NIST
United States Department of Commerce
Technology Administration
National Institute of Standards and Technology

NISTIR 5059

Report of the Workshop on Thermophysical Properties of Ammonia/Water Mixtures

D.G. Friend and W.M. Haynes

NISTIR 5059

Report of the Workshop on Thermophysical Properties of Ammonia/Water Mixtures

D.G. Friend and W.M. Haynes

Physical and Chemical Properties Division
Chemical Science and Technology Laboratory
National Institute of Standards and Technology
Boulder, Colorado 80303-3328

February 1997

U.S. DEPARTMENT OF COMMERCE, William M. Daley
TECHNOLOGY ADMINISTRATION, Mary L. Good, Under Secretary for Technology
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, Arati Prabhakar, Director

Report of the

Workshop on Thermophysical Properties of Ammonia/Water Mixtures

Wednesday, June 26, 1996
Physical and Chemical Properties Division
National Institute of Standards and Technology
325 Broadway
Boulder, Colorado 80303

Abstract

A workshop on the *Thermophysical Properties of Ammonia/Water Mixtures* was held in Boulder, Colorado on June 26, 1996. The purpose of this Workshop was to gather together representatives of industry who have an interest in ammonia/water as a working fluid in various processes, with representatives of governmental agencies who are concerned with these technologies. Major objectives of the meeting were to determine the thermophysical properties required to advance technologies based on this mixture as a working fluid and to establish a mechanism for obtaining the required data and models. Staff members from the host National Institute of Standards and Technology division and representatives from industry reported on current activities in this area as well as future needs. The consensus conclusion was that accurate thermodynamic, transport, and kinetic properties are needed over broad ranges of temperature, pressure, and composition, and that a suitable process must be implemented to ensure that accurate experimental data and models will be available in the shortest possible time.

Keywords

ammonia, Kalina cycle, mixtures, properties, water, working fluid

Table of Contents

Appendices

Tables and Figures

Introduction

The National Institute of Standards and Technology (NIST) is the principal U.S. government agency with a mandate from Congress to provide scientific and technological assistance to industry. This responsibility includes the development of standard reference data for fluid systems of industrial importance, an activity in which NIST has been involved for more than 40 years. Pure steam (water) and ammonia have been subjects of extensive research at NIST, and the ammonia/water system has recently received attention as a working fluid for thermal power cycles. In addition to its importance in potential power plant applications, accurate properties data for ammonia/water mixtures are important when this binary fluid is used as the working fluid in other processes, such as absorption refrigeration cycles.

The Physical and Chemical Properties Division (formerly the Thermophysics Division) of NIST has been involved in a project (funded by the Department of Energy, Geothermal Division) to help to establish standard reference data for the thermophysical properties of the ammonia/water binary fluid system over a restricted range of interest for geothermal power cycles. In particular, we are investigating properties in the temperature range from 280 to 450 K (44 to 350 °F), with a maximum pressure of 3.5 MPa (500 psia), and with compositions in the range 0.8 to 1.0 ammonia (mole fraction[1]). This project involves the evaluation of literature data, experimental measurements, and the development of models for the thermodynamic and transport properties over these ranges. More general application of ammonia/water working fluids requires standards and properties data over a much larger region of the phase diagram. A Certified Research Need established by the International Association for the Properties of Water and Steam (IAPWS-ICRN) indicated a broad industrial interest in properties for this system at temperatures up to 866 K (1100 °F), at pressures to 34.5 MPa (5000 psia), and for the complete range of compositions. These ranges have been substantiated through NIST interactions with industry. Accurate properties data over these ranges are needed to design, evaluate, and optimize power plants using ammonia/water mixtures as the working fluid.

With these considerations in mind, the major objectives of the Workshop were:

(a) to present the current status of thermophysical properties data and models for the ammonia/water system,

(b) to identify existing research facilities and capabilities for studies of the thermophysical properties of the ammonia/water system,

(c) to identify industrial needs (priorities, properties, ranges, accuracy, etc.) for the thermophysical properties of the ammonia/water systems, and

(d) to develop a plan to provide the data and models to satisfy industrial needs.

---

[1] Because the molar masses of water and ammonia are so close, the distinction between molar concentration and mass concentration is not important for the current discussions.

Presentations were made by NIST staff and representatives from industry and other government agencies to achieve these goals. However, an important part of the Workshop involved informal discussions among the Workshop participants in developing a plan to provide industry with the essential property information required for processes using ammonia/water mixtures as the working fluid. This report serves as a summary of the content and discussions of the Workshop. The presenters have kindly agreed to allow copies of their transparencies to be included in this document. Several attendees of the Workshop from NIST were asked to record certain portions of the discussions, and their notes were used to provide some of the content of this report. Although a consensus was achieved in the identification of priorities, ranges, required tolerances, etc., this report summarizes the opinions and interpretation of the authors and does not imply endorsement by any other attendees of the Workshop.

Workshop Participants and Agenda

The list of workshop attendees, including contact addresses and phone numbers, is given in Appendix A. A representative was present from each of the major domestic industrial concerns that have been identified as having a strong interest in ammonia/water mixtures for power generation. The final meeting agenda, as distributed at the Workshop, is included as Table 1.

Workshop Presentations

W. M. (Mickey) Haynes (NIST): Opening Remarks

W. M. Haynes opened the program by presenting an overview of the activities and responsibilities of NIST with respect to thermophysical properties research. The presentation included some historical perspective about the activities in this area, illustrated the broad scope of the research, focussed on particular programs analogous to a projected program on ammonia/water properties, and discussed the ongoing work on this fluid. He anticipated the later discussions on the experimental and modeling aspects of a program on ammonia/water properties and summarized the goals and format of the Workshop. Copies of the transparencies used in this presentation are included in Appendix B of this report. The Certified Research Need on ammonia/water properties developed by the International Association for the Properties of Water and Steam was one topic of discussion; this document is included in its entirety as Appendix C.

M. Tribus (Exergy): Status of Projects using Ammonia/Water Mixtures

The discussion concerning the industrial perspective on ammonia/water mixtures was opened with a presentation by M. Tribus; notes prepared by Dr. Tribus are included in Appendix D.[2] M. Tribus spoke of the existing System 1 facility which has operated for more than 4000 hours in a 3.2 MW bottoming cycle plant, as well as plans for facilities based on combined cycles, direct fired, geothermal, and waste incineration. He described the computer program WATAM for ammonia/water properties and a joint project with the Russian Academy of Sciences to make additional measurements. (A summary of this work by Baranov et al. is included as Appendix E of this report.) In addition, heat transfer studies and research on the condensation itself are being conducted; tests of the effects of impurities (on corrosion, in particular) are part of the Canoga Park project, and further

---

[2] Except where attributed to NIST authors, the content of individual sections of this volume has not been reviewed or edited by the National Institute of Standards and Technology. NIST, therefore, accepts no responsibility for comments or recommendations therein. The mention of trade names in this volume is in no sense an endorsement or recommendation by the National Institute of Standards and Technology.

information on decomposition, in addition to stability tests, is required. During the discussions, it was noted that properties for mixtures with ammonia concentrations as low as 0.3 are required at moderate temperatures for pressures in the range 0.7 to 1 MPa (100 to 150 psia) in the distillation/condensation subsystem (DCSS); for the supercritical stages of the cycle, ammonia concentrations near 0.85 are used with an upper temperature limit near 894 K (1150 °F) at pressures to 20.68 MPa (3000 psia).

Table 1. Agenda.

Workshop on
Thermophysical Properties of Ammonia/Water Mixtures

Physical and Chemical Properties Division
National Institute of Standards and Technology
325 Broadway, Boulder, Colorado
Wednesday, June 26, 1996

8:30 a.m.	**Opening Remarks** – Mickey Haynes, NIST
9:00 a.m.	**Industrial Perspective** *Status of ProjectsUsing Ammonia/Water Mixtures* – Myron Tribus, Exergy, Inc. *Fluid Properties Requirements of Kalina Cycle for Direct Coal-Fired Plants* – Frank Gabrielli, ABB Power Plant Laboratories, Combustion Engineering, Inc. *Fluid Property Needs for Geothermal Power Cycles* – Jeff Hahn, U.S. Department of Energy, Golden Field Office *Property Needs for Absorption System* – Abdi Zaltash, Oak Ridge National Laboratory *The Importance of Standardized Data on Ammonia/Water Mixture Properties for Economical Design and Operation of Kalina Combined Cycle Power Generation Systems* – Bijan Davari, General Electric, Power Generation Engineering
10:20 a.m.	**BREAK**
10:40 a.m.	**Status of Data and Models for Ammonia/Water** – Dan Friend, NIST
11:30 a.m.	**LUNCH**
1:00 p.m.	**Overview of Experimental Capabilities at NIST** – Mark McLinden, NIST
1:45 p.m.	**Lab Tour** Calorimetry – Joe Magee Thermal Conductivity, Viscosity – Rich Perkins
2:30 p.m.	**BREAK**
2:40 p.m.	**Summary of Research Facilities/Capabilities for Ammonia/Water** –Mickey Haynes/Dan Friend, NIST
3:00 p.m.	Discussion/Planning Session
4:30 p.m.	**Adjourn**

F. Gabrielli (ABB Power Plant Laboratories): Fluid Properties Requirements of Kalina Cycle for Direct Coal-Fired Plants

F. Gabrielli focussed on the direct-fired technology; copies of his transparencies are included as Appendix F. He noted the predicted 10 to 20% increase in efficiency projected for the Kalina cycle plant compared to a conventional Rankine plant. The fluid composition of interest ranges from 35 percent (at low pressures and temperatures) to about 90% ammonia. The pressure ranges from about 0.1 MPa (15 psia) to 18.4 MPa (2700 psia) with temperatures from ambient to about 811 K (1000 °F). The properties of greatest interest to this technology include heat capacity (or enthalpy), surface tension, viscosity, thermal conductivity, and density.

