilibria of water + n-decane provide a severe test of an equation of state. Figure 4 shows the phase equilibrium ratios of water and decane that are calculated from the augmented BACK equation of state developed in this research compared to the experimental data. Quantitative agreement is obtained for both the VLE and LLE.

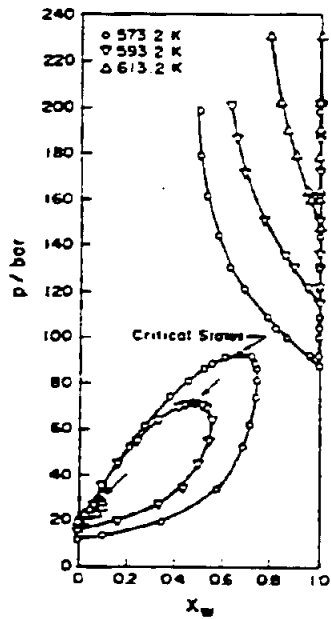


Fig. 2. Isothermal pressure-composition phase boundary curves.

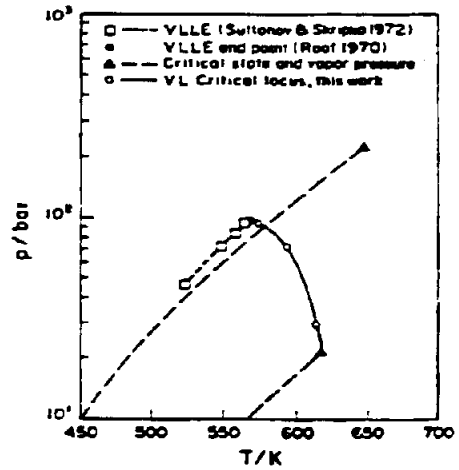


Fig. 3. The critical states and VLE coexistence states on the p - T plane.

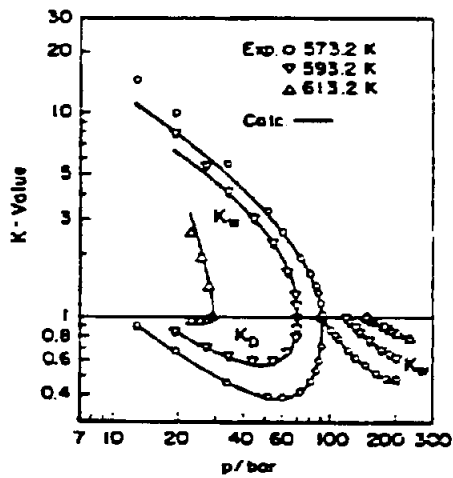


Fig. 4. Experimental and calculated K -values.

A Group Contribution Equation of State

A group contribution equation of state called the Chain-of-Rotators Group Contribution (CORGC) equation has been developed (14,15) for the description of liquid and gas states and liquid-gas equilibria for wide ranges of temperature and pressure. The equation parameters are expressed as contributions of groups which are the structural units of molecules. Since a large number of molecules are made of a small number of groups such as methyl CH_3 , methylene CH_2 , aromatic CH , cyclic CH_2 , etc., a group contribution equation of state applies to large classes of pure fluids and mixtures with the parameters of a relatively small number of groups. We have determined the CORGC equation parameters for 20 groups making it possible to describe fluid phase equilibria and thermodynamic properties of large classes of fluids. The group contribution method is particularly suitable for oil fractions for which the group composition can be determined by instrumental analysis such as NMR, but the molecular composition may remain unknown. Appendix I presents the equilibrium vaporization of oils calculated by the CORGC equation. The calculations are confirmed by extensive experimental data.

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Appendices - Publications from this Research

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Proposed Research
12/1/90 - 11/30/92
Group Contribution Thermodynamics of Fluids

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ABSTRACT

Thermodynamics of polar and non-polar fluids and their mixtures will be investigated in light of recent advances in understanding micro structures of fluids. Group contribution molecular models will be developed for computer simulation of molecules in the fluid state. Potential functions of the interactions of groups will be obtained for groups of common occurrence for the computer simulation calculation of thermodynamics and phase equilibria of large classes of molecules and their mixtures.

Introduction

Thermodynamics and phase equilibria of fluids and fluid mixtures are of fundamental interest to chemical, petrochemical, and biochemical processes. Quantitative description of fluid properties is indispensable for separation and mass transport operations and is required for the engineering and design of processes. Development of computer aided design of chemical processes has shed new light on the significance of systematic prediction. Generally 70-90% or more of the computing for process design on the computer are taken up by phase equilibrium and thermodynamic calculations. As new processes are developed for new chemicals, and as processing conditions are pushed to more extreme temperature and pressure, new thermodynamic and phase equilibrium knowledge will be in demand.

Theoretical and correlational methods are needed to describe fluids at diverse temperatures, pressures, and compositions. Experimental data are needed but are rarely directly useful to meet the demand at the great variety and diversity of states of interest.

Much progress has been made in recent years to develop methods for the description of fluids. Group contribution methods have been especially noteworthy. Since the large number of molecules of interest in chemical processes are made up of a relatively small number of groups or structural units such as the methyl CH_3 , methylene CH_2 , hydroxyl OH , etc., a group contribution method is generally useful for the large classes of molecules that are made up of the groups described in the method. Once the group parameters are determined, molecular fluids for which no experimental data are available can be calculated. Only the molecular structure is required to be known.

The greatest success of the group contribution method has been in the description of non-ideal solution behavior and hence low pressure vapor-liquid equilibrium. Nitta *et al.* (1) developed their method based on cell theory. Subsequent work (2) extended the method to 15 groups. The ASOG (Analytical Solution of Groups) method of Wilson and Deal (3) and Derr and Deal (4) has been in wide use. Kojima and Tochigi (5) reported parameters for 31 groups. The UNIFAC method originally due to Fredenslund, Jones, and Prausnitz (6) has been made very extensive by much successive work. The monographs by Fredenslund, Gmehling, and Rasmussen (7), and by Kojima and Tochigi (8) present parameters for a large number of groups.

Group contribution method has been applied to equation of state development. Cunningham (9) and Majeed and Wagner (10) developed the Parameters-From-Group Contribution (PFGC) equation of state using a modified Flory-Huggins Theory to account for molecular size difference and modified Wilson equation for the attractive energy. Skjold-Jorgensen (11) developed a group contribution equation of state (GCEOS) built on a Carnahan-Starling repulsive pressure. This method requires pure component critical properties and a large number of group parameters. Georgeton and Teja (12) developed a group contribution equation from the Perturbed Hard Chain equation of Beret and Prausnitz (13), but only five groups have been reported. Gupte *et al.* (14) combined the van der Waals equation with the UNIFAC model. Vapor pressures are required in the calculations, and the method is not applicable to non-condensable light gas containing fluids. Pulis (15) *et al.* developed The Chain-of-Rotators group contribution (CORGC) equation from the Chain-of-Rotator equation of Chien *et al.* and reported equation of state parameters for 20 non-polar and weakly polar groups. Group contribution equations of state have not achieved as much success as the non-ideal solution

group contribution models. They are either for non-polar fluids only or said to be for all fluids but really not so good for polar fluids. In general the accuracy and scope of group contribution equations of state are in need of improvement.

A new group contribution method is emerging for the description of fluids. This method is molecular simulation on the computer. In this method the interaction of molecules is decomposed into the interaction of the groups of the molecules and numerical calculations are made of the statistical mechanics of the interactions to yield the thermodynamics and phase equilibria of the fluid. The method of molecular simulation on the computer is capable of representing non-ideal solution behavior and equation of state properties. The objective of the proposal research is to develop the method for the description of the thermodynamics of fluids.

Group Contribution Molecular Simulations of Fluids and Mixtures

In molecular simulation one calculates the thermodynamics of a fluid by taking averages of the molecular interactions for a large number of molecular configurations. Molecular simulation has been a valuable tool for studying micro structure of fluids and for testing molecular theories. As a result of recent development in simulation methods and in computing power, molecular simulation is becoming a new method of calculation of thermodynamic properties for technological applications. The proposed research to develop a group contribution molecular model is aimed at making molecular simulations useful for technological purposes.

Molecular simulation is a rigorous method of calculation based on the structure of the molecules. It is free of simplifying assumptions that are required in developing equations of state or solution theories. All group contribution methods so far developed invoke the unstated assumption that only the number and kind of groups matter, and that the structure of the molecule does not. In fact molecular structure is not accounted for in all current group contribution methods. In contrast, molecular structure will be rigorously expressed in molecular simulations.

A major and fundamental deficiency of current group contribution methods is that they are limited to mono-functional molecules. The methods fail catastrophically for compounds containing more than one strong functional group in a molecule (16). The thermodynamic correlations depend on the micro structure to be unchanged from the experimental states, which belong to the mono-functional molecules. As the micro structure of the poly functional molecular fluids is different, the correlations no longer apply. Molecular simulation calculations will be free from such deficiencies, as it will produce the appropriate micro structure in the simulation calculations.