J. Hahn (U. S. Department of Energy): Fluid Property Needs for Geothermal Power Cycles

J. Hahn addressed the requirements for ammonia/water systems related to geothermal power technology; copies of his transparencies are included in Appendix G. There was a discussion of the role of the federal government and the Department of Energy in the continuum from research through development and into commercialization of a technology. The competitive process which has led to support for the Kalina cycle was described, and it was noted that most applications in this area are for temperatures less than 450 K (350 °F). Better thermophysical property estimates will allow improved condenser design and will lead to optimization of the mixture ratios used in the cycle.

A. Zaltash (Oak Ridge National Laboratory): Property Needs for Absorption Systems

A. Zaltash spoke about properties for ammonia/water mixtures as required for absorption refrigeration applications; copies of his transparencies are included in Appendix H. In particular, work related to the Hi-Cool program (gas driven system generally using waste heat and for use in southern climates) and generator/absorber heat exchanger (GAX) technology (heat pumps, generally used in northern climates) was discussed. A summary of available experimental data and various correlating equations was presented. When different property formulations were used in a cycle simulation, differences of 5 to 6% and up to 10% in the coefficient of performance were calculated. Properties of main interest were the vapor-liquid equilibrium, enthalpy, viscosity, thermal conductivity, and density over the full composition range with temperatures from 233 to 561 K (−40 to 550 °F) with an upper pressure of 8 to 10.3 MPa (1200 to 1500 psia). There is some interest in the location of the solid line and in corrosion inhibitors which can be used in the mixture.

B. Davari (General Electric Power): The Importance of Standardized Data on Ammonia/Water Mixture Properties for Economical Design and Operation of Kalina Combined Cycle Power Generation Systems

B. Davari addressed the issues of concern to combined cycle applications. Much of this material was previously discussed by B. Davari's colleagues at the recent Power-Gen Europe '96 conference; the report by Bjorge *et al.* is included as Appendix I. It was noted that when property calculations were done using the WATAM computer program, efficiency increases of 2.5 to 5 percent (depending on the heat source) were found when comparing the Kalina cycle to a Rankine process using the same heat source. The ranges of the variables for the heat recovery vapor generator (HRVG), the vapor turbine (VT), and the distillation/condensation system (DCSS) were discussed. For the HRVG and VT, data are required for ammonia concentrations from 0.7 to 0.85 (outside of the vapor-liquid equilibria zone) with temperatures in the range of 320 to 867 K (116 to 1100 °F) and pressures in the range of 1 to 22 MPa (150 to 3200 psia). For the distillation/condensation unit, more modest temperatures and pressures are found, but the composition range extends from 0.45 to 0.95 ammonia. The sizing issues involved in the design of the system are critically dependent on the mixture properties; some of the key properties required are sound speed, entropy, and enthalpy.

D. Friend (NIST): Status of Data and Models for Ammonia/Water

D. Friend reported on the bibliographic and modeling activities which have been underway at NIST; copies of his transparencies are included as Appendix J. He pointed to several previous studies of the system and summarized the available experimental data and regions in which the data are sparse or nonexistent. He described the models available for the critical region as well as efforts based on classical extended corresponding states models and an alternative two-fluid Helmholtz energy model for use over broader regions of the phase diagram. Some comparisons between experimental data and the models were given, and the large uncertainty in the extrapolation region for the heat capacity was noted. Three papers, describing the data situation, a preliminary thermodynamic formulation, and properties in the critical region, are nearing completion.

M. McLinden (NIST): Overview of Experimental Capabilities at NIST

M. McLinden discussed the experimental facilities available at NIST and how they might be brought to bear on the data requirements for the ammonia/water mixtures; copies of his transparencies are included as Appendix K. The types of property measurements that can be carried out at NIST include vapor-liquid equilibrium (VLE), surface tension, viscosity, isochoric heat capacity, enthalpy, density (PVT), thermal conductivity, thermal diffusivity, and sound speed. The high temperature (to 523 K) twin-cell calorimeter, VLE equipment, and transient hot-wire apparatus (thermal conductivity) have been used for ammonia/water measurements over limited ranges of temperature, pressure, and composition. Questions related to materials compatibility, sample handling, and safety have been resolved with respect to an experimental program for the mixture. Modifications to some of the apparatus, to further increase the temperature range, may be feasible at modest cost; new equipment would be required to fully cover the interests in ammonia/water properties.

Laboratory Tours: Calorimetry and Transport Properties

The Workshop attendees were divided into two groups to visit some of the laboratory facilities at NIST to discuss experimental details with the staff researchers. J. Magee described the calorimetry program. The twin-cell calorimeter (see Figure 1) is used to measure isochoric heat capacities; the reference cell is used to minimize the effects of parasitic heat loss during the measurements. The total enthalpy (flow) calorimeter directly measures the enthalpy difference between two state points in a steady-state flowing system. R. Perkins showed the apparatus available for transport property measurements. The hot-wire thermal conductivity cells are normally run in a transient mode in which a pulse of heat is generated in a long thin wire (which approximates an infinite line source of heat) which also acts as a thermometer in the determination of thermal conductivity; see Figure 2. In addition to the new vibrating wire viscometers, a capillary viscometer and two quartz-crystal viscometers are used to measure fluid viscosity.

W. M. Haynes and D. Friend (NIST): Summary of Research Facilities and Capabilities for Ammonia/Water Measurements

W. M. Haynes and D. Friend presented a summary of their findings concerning laboratory facilities which may be available for the determination of ammonia/water thermophysical properties, especially in the region of high temperatures and pressures, where the lack of data is a very serious concern; copies of their transparencies, containing a list of such facilities, are included as Appendix L. Although the list is extensive, it may not be complete; the information was gathered from the literature and our familiarity with other laboratories engaged in thermophysical property measurements. We were able to contact directly many of the researchers included in order to determine interest and capabilities in this area; for other listings, we have not collected any further information concerning current activities. During the discussion of this item, it was noted that Prof. Keller of Siegen, Germany, the laboratories of Professor Teja at the Georgia Institute of Technology, Dr. Simonson at Oak Ridge National Laboratory (for heat capacities), and Dr. Vladimir Meyer at the Pascal Laboratory in France might be useful contacts. Among the laboratories which were contacted, several expressed an interest in joining an effort to improve the data situation for ammonia/water mixtures. However, in essentially every case, apparatus limitations (in temperature, pressure, or materials compatibility), prior commitments, and financial constraints would not allow an immediate measurement program of the required scope. It may be feasible and appropriate to include some of these laboratories in a large-scale coordinated effort to provide adequate data and coverage.

Discussion and Planning Session

During the discussion sessions, several technical points concerning the existing data, thermodynamic models, and experimental procedures were brought up. It was noted, during this discussion, that the zero points of the enthalpy and entropy of the mixture system were essentially fixed by the choices made for the pure fluid properties: for water, the internal energy and entropy of the liquid at its triple point are assigned a value of zero; for ammonia, the zero of energy is taken as that of the ideal gas at 0 K and 0.101 325 MPa (1 atm). Different conventions are quite common—for refrigerant systems, the American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE) sets a zero at −40 °C at saturation while the International Institute of Refrigeration uses 0 °C for its fixed point.

There was some discussion of the dynamic feedback process used to develop standard thermophysical property formulations. In the course of a comprehensive program to establish standard reference property surfaces, the experimental and modeling aspects are often conducted simultaneously. As new property data are obtained, interim correlations are improved; typically, an annual update is made to the computer models. As the models are further developed, shortcomings in the data situation (including gaps in the data, inconsistent data, suspect data) may be identified; the experimental data acquisition program is then modified to address these problems. The research effort on the properties of air was again used as an analogy for a projected 4 to 6 year comprehensive program on ammonia/water properties; during that effort, the regular, but preliminary, results proved beneficial to the sponsoring organizations.

The interests of the major participants in a program to develop standard reference data for the ammonia/water binary system were summarized. In addition to the direct commercial interests, the Department of Energy, the Electric Power Research Institute, and the National Institute of Standards and Technology are very important for this project. Some bilateral projects in this area already are in progress among these parties. It was noted that although the geothermal areas within the Department of Energy may have already obtained their required data, other programs within the Department retain an intense interest in the subject. Finally, the very stringent time constraints faced by the attendees were discussed. In some cases, engineering design studies must be completed in the very near future, to maintain the required schedule; critical thermophysical property data required for this process are simply not currently available.

The question of specific industrial needs was then considered. In particular, it was noted that stability studies and the kinetics of the related chemistry still require some effort. This is described in the IAPWS CRN included above. Some research efforts concerning catalysis are underway in Japan; questions concerning inhibitors—chromates and molybdates—still should be addressed. Despite these concerns, however, a statement was made that a plant could be built now, but property data are required for design optimization and for guarantees. There was a consensus that the mixture should be studied over the entire composition range. The current temperature range of interest is 233 to 895 K (−40 to 1150 °F) with pressures to 22 MPa (3200 psia) with the possibility of increasing to about 25 MPa (3600 psia) in the near future. This is somewhat less than described in the ICRN, which seeks information to pressures of 34.5 MPa. It was emphasized that the turbine inlet region encounters both high pressures and high temperatures, so that the pressure maximum is not relaxed at the higher temperatures.

Specific properties of interest include the surface tension (for design of two-phase condensers), as well as PVT (density), VLE, isochoric and isobaric heat capacity, enthalpy, entropy, and sound speed. It was noted that a Helmholtz energy formulation can be used to obtain all of these quantities in a completely self-consistent manner provided that sufficient accurate experimental data are available. Also, the sound speed may be most closely related to direct entropy measurements. In addition, information on the thermal conductivity and viscosity are required for design work.

It is difficult to determine precise uncertainty requirements for properties; however, the following estimates were established by consensus; these estimates considered both the capabilities of various apparatus at NIST and the true needs for plant design and optimization. In general, industrial needs can be satisfied by the experimental uncertainty that can be achieved currently. For the densities, uncertainties from 0.1 to 0.2% are desirable; for the heat capacities, C_v and C_p, 0.5 to 1% is adequate; for sound speed, an uncertainty of 0.05% is appropriate. For the vapor-liquid equilibrium properties, an uncertainty of 0.1% in pressure for well defined mixtures is feasible. Composition measurement is difficult (because the ammonia escapes), and boric acid titration was used in the Cornell University studies. Also, current mixture thermodynamic models may have difficulty achieving these accuracies over the broadest range of independent variables. The interfacial tension (surface tension) can have uncertainties ranging from 0.1 to 0.5 mN/m; this is strongly dependent on the composition. There is some question whether a dynamic or equilibrium determination of the interfacial tension is more appropriate. For the transport properties, an uncertainty of 1% in the thermal conductivity and 2% in the viscosity can be expected.

For a typical application, a guarantee of 0.5% in the turbine performance requires knowledge of the mass flow and energy flow of the process stream; an agreed-upon formulation for the properties of the mixture must be used in such situations. The uncertainties in the transport properties are generally much better than those obtained in the heat transfer calculations. Independent studies of the heat transfer, including the turbulent regime, may be required. In addition, mass diffusion (Soret effect) may also play a factor in later stages of the design work. In Table 2, we summarize the discussion of property needs and uncertainties. Greater errors may be tolerable during the next few years; however, as the technology is further developed, the uncertainty requirements will be refined during this period.

Table 2. Summary of property needs for ammonia/water mixtures.

Ranges of conditions:

Composition	full range	
Temperature	233 to 895 K	−40 to 1150 °F
Pressure	to 22 MPa	to 3200 psia
(future need	to 25 MPa	to 3600 psia)

Thermodynamic properties (from Helmholtz energy formulation):

Property	Uncertainty
PVT (density)	0.1 – 0.2%
VLE (phase equilibria)	0.1% in P, 0.1% in composition
Isochoric heat capacity	0.5 – 1%
Isobaric heat capacity	0.5 – 1%
Enthalpy	
Entropy	
Sound speed	0.05%

Transport properties:

Thermal conductivity	1%
Viscosity	2%
Mass diffusion (future need)	

Other properties:

Surface tension	0.1 to 0.5 mN/m
Stability; kinetics	
Catalysis	

Conclusions

There was a strong consensus that thermophysical properties are vitally important in the design stages of power plants based on ammonia/water working fluids. For this purpose, accuracy requirements are not stringent, but current information that is required to make some of the critical design decisions is missing. As the technology matures, better thermophysical property models will be required to improve and optimize the designs. Although no clear mechanism was identified to establish the required data base, steps toward this process have now been taken. In particular, it will require additional effort to achieve satisfactory funding. Many of the participants in the Workshop gave a general commitment to work together to achieve the desired goals. They intend to work together on funding options, to maintain communication concerning research results and requirements, and to meet again, as appropriate, to re-assess the status of properties work on the ammonia/water binary mixtures.

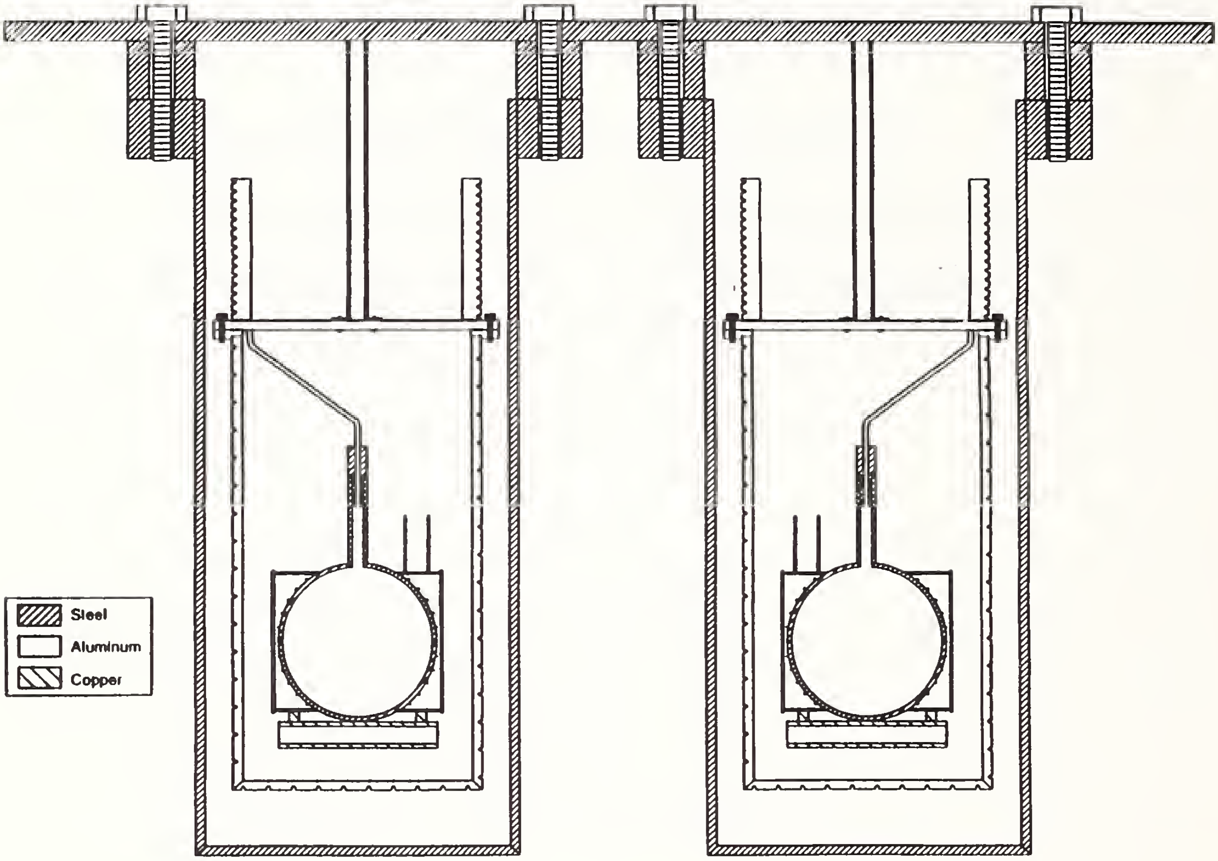


Figure 1. Schematic of twin-cell calorimeter.