Molecular simulation is indifferent to experimental difficulties such as those of extreme temperatures or pressures. The calculations are carried out on the computer just as readily as for states experimentally easy to attain. Molecular simulation of polar and non-polar molecular fluids have been carried out in studies of micro structure of fluids by Jorgensen and coworkers (17), Bolis *et al.* (18), Karlstrom *et al.* (19), and Weiner *et al.* (20). The interest was conformation, hydrogen bonding, atom-atom correlation function, hydrophobicity, and the like, while configurational energy and density were marginally addressed, phase equilibria were not

touched.

In the proposed research molecular interaction will be represented as the combined mutual interactions of the groups. The potential function of interaction will be obtained for groups of common occurrence such as CH₃ (aliphatic), CH₂ (aliphatic), CH (aromatic), OH (alcohol), CO (of ketone), NH (of amide), NH₂ (of amine), CO (of aldehyde) etc. Hydrogen atoms in these groups are generally implicit, except when they are charged, in which case they are explicit.

The representation of molecules also requires structural geometrical information such as lengths, angles, and rotational properties of bonds. These are available in the literature, e.g., CRC Handbook, for the common bonds of interest in this research.

The group interaction potential functions and the structural geometries complete the description of molecules for molecular simulation calculations of their thermodynamics.

We have carried out a limited amount of molecular simulation calculations. Our experience indicates that the OPLS (Optimized Potential for Liquid Simulation) form of Jorgensen *et al.* (17) gives good accurate simulation results when it is improved. The OPLS is Lennard-Jones potential plus columbic potential for the electric charges at the poles. Our improvement is to make the Lennard-Jones parameters σ and ϵ temperature dependent. We adopt for σ Barker's formula for the hard sphere diameter, and for ϵ the formula for u^0 in BACK equation of state. In this way, we retain the great advantage of simplicity of Lennard-Jones while allowing the departure of the model potential from the true to be corrected as a temperature dependence.

An important part of the proposed research is the demonstration of calculated thermodynamics and fluid phase equilibria from the resulting group contribution molecular model. Since the model is very generally applicable to include solution non-ideality and equation of state calculations, the demonstration will have to be extensive. As the potential function of a new group is developed, a new class of fluids becomes accessible to calculations. The demonstration will then be made for that new class. We will emphasize calculations that are beyond the capabilities of current correlations: polar fluids and mixtures at high pressures, molecules that contain more than one strong functional group, and effect of molecular structural differences.

Molecular simulation requires long calculations on the computer to obtain thermodynamic properties of interest. Thanks to advances in computer technology, the cost of molecular simulations is no longer exorbitant but still more than equation of state or solution theory calculations. Gubbins (21) presented in a 1989 article the following cost figures for determining binary vapor-liquid equilibria including 4-5 isotherms:

Method	Cost, \$	Time
Redlich-Kwong eq.	10	0.1 h
Perturbation theory	100-1000	1 h
Molecular simulation	3000	4 h
Lab experiment	30,000	60 days

The computing time is shown for a then current supercomputer. With the new work stations the cost has come down by about a factor of 3. Molecular simulation has a place in between equation of state calculations and laboratory experiments.

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Facilities

Computing facilities at the Purdue University Computing Center are among the best at any university in the United States. Large-scale systems operated by the center include two vector supercomputers: an ETA-10P running UNDX (trademark of Bell Laboratories) and a CDC Cyber 205 with the VSOS operating system. An IBM 3090-180E mainframe provides VM/CMS service. Two sequent systems, a Symmetry S81 and a Balance B21000, serve large numbers of students with multi-processor UNIX systems. Five dual-processor DEC VAX-11/780 systems also run UNDX. The center operates a few DEC PDP-11/70 RSTS/E minicomputer systems and several microcomputer labs.

We are making use of the Cyber 205 and will continue to use it for long runs. For program development, debugging, and short calculations, we use a Sun Sparc work station maintained in our research group shared by several students. We request a new work station to be added to our laboratory, as it is extremely helpful to have the computer readily accessible for program development, debugging, and short calculations.