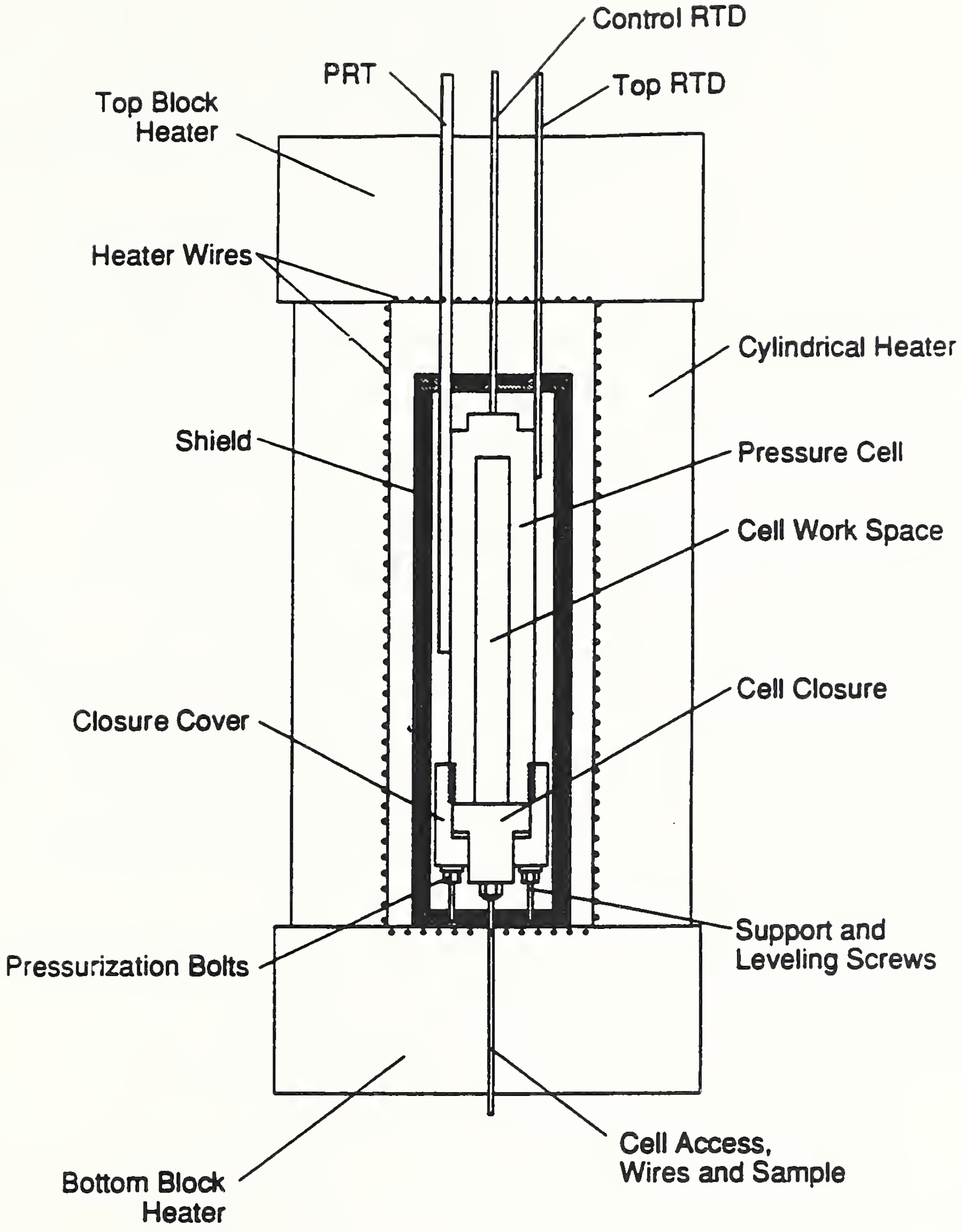


Figure 2. Schematic of transient hot-wire thermal conductivity apparatus.

APPENDIX A.

ATTENDANCE LIST

THERMOPHYSICAL PROPERTIES OF AMMONIA/WATER MIXTURES WORKSHOP

Wednesday, June 26, 1996

Non-NIST Attendance List

Name	Company	Phone/Fax #
Bharathan, Desikan	NREL 1617 Cole Blvd. Golden, CO 80401	(303) 384-7418/7495
Biar, Mark	EFCO 3501 W. 11th St. Houston, TX 77008	(713) 803-4700x411/869-8088
Bliem, Carl J.	CJB Consulting 7401 Rozena Dr. Longmont, CO 80503	(303) 651-7286/772-9484
Davari, Bijan	General Electric Power 1 River Rd. Bldg. 40 - 4th South Schenectady, NY 12345	(518) 385-9556/5041
Gabrielli, Frank	ABB Power Plant Laboratories Combustion Engineering, Inc. P.O. Box 500, CEP 9007-1204 2000 Day Hill Road Windsor, CT 06095-0500	(860) 285-5746/2513 frank.gabrielli@usppl.mail.abb.com
Gawlik, Keith	NREL 1617 Cole Blvd. Golden, CO 80401	(303) 384-7515/7540 kgawlik@bldgs.nrel.gov
Hahn, Jeffrey	U.S. Dept. of Energy 1617 Cole Blvd. Golden, CO 80401	(303) 275-4775 Hahnj@tcplink.nrel.gov

Thermophysical Properties of Ammonia/Water
Mixtures Workshop
Wednesday, June 26, 1996

Non-NIST Attendance List (Cont'd)

Name	Company	Phone/Fax #
Hassani, Vahab	NREL 1617 Cole Blvd. Golden, CO 80401	(303) 384-7464/7495 vahab.hassani@nrel.gov
Ito, Takehiro	Kyushu University 6-10-1 Hakozaki, Higashi-ku 812 Fukuoka, Japan	81 (92) 642-3397/3400 tito@mech.kyushu-u.ac.j
Rawls, Patricia	U.S. Department of Energy Pittsburgh Energy Technology Ctr. P.O. Box 10940 Pittsburgh, PA 15236-0940	(412) 892-5882/4818 rawls@petc.doc.gov
Rhodes, Lawrence	Exergy, Inc. 22320 Foothill Blvd., #540 Hayward, CA 94541	(510) 537-5881/8621 exrg@aol.com
Tribus, Myron	Exergy, Inc. 22320 Foothill Blvd., #540 Hayward, CA 94541	(510) 537-5881/8621 104055.2603@compuserv.com exrg@aol.com
Zaltash, Abdi	Oak Ridge National Laboratory P.O. Box 2008, Bldg. 3147 Oak Ridge, TN 37831-6070	(423) 574-4571/9338 A1Z@ORNL.GOV

THERMOPHYSICAL PROPERTIES OF AMMONIA/WATER MIXTURES WORKSHOP

Wednesday, June 26, 1996

NIST Attendance List

Name	Phone #	E-Mail #
Rich Kayser	(301) 975-2483	richard.kayser@nist.gov
Mickey Haynes	(303) 497-3247	haynes.@micf.nist.gov
Dan Friend	(303) 497-5424	dfriend@boulder.nist.gov
Mark McLinden	(303) 497-3580	markm@bldrdoc.gov
Jim Rainwater	(303) 497-5376	rainwater@boulder.nist.gov
Joe Magee	(303) 497-3298	magee@boulder.nist.gov
Cindy Holcomb	(303) 497-3437	holcomb@boulder.nist.gov
Rich Perkins	(303) 497-5499	perkins@boulder.nist.gov
Adam Nowarski (University of Cracow)	(303) 497-7752	nowarski@boulder.nist.gov
Sandy Klein (University of Wisconsin)	(303) 497-3040	klein@engr.wisc.edu
Torsten Lüddecke (University of Hannover)	(303) 497-5207	

APPENDIX B.

W. M. (MICKEY) HAYNES: OPENING REMARKS

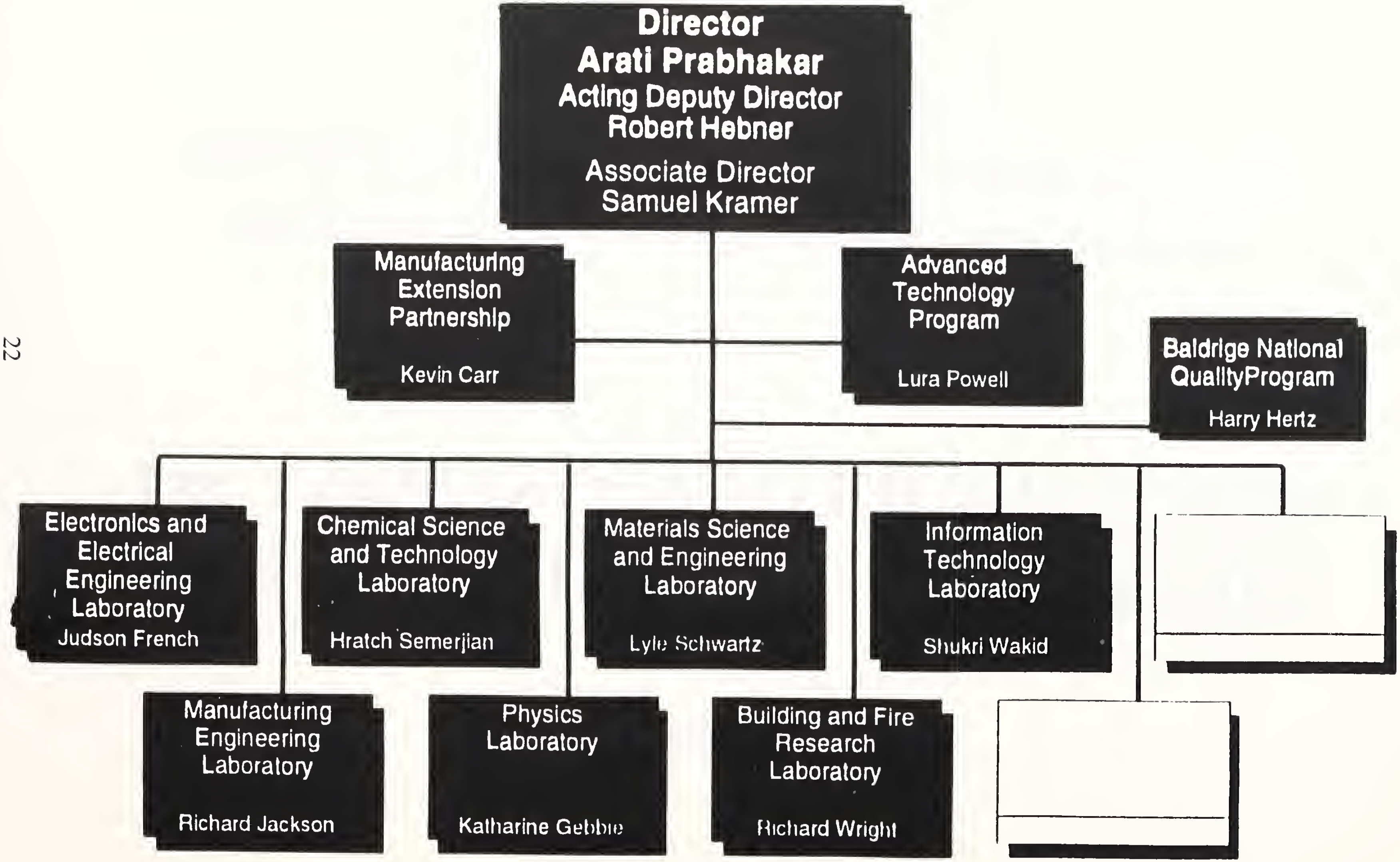
Workshop on

THERMOPHYSICAL PROPERTIES OF AMMONIA/WATER MIXTURES

Physical and Chemical Properties Division
National Institute of Standards and Technology
Boulder, Colorado

June 26, 1996

National Institute of Standards and Technology



Director
Arati Prabhakar
Acting Deputy Director
Robert Hebner
Associate Director
Samuel Kramer

Manufacturing Extension Partnership
Kevin Carr

Advanced Technology Program
Lura Powell

Baldrige National QualityProgram
Harry Hertz

Electronics and Electrical Engineering Laboratory
Judson French

Manufacturing Engineering Laboratory
Richard Jackson

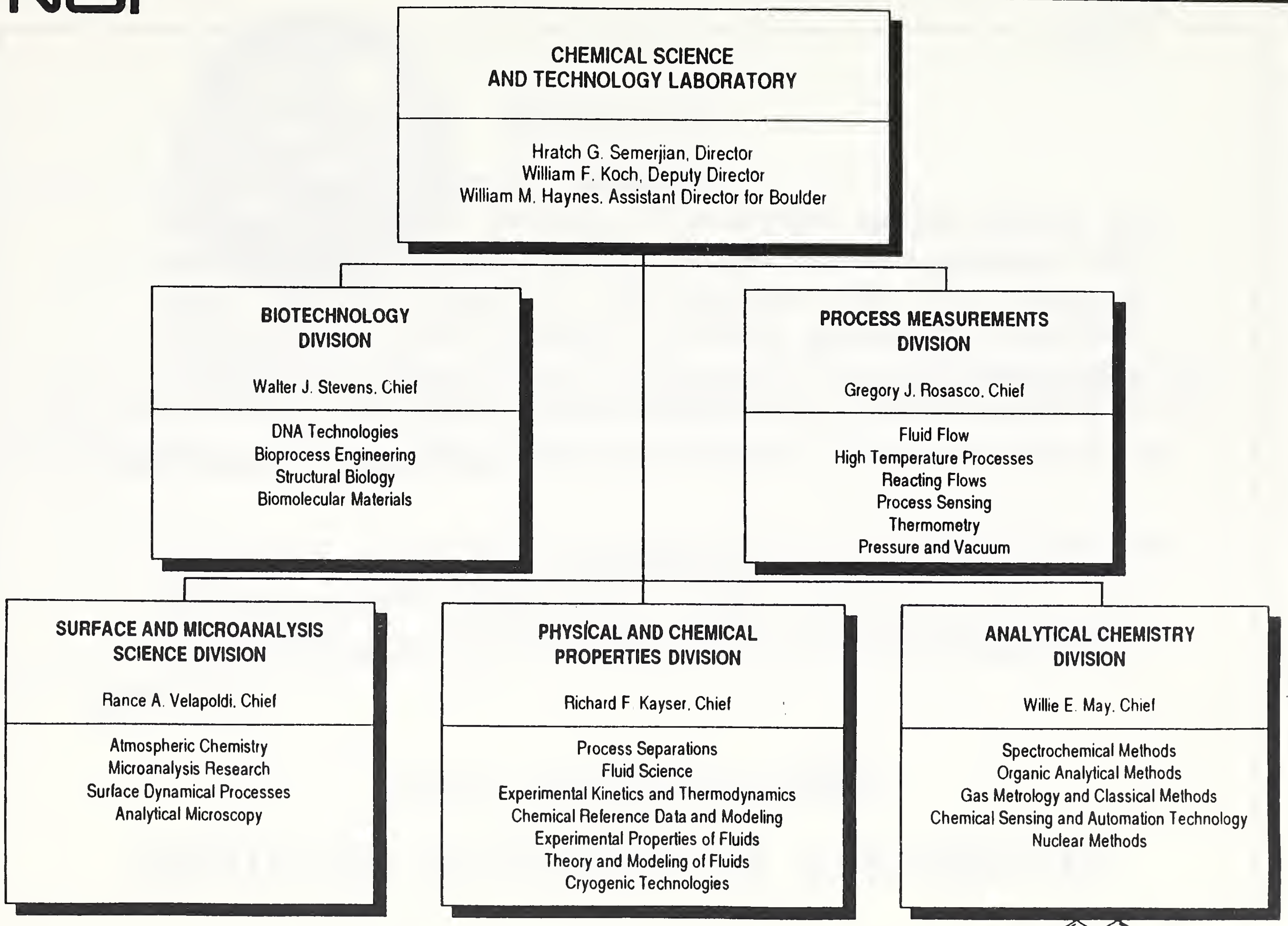
Chemical Science and Technology Laboratory
Hratch Semerjian

Physics Laboratory
Katharine Gebbie

Materials Science and Engineering Laboratory
Lyle Schwartz

Building and Fire Research Laboratory
Richard Wright

Information Technology Laboratory
Shukri Wakid



CHEMICAL SCIENCE AND TECHNOLOGY LABORATORY

Hratch G. Semerjian, Director
William F. Koch, Deputy Director
William M. Haynes, Assistant Director for Boulder

BIOTECHNOLOGY DIVISION

Walter J. Stevens, Chief

- DNA Technologies
- Bioprocess Engineering
- Structural Biology
- Biomolecular Materials

PROCESS MEASUREMENTS DIVISION

Gregory J. Rosasco, Chief

- Fluid Flow
- High Temperature Processes
- Reacting Flows
- Process Sensing
- Thermometry
- Pressure and Vacuum

SURFACE AND MICROANALYSIS SCIENCE DIVISION

Rance A. Velapoldi, Chief

- Atmospheric Chemistry
- Microanalysis Research
- Surface Dynamical Processes
- Analytical Microscopy

PHYSICAL AND CHEMICAL PROPERTIES DIVISION

Richard F. Kayser, Chief

- Process Separations
- Fluid Science
- Experimental Kinetics and Thermodynamics
- Chemical Reference Data and Modeling
- Experimental Properties of Fluids
- Theory and Modeling of Fluids
- Cryogenic Technologies

ANALYTICAL CHEMISTRY DIVISION

Willie E. May, Chief

- Spectrochemical Methods
- Organic Analytical Methods
- Gas Metrology and Classical Methods
- Chemical Sensing and Automation Technology
- Nuclear Methods

Chemical Science and Technology Laboratory

[illegible]

National Institute of Standards and Technology

Mission:

To promote U.S. economic growth by working with industry to develop and apply technology, measurements, and standards. NIST's direct customer is U.S. industry.

Laboratory Programs:

A strong laboratory effort planned and implemented in cooperation with industry and focused on infrastructural technologies, such as measurements, standards, evaluated data, and test methods. The benefits from such enabling technologies typically spread across entire industries, and the investments needed to produce them cannot be recovered by individual companies.

Chemical Science and Technology Laboratory

Mission

As the Nation's Reference Laboratory, CSTL's Mission is to provide the chemical measurement infrastructure to:

- enhance U.S. industry's productivity and competitiveness;
- assure equity in trade; and
- improve public health, safety, and environmental quality.

Chemi[illegible]
Science and
Technology
Laboratory

Goals

Measurement Standards

to establish CSTL as the pinnacle of the traceability structure for measurements in chemistry, chemical engineering and biotechnology, and provide the fundamental basis of the nation's measurement system

Chemical and Process Information

to assure that U.S. industry has access to accurate and reliable data and predictive models to determine the chemical and physical properties of materials and processes

Measurement Science

to anticipate and address next generation measurement needs of the nation, by performing cutting-edge research in measurement science

Properties of Fluids Program - History

- 35 years of experience in thermophysical properties
- Cryogenic fluids
- Steam and ammonia
- Natural gas and LNG
- Supercritical fluids
- Alternative refrigerants
- Aqueous systems

Major Programs

- Properties of Alternative Refrigerants
- Properties of Aqueous Systems
- Properties of Natural Gas Systems
- Properties of Supercritical Fluids
- Predictive Computer Packages for Pure Fluids and Mixtures
- New Apparatus Development
- Theoretical Studies
- Neutron and Light Scattering Studies of Complex Fluid Systems and Processes

- **Cryogenic Research (1950's)**

  space program

  oxygen, hydrogen, nitrogen

- **Properties of Natural Gas Systems**

  methane, ethane, propane, butanes, carbon dioxide, etc.

  methanol, ammonia, hydrogen sulfide, benzene, toluene

  gas mixtures, LNG, natural gas liquids (NGLs)

  custody transfer

  sound speeds for sonic nozzle metering

  PVT reference data

- Properties of Alternative Refrigerants

  Montreal Protocol–1987

  PVT, heat capacity, sound speed, critical properties, VLE, viscosities, thermal conductivities, surface tension, dielectric constant

  standard reference data for selected fluids

  screening measurements for "long-shot" fluids

  computer package for SRD and prediction

  coordination with IEA, ARI, etc.