**Curriculum Vitae of
Kwang-Chu Chao**

Present Positions:

Professor of Chemical Engineering, Purdue University (1968 -)
Harry Creighton Peffer Distinguished Professor of Chemical Engineering, Purdue
University (1989 -)

Degrees:

Ph.D., Chemical Engineering, Wisconsin-Madison, 1956
M.S., Chemical Engineering, Wisconsin-Madison, 1952
B.S., Chemical Engineering, National Chekiang University, Hangzhou, China, 1948

Experience:

Oklahoma State University, Associate Professor, 1964-1968
Illinois Institute of Technology, Associate Professor, 1963-1964
Chevron Research Co., Research Engineer, 1957 - 1963
University of Wisconsin, Research Associate, 1956 -57
Taiwan Alkali Co., Chemical Engineer, 1952-54; 1948-51

Memberships:

American Institute of Chemical Engineers
American Chemical Society
American Association of University Professors
American Society of Engineering Education

Professional Activities:

American Institute of Chemical Engineers - National Program Committee
Area 1a, 1971-80, 1982-85; Central Oklahoma Section, Secretary, 1956-67,
Vice Chairman, 1967-68

Panel of Experts for the evaluation of research needs in coal liquefaction,
Department of Energy, 1988.

Editorial Boards:

AICHE Journal (1977-81)
Industrial and Engineering Chemistry Annual Reviews (1970-74)

Biographical Listings:

Who's Who in America, Who's Who in the World, Who's Who in Engineering, American Men and Women of Science, International Scholars Directory, Dictionary of International Biography, International Who's Who in Community Service, Community Leaders and Noteworthy Americans, Men of Achievement, America's Names and Faces Library, Who's Who in the Midwest, Personalities of the West and Midwest, Who's Who in Technology Today, Who's Who of Sino-American, International Who's Who in Engineering, Personalities of America, The International Directory of Distinguished Leadership, Who's Who in Society

Honors and Awards:

American Institute of Chemical Engineers, Fellow (1976)
Honorary Professor, Beijing Institute of Chemical Technology (1984)
Honorary Professor, Zhejiang University (1988)
Plenary Lecturer, International Symposium in Thermodynamics in Chemical Engineering and the Chemical Industry, Beijing, China, May 1988
Lecturer, International Scientist National Science Council, Taiwan (1989)

External Graduate Degree Examiner:

McGill University
University of Ottawa
The University of Alberta

Publications of K.C. Chao since 1985

1. H. Kim, H.M. Lin, and K.C. Chao, "Cubic Chain-of-Rotators Equation of State" *Ind. Eng. Chem. Fundam.*, *25*, 75-84 (1986).
2. H.Y. Kim, H.M. Lin, and K.C. Chao, "Vapor-Liquid Equilibrium in Binary Mixtures of Carbon Dioxide + Phenyloctane and Carbon Dioxide + 1-Hexadecene", *AIChE Symposium Series*, Vol. 81, No. 244, p. 86-89 (1985).
3. Z. Jin, H.M. Lin, R.A. Greenkorn, and K.C. Chao, "Vapor-Liquid Equilibrium in Binary Mixtures of Propylene and Propylene Oxide", *AIChE Symposium Series*, Vol. 81, No. 244, p. 90-95 (1985).
4. E.J. Kolodziej, Z. Jin, R.A. Greenkorn, and K.C. Chao, "Vapor-Liquid Equilibrium in Binary Mixtures of Propylene Oxide with 1,2-Dichloropropane and with tert-Butanol", *AIChE Symposium Series*, Vol. 81, No. 244, p. 80-85 (1985).
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6. T.M. Guo, H. Kim, H.M. Lin, and K.C. Chao, "Cubic Chain-of-Rotators Equation of State 2. Polar Substances", *I&EC Process Des. Devel.*, *24*, 764-767 (1985); "Cubic Chain-of-Rotators Equation of State for Polar Fluids", *Fluid Phase Equilibria* *24*, 43-61 (1985).
7. T.M. Guo, H.M. Lin, and K.C. Chao, "Cubic Chain-of-Rotators Equation of State 3. Mixtures of Polar Substances", *I&EC Process Des. Devel.*, *24*, 768-773 (1985).
8. H. Kim, H.M. Lin, and K.C. Chao, "Vapor-Liquid Equilibrium in Binary Mixtures of Propane and n-Butyraldehyde", *AIChE Symposium Series*, Vol. 81, No. 244, p. 144-146 (1985).
9. H. Kim, C.M. Dinh, W.A. Leet, H.M. Lin, and K.C. Chao, "Vapor-Liquid Equilibrium in Mixtures of Carbon Dioxide + Diethylamine + Water", *AIChE Symposium Series*, Vol. 81, No. 244, p. 147-150 (1985).
10. Z.L. Jin, H.M. Lin, R.A. Greenkorn, and K.C. Chao, "Vapor-Liquid Equilibrium in Binary Mixtures of Methylene Chloride and Ethanol", *AIChE Symposium Series*, Vol. 81, No. 244, p. 151-154 (1985).
11. Z.L. Jin, H.M. Lin, R.A. Greenkorn, and K.C. Chao, "Vapor-Liquid Equilibrium in Binary Mixtures of tert-Butyl-Methyl Ether + n-Hexane and + Benzene", *AIChE Symposium Series*, Vol. 81, No. 244, p. 155-160 (1985).
12. Z.L. Jin, H.M. Lin, R.A. Greenkorn and K.C. Chao, "Vapor-Liquid Equilibrium in Binary Mixtures of Propylene Oxide + Methyl Acetate", *AIChE Symposium Series*, Vol. 81, No. 244, p. 161-164 (1985).
13. H.M. Lin, H. Kim, W.A. Leet, and K.C. Chao, "A New Vapor-Liquid Equilibrium Apparatus for Elevated Temperatures and Pressures", *I&EC Fundamentals*, *24*, 260-262 (1985).
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15. C.M. Dinh, H. Kim, H.M. Lin, and K.C. Chao, "Vapor-Liquid Equilibrium in Water + m-cresol + Hydrogen Mixtures at High Temperatures and Pressures," *J. Chem. Eng. Data*, 30, 326-327 (1985).
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31. F.N. Tsai, S.H. Huang, H.M. Lin, and K.C. Chao, "Solubility of Methane, Ethane, and Carbon Dioxide in a Mobil Fischer-Tropsch Wax and in n-Paraffins", *Chem. Eng. J.* 38, 41-46 (1988).
32. S.H. Huang, H.M. Lin, and K.C. Chao, "Solubility of Carbon Dioxide, Methane, and Ethane in n-Eicosane", *J. Chem. Eng. Data*, 33, 145-147 (1988).
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36. S.H. Huang, H.M. Lin, and K.C. Chao, "Solubility of Carbon Dioxide, Methane, and Ethane in n-Octacosane", *J. Chem. Eng. Data*, 33, 143-145 (1988).
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44. Gang Chen and Kwang-Chu Chao, "Vapor-Liquid Equilibrium in Mixtures of Methyl Formate + Acetone", *AIChE Symposium Series*, submitted.