- Supercritical Fluid Properties

  industrial consortium

  pipeline CO_2

  supercritical fluid extraction of chemical products

  inorganics, alkanes, cycloalkanes, alkenes, aromatics

NIST

Properties of Fluids Program

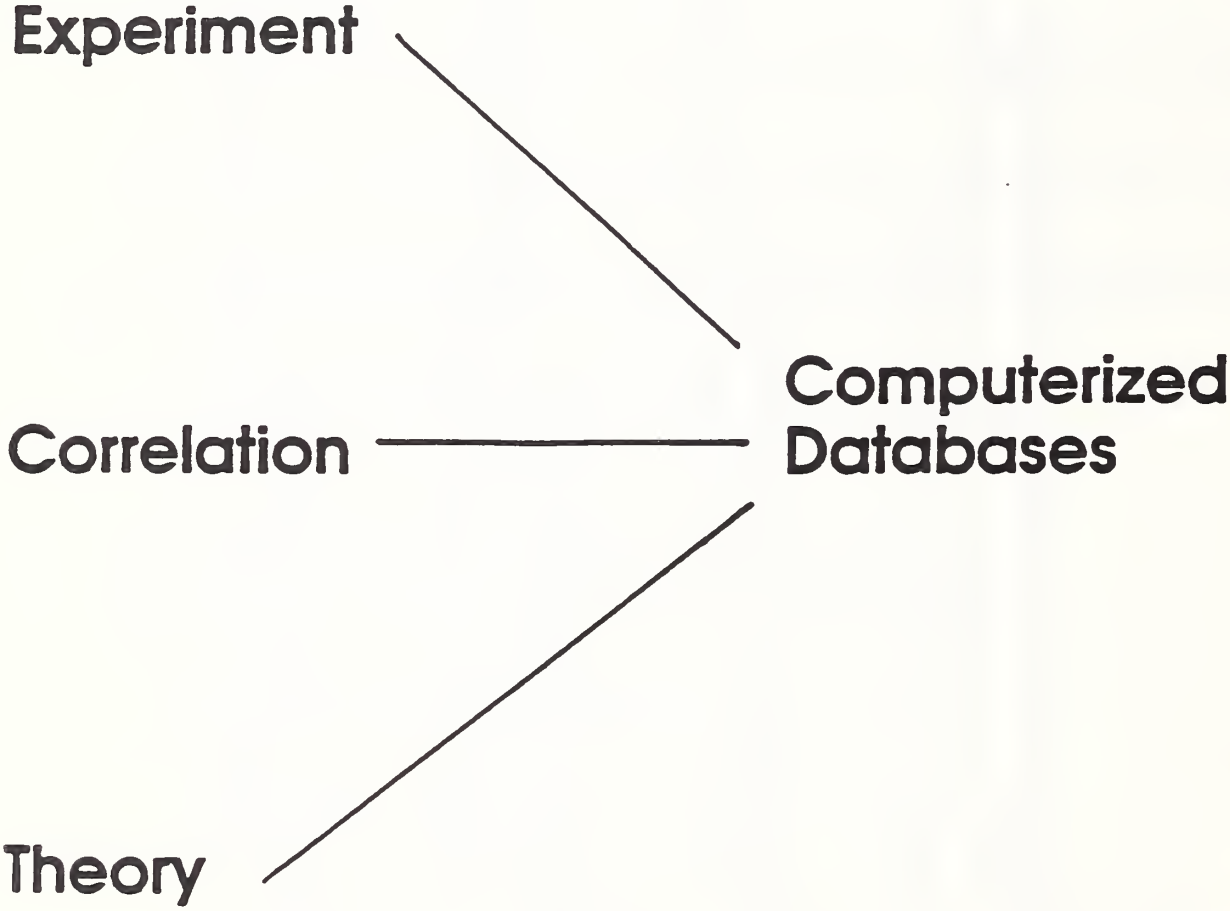
- **Thermodynamic Properties**
  PVT (pressure-volume-temperature),
  heat capacity, sound speed

- **Transport Properties**
  Thermal conductivity, viscosity, diffusion

- **Phase Equilibria**
  VLE (vapor-liquid equilibria), coexisting densities,
  vapor pressures, fugacity

- **Other Properties**
  surface tension, dielectric constant, refractive index

Integrated Program



Experiment

Correlation

Theory

Computerized
Databases

Properties of Fluids Program

- Measurement techniques
- Experimental data
- Critical evaluation and correlation
- Theoretical models
- Neutron and light scattering studies
- Computer simulation
- Standard reference data
- Computer packages

NIST Air Properties

Goal:

Develop the means to accurately model the thermodynamic and transport properties of air and related O_2 - N_2 mixtures down to the solid line

Problems with Existing Air Properties

- Limited data below 200° R
- No data below 140° R
- No data down to solid line
- Lack of vapor-liquid equilibria (VLE) data
- Lack of data for other $O_2 + N_2$ compositions
- Systematic errors in Russian correlation
- Inconsistent critical region data
- Complete lack of derived property data
- Complete lack of transport property data

Technical Plan

- Prepare preliminary EOS and computer code
  - √ Thermodynamic Properties - corresponding states
  - √ Transport Properties NIST - TRAPP
  - √ Surface Tension Model
- Perform accurate property measurements (update EOS and computer code)
  - √ Heat Capacity - improve EOS performance
  - √ PVT
  - √ VLE
  - √ Sound Speed
  - √ Transport Properties (thermal conductivity, viscosity)
- Prepare final EOS and computer code

Major Accomplishments

- Comprehensive measurements of thermodynamic, transport, and phase equilibria properties of air
- Standard reference equation of state for air
- Predictive models for thermophysical properties of mixtures of nitrogen, oxygen, and argon
- Computer packages for properties of air and related mixtures

IAPWS Certified Research Need (ICRN)
Thermophysical Properties of Ammonia/Water Mixtures

Results

1. Evaluation of performance of power plants

2. Optimization of economic performance of power plant systems/components

3. Design, operation, and calibration of control systems

IAPWS Certified Research Need (ICRN)
Thermophysical Properties of Ammonia/Water Mixtures

<u>Needs</u>

1. Thermodynamic Properties (enthalpy, entropy, density, surface tension)
    - Temperatures to 866 K (1100°F)
    - Pressures to 34.5 MPa (5000 psia)
    - Complete range of compositions

2. Transport Properties (viscosity, thermal conductivity)

3. Stability of Ammonia/Water Mixtures

Project Goal

Standard reference quality model for accurate prediction of the thermophysical (thermodynamic, transport, phase equilibria) properties of ammonia/water mixtures over the ranges of temperature, pressure, and composition important to industrial applications.

Major Objectives of Workshop

1. **To identify industrial needs** for the thermophysical properties of ammonia/water mixtures

2. **To present the current status** of thermophysical property data and models for the ammonia/water system

3. **To identify projects and facilities/capabilities** for studies of the thermophysical properties of the ammonia/water system

4. **To develop a plan to provide the data and models to satisfy industrial needs**

Thermophysical Properties of Ammonia/Water Mixtures

- Geothermal applications
- Temperature range of 280 to 450 K (44 to 350°F)
- Pressures to 3.5 MPa (500 psia)
- Compositions from 80 to 100% ammonia by mass
- Supported by DOE (Geothermal Division)
- Complete by September 1996

Thermophysical Properties of Ammonia/Water Mixtures

- Experimental Measurements
  - PVT
  - Heat capacity
  - Thermal conductivity
  - Vapor-liquid equilibria
- Compilation and Critical Evaluation of Available Data
- Modeling
  - Critical region
  - Extended corresponding states
  - Helmholtz free energy

Calorimetric Properties of Ammonia/Water Mixtures

- Temperature range of 300 to 523 K (80 to 482°F)
- Pressures to 20 MPa (2900 psia)
- Composition range of 0.6 to 0.8 mass fraction NH_3
- Heat capacities at constant volume (C_V) using twin cell calorimeter
- 0.5% uncertainty in C_V
- Comparisons with models
- Supported by ABB Combustion Engineering Systems
- Complete by January 1997

Properties of Ammonia

- Experimental Measurements
  - PVT - 200 to 400 K (-100 to 260°F)
  - Heat capacities
  - Viscosity > 200 to 473 K (-100 to 392°F)
  - Thermal conductivity
- Pressures to 35 MPa (5000 psia)
- Models
  - New equation of state
  - New transport property models
- Supported by DOE (Office of Building Technologies, Building Equipment Division)
- Complete by July 1997

APPENDIX C.

IAPWS CERTIFIED RESEARCH NEED

IAPWS Certified Research Need - ICRN

Thermophysical Properties of Ammonia-Water Mixtures

The IAPWS Working Group - Thermophysical Properties of Water and Steam has examined the published work in the area of the thermodynamic and transport properties of ammonia-water mixtures required for accurate system design of power plants and has found that the existing information is deficient in a number of respects.

The available information is not sufficiently accurate and comprehensive to permit:

(a) the evaluation of the performance of power plants now under construction and soon to be constructed,

(b) the optimization of the economic performance of power plant systems and the proper economic sizing of components, and

(c) the design, operation, and calibration of control systems used to monitor and control power plants which use ammonia/water mixtures as their working fluids.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will liaise between research groups.

Issued by the

International Association for the Properties of Water and Steam

President:	**J.R. Cooper** **Queen Mary and Westfield College** **London E1 4NS England**
Executive Secretary:	**Dr. R.B. Dooley** **Electric Power Research Institute** **Palo Alto, California 94304 USA**

IAPWS Certified Research Need - ICRN

Thermophysical Properties of Ammonia/Water Mixtures

Background:

For over a century, power plants have been in service utilizing water as their working fluid. In recent years, accurate formulations of the thermophysical properties of steam (enthalpy, entropy, density, temperature, pressure, thermal conductivity, viscosity) have been developed with international cooperation through IAPWS. These formulations and the steam tables derived from them are used in the design and testing of turbines, boilers, condensers, heat exchangers, pumps, and other equipment. These steam properties are also used by system designers to specify the performance of the components which make up a modern power plant. The properties are also required by the owner at the time the power plant is accepted to check the performance guarantees and to monitor the performance of the system over time, particularly for degradations in efficiency.

Validated thermophysical properties are also required for calculations concerning the safety of power plants. Various control equipment is designed to shut power plants down when operating parameters exceed the specified criteria. These conditions are determined on the basis of measurements which, in turn, are interpreted with the aid of the steam tables.

Steam turbine power plants costing as much as a billion dollars are bought and sold with guaranteed performance quoted to within 0.25%. In many cases, performance is warranted with the possibility of substantial liquidated damages being paid for failure to meet warranties. Whether the seller is liable for these damages depends upon measurements which, in turn, are again interpreted with the aid of steam properties.

Recent developments indicate that improved thermodynamic performance can be obtained from power plants if the present working fluid, water, is replaced by a mixture of ammonia and water. The mixtures used cover the entire range of compositions, from 0 to 100% ammonia. The cycle is described in "Development of the Adjustable Proportion Fluid Mixture Cycle" by C.H. Marston (Mechanical Engineering, Vol. 114, No. 9, Sept. 1992, p. 76-81). The best known such cycle is the Kalina Cycle.

In addition to their importance in potential power plant applications, accurate properties data for ammonia/water mixtures are also important for use in the design and operation of absorption refrigeration systems.

1. The Range of Thermodynamic Properties Required

The applications of ammonia-water mixtures in power plant design include very high temperature systems, as occur in the use of coal in "direct fired" power plants (866 K) to more modest temperatures, such as those in nuclear reactors (644 K), and relatively low temperatures in geothermal and industrial waste heat systems (373-473 K). The pressures used may vary from feed pump delivery pressures of 34.5 MPa down to condenser pressures of 0.002 MPa.

For every combination of pressure, temperature, and mass fraction of ammonia, it is necessary to have values of the specific enthalpy, entropy, and density.

Because of the importance of boiling and condensation phenomena in these cycles, it is also essential to have good information on the surface tension of ammonia-water mixtures.

2. The Range of Transport Properties Required

The proper design of turbines and pumps together with the design of heat exchangers requires in addition to the thermodynamic properties, good knowledge of the viscosity and thermal conductivity of ammonia-water mixtures over the complete range of temperatures and pressures cited for thermodynamic properties.

3. Stability of Ammonia-Water Mixtures

The constituents of ammonia-water mixtures will decompose significantly at high temperatures. The effect of different construction materials as catalysts has not been established.

Ammonia decomposition is heterogeneous, that is, it is enhanced by contact with a heated surface and occurs near the walls of a flow stream. It is desirable to operate the equipment at as high a temperature as possible. Therefore, there is a need to characterize the catalytic nature of different materials which may be of interest in high temperature plant components (superheaters, for example).

4. Previous Work and Current Studies

An important bibliography of experimental work on the ammonia-water system was published in 1986 by the U.S. National Bureau of Standards (predecessor to the National Institute of Standards and Technology - NIST): **NBS Special Publication 718 -- Bibliographies of Industrial Interest: Thermodynamic Measurements on the Systems CO_2-H_2O, $CuCl_2$-H_2O, H_2SO_4-H_2O, NH_3-H_2O, H_2S-H_2O, $ZnCl_2$-H_2O, and H_3PO_4-H_2O**, by B.R. Staples *et al.* This report and an experimental study by Gillespie *et al* (AIChE symposium Series, 256; Vol. 83, 1987: **Vapor-Liquid Equilibrium Measurements on the Ammonia-Water System from 313 K to 589 K**) were sponsored by the Design Institute for

Physical Property Data of the American Institute of Chemical Engineers. The 1964 report of the U.S. Institute of Gas Technology (Research Bulletin No. 34; **Physical and Thermodynamic Properties of Ammonia-Water Mixtures**, by Marcriss *et al.*) presents tabulated thermophysical properties for the water-rich system up to about 500 K and for the ammonia-rich fluid up to 390 K.

Among the more recent studies, the article by Smolen *et al.* (**Vapor Liquid Equilibrium Data for the NH_3-H_2O System and Its Description with a Modified Cubic Equation of State**, J. Chem. Eng. Data 36; 202, 1991) can be cited. In this paper, as well as many others, an attempt to describe the system with a simple (i.e. cubic) thermodynamic surface is made. It is noted throughout the literature there is a concentration on VLE data (to the near exclusion of single-phase properties). Finally, it is also noted that even the VLE data exhibit large inconsistencies when comparing the results of different studies.

Current work is underway at NIST to begin the development of standard reference thermophysical properties for the ammonia-water system for geothermal applications. It is necessary that any mixture of thermodynamic surface must reduce to a water formulation such as that of IAPS 84 and to an ammonia surface for instance (Haar and Gallagher, **Thermodynamic Properties of Ammonia**, J. Phys. Chem. Ref. Data 7; 635, 1978) for the pure components. The theoretical models being examined include scaled equations in the region of the critical locus for VLE calculations and extended corresponding states algorithms to calculate mixture properties. The work at NIST includes a limited measurement program to resolve the major discrepancies in the experimental VLE database and to supply selected data over limited ranges where none are currently available. These new data will have a major impact on the development of standard reference models for applications in the range of geothermal power cycles. Additional funding, as well as collaboration with other domestic and international groups, will be required to achieve a definitive study of the ammonia-water system. The NIST program does not currently address the questions concerning surface tension or the stability and catalysis issues which are also extremely important.

IAPWS Contact: W.T. Parry
General Electric Company
Steam Turbine Design & Development
1 River Road, Building 55 - Room 169
Schenectady, New York 12345 U.S.A.
Telephone: 518-385-0577
Fax: 518-385-1504

ICRN Issue Date: June 1994

ICRN Expiration Date: June 1997

APPENDIX D.

M. TRIBUS: STATUS OF PROJECTS USING AMMONIA/WATER MIXTURES

Notes for presentation at Boulder

Myron Tribus

Status of our technological development: Several systems have been developed. There is no single Kalina cycle. Rather there is a family of cycles, each designed to meet a particular need.

System 1 has been built and operated for several years at Canoga Park. It is now being modified by the addition of a small gas turbine. Heretofore we have used hot gases from the SETI tests at ETEC. However, they have come to an end and we need to be self sufficient. This small 8 MW combined cycle plant will have an efficiency which will exceed that of many existing large plants.

Here is a run down on the status of our current designs.

Cycle and Licensee	η	#	**Comment**
Combined Cycle (GE)	**59%**	**2**	**Using GE 9FA engine**
Direct Fired (ABB)	**(net)**	**1**	**Cycle efficiency = 52%.**
Subcrit	**45%**		
Supercrit	**47%**		
Geothermal (Ansaldo)	**1.2x** **2 x**	**4**	**Multiples of Rankine**
Waste Incineration (Ebara)	**1.35x**	**1**	**Multiples of Rankine**

X = Ratio Kalina/Rankine efficiencies in same boundary conditions.

Because of the number of projects in development, there is great interest in the properties of Water-Ammonia mixtures. We have developed our own computer program, WATAM, over a period of about 16 years. We have checked it against all the experimental data we could find and have used the best we knew to extrapolate into regions where there are no properties. We recently contracted with the Russian Academy of Sciences to make more measurements. A copy of their summary report is available at this meeting.

We are also conducting studies of heat transfer. As we attempt more and more detailed analysis of our data, the properties of mixtures will be crucial.

We hope that this work will be expanded. The promise of the Kalina cycle for fuel saving, pollution reduction, cost reduction and flexibility is very great. As more people become involved, the potential savings in cost and time provide a very strong basis for this research.

APPENDIX E.

THE INVESTIGATION OF AMMONIA-WATER GAS AND LIQUID MIXTURES PROPERTIES; A. BARANOV ET AL.

The investigation of ammonia - water gas and liquid mixtures properties.

*Baranov A.N., *Churagulov B.R., Kalina A.I., **Sharikov F.Yu., ***Zharov A.A., ****Yaroslavtsev A.B.

**Lomonosov Moscow State University, **St.-Peterburg State University, ***Zelinsky Institute of Organic Chemistry Russian Academy of Sciences, ****Higher Chemical College Russian Academy of Sciences.*

Correct knowledge of the thermodynamic properties of ammonia-water mixtures is very important for the fruitful operation of the power generation Kalina cycle [1]. The specific volumes of NH_3-H_2O liquid and gaseous solutions plays a key role on the calculation of these properties. Unfortunately the knowledge of gas mixture properties at the high temperatures and pressures is scanty. The known data on the compressibility of liquid solutions is of low accuracy. The main purpose of this work was to investigate the volumetric and some of the calorimetric properties of ammonia-water liquid and gaseous solutions.

I. *Specific volume of gas mixtures.*

Ammonia from a gas cylinder 1 (Fig. 1) was distilled in the corrosion-proof steel vessel 2, which was cooled by dry ice. Then vessel 2 was cooled by liquid nitrogen and the frozen ammonia was evacuated. The procedure was repeated as many times as traces of gaseous ammonia remained in the system. Then ammonia from gas cylinder 2 under its own pressure was supplied into the amalgamator intermediate device 3 and water was also transferred in the intermediate device 3 with the help of pump 16. The mixture under a pressure of 8-12 at was then manually stirred and supplied into the PVT cell.