45. R.J. Lee and K.C. Chao, "Equation of State for Square-Well Fluids", *Molecular Physics*, 65, 1253-1256 (1988).
46. Rong-Jwyn Lee and Kwang-Chu Chao, "Local Composition Embedded Equations of State for Strongly Non-ideal Mixtures", *I&EC Research*, 28, 1251-1261 (1989).
47. M.J. Lee and K.C. Chao, "Augmented BACK Equation of State, Part II Polar Fluid Mixtures", *AIChE Journal*, 34, 1773-1780 (1988).
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49. John D. Pults, Robert A. Greenkorn, and Kwang-Chu Chao, "Chain-of-Rotators Group Contribution Equation of State", *Chem. Eng. Sci.*, 44 2553-2564 (1989).
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51. Qi Wang and Kwang-Chu Chao. "Vapor-Liquid Equilibrium for Binary Mixtures of Butylene Oxide + n-Butyraldehyde, Butylene Oxide + iso-Butyraldehyde, and Methyl Acetate + Butylene Oxide", *AIChE Symposium Series*, submitted.
52. Chun-Lan Peng and Kwang-Chu Chao, "Vapor-Liquid Equilibria in Binary Mixtures of Isopropyl Acetate + n-Hexane and Isopropylacetate + Ethanol", *AIChE Symposium Series*, submitted.
53. M.J. Lee and K.C. Chao, "Polar Pressure of Water and Simplified Augmented BACK Equation of State", *Fluid Phase Equilibria*, accepted.
54. Qi Wang and Kwang-Chu Chao, "Vapor-Liquid and Liquid-Liquid Equilibria and Critical States of Water + n-Decane Mixtures", *Fluid Phase Equilibria*, in press.
55. Zong-Xiang Wang, John D. Pults, Robert A. Greenkorn, and Kwang-Chu Chao, "Equilibrium Vaporization of Oils by the Chain-of-Rotators Group Contribution Equation of State", *Chem. Eng. J.* submitted.
56. Chun-Lan Peng and Kwang-Chu Chao, "Simplification of the Augmented BACK Equation of State", *AIChE Journal*, submitted.

Book:

K.C. Chao, and R.L. Robinson, Jr., ed., "Equations of State - Theories and Applications, 597 pp. ACS Symposium Series 300, Am. Chem. Soc., Washington, D.C., 1986.

Handwritten note:
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