The PVT cell was evacuated to a pressure of 0.1 torr and was heated to a specified temperature with the help of air thermostat 5 and maintained as long as the fluctuations of temperature were kept within the limits of the measurement error (±0.1K). Then valve 25 was closed and the cell content was transferred to the evacuated trap 13 and 14 cooled by liquid nitrogen. The volume of gases not condensed at liquid nitrogen temperature (N_2 and H_2 - if they were formed as a result of ammonia decomposition during the experiments) was measured. Traps 13 and 14 were sealed off, weighed, and the substances were analyzed for the ammonia content.

We have investigated the specific volumes of water-ammonia gas mixture in the range of temperature 623 - 873 K and pressures from 32 up to 250 bar. Some of results of our investigation are given in Fig. 2. The ammonia and water forms almost ideal gas solution at low temperatures. Some deviations took place at the high pressures, but they became negligible with a rise of temperature (Fig. 2).

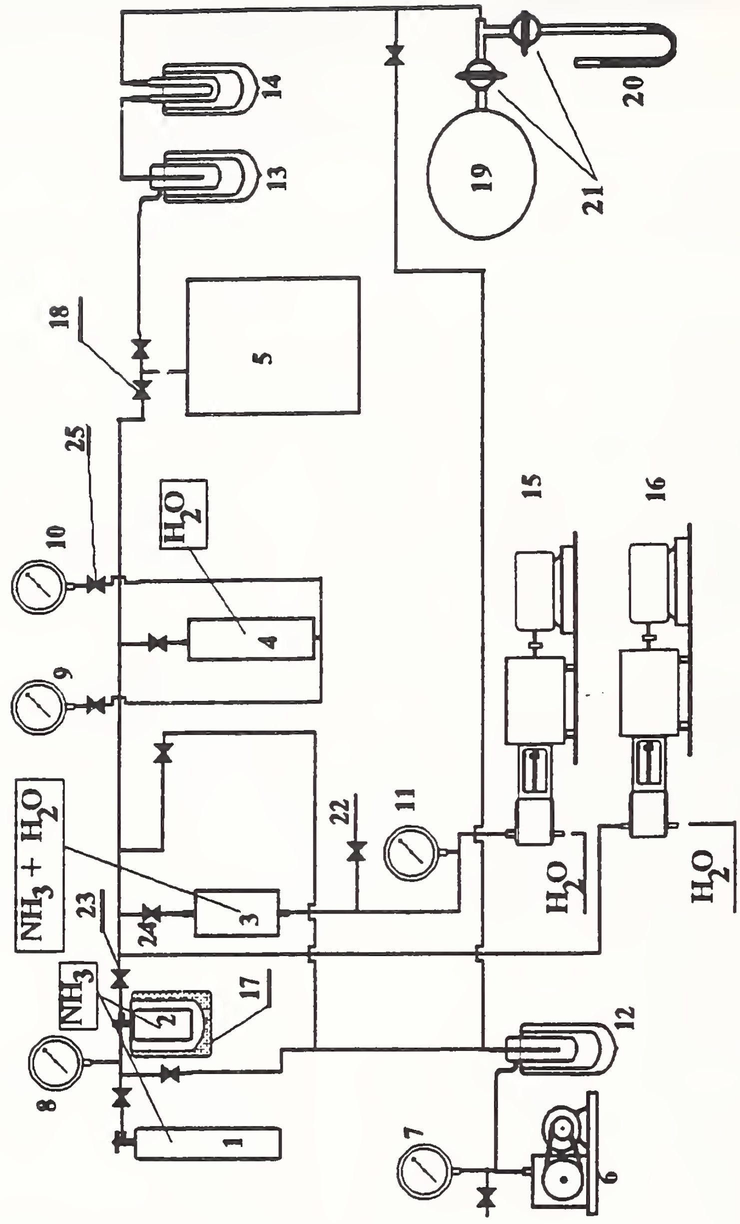


Fig. 1. Schematic diagram of the installation for PVT measurements of ammonia-water mixtures in the temperature range up to 873 K and pressures up to 40 MPa.

1- cylinder with ammonia; 2- vessel for ammonia recondensation; 3- intermediate vessel used for mixing; 4- buffer vessel with water, preventing ammonia contact with metal parts of the manometer; 5- air thermostat with a PVT cell; 6- vacuum pumps; 7- vacuumeter, 8,-11 - manometers, 12- trap with liquid nitrogen, 13,14- vessels for probes of the ammonia - water mixture withdrawn from the PVT-cell, 15- plunger high-pressure pump; 16-accurate displacement pump with sapphire rods and valves; 17- foam plastic vessel with dry ice or with liquid nitrogen; 18,22-27-two-way valves; 19- glass calibrated volume vessel; 20 - Hg manometer; 21- vacuum valves.

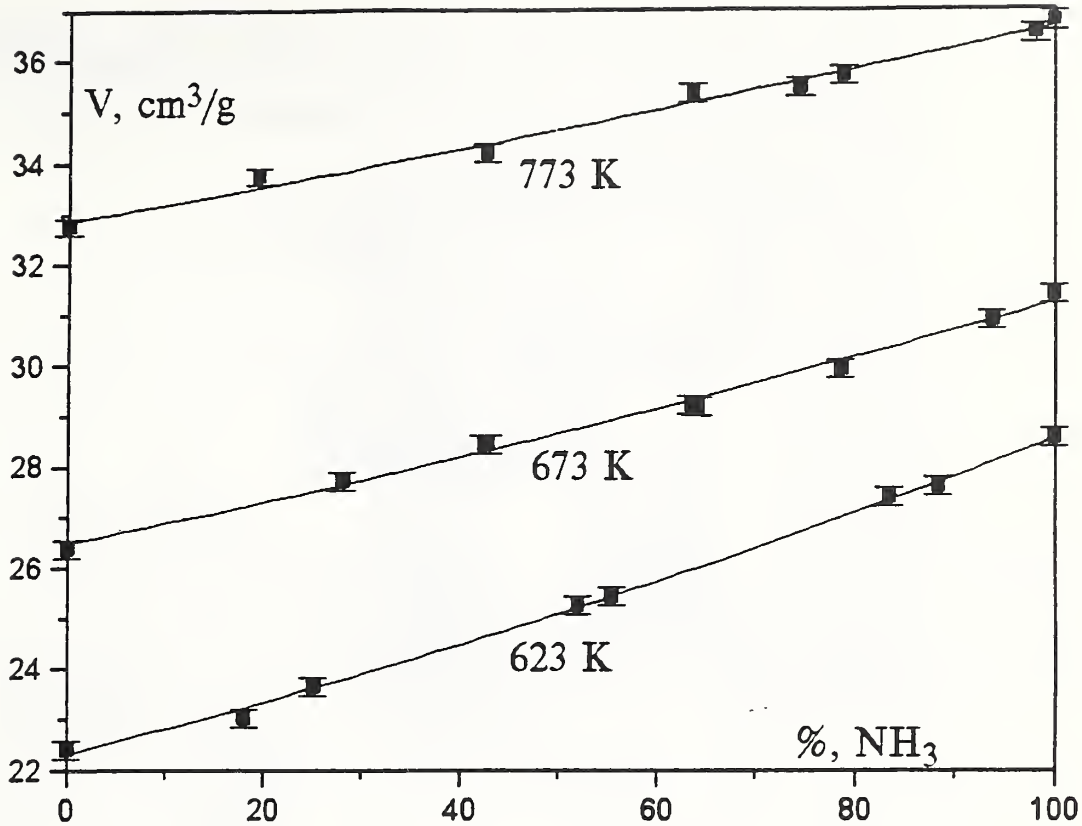


Fig. 2. Comparison of the specific volumes of ammonia - water gas mixtures at various temperatures and NH_3 contents. P = 100 bar.

II. *Measurement of compression of ammonia-water liquid solutions.*

The schematic diagram of the installation, used for high-pressure experiments with water - ammonia solutions is presented in Fig. 3. The installation is made of special corrosion-proof steel with increased strength. The top of the channel of the high-pressure chamber is closed by diaphragm through a brass seal, which is secured by a wing nut. To prevent heat loss through cross brace (2), the high pressure chamber was fixed on a special union, which was also kept at a constant temperature by thermostatic control. The installation was heat-insulated with asbestos. These measures have allowed us to create inside the HP chamber channel a nongradient zone in a range of temperatures up to 430 K. The preliminary study of thermostatic control modes at various temperatures and pressures was performed before the experiments with compression of solutions. The time to establish thermal equilibrium ranged from 1 (at 300 K) to 6 hours (at 425 K).

For the investigation of the compression of water - ammonia solutions a Gibson piezometer was used [2]. Piezometers are made of Pyrex glass and are vessels with a sealing capillary in the bottom (Fig. 4). The cell is immersed in mercury in a stainless steal beaker. During the compression experiments, mercury enters the capillary and drops onto the piezometer bottom.

Upon pressure reduction the excess liquid leaves the piezometer through the capillary. The compression of the solution was calculated from the weight of mercury left in the piezometer. After the experiments, ammonia solutions were neutralized with a 1N H_2SO_4 solution and the excess of acid was titrated by a 0.1N NaOH solution.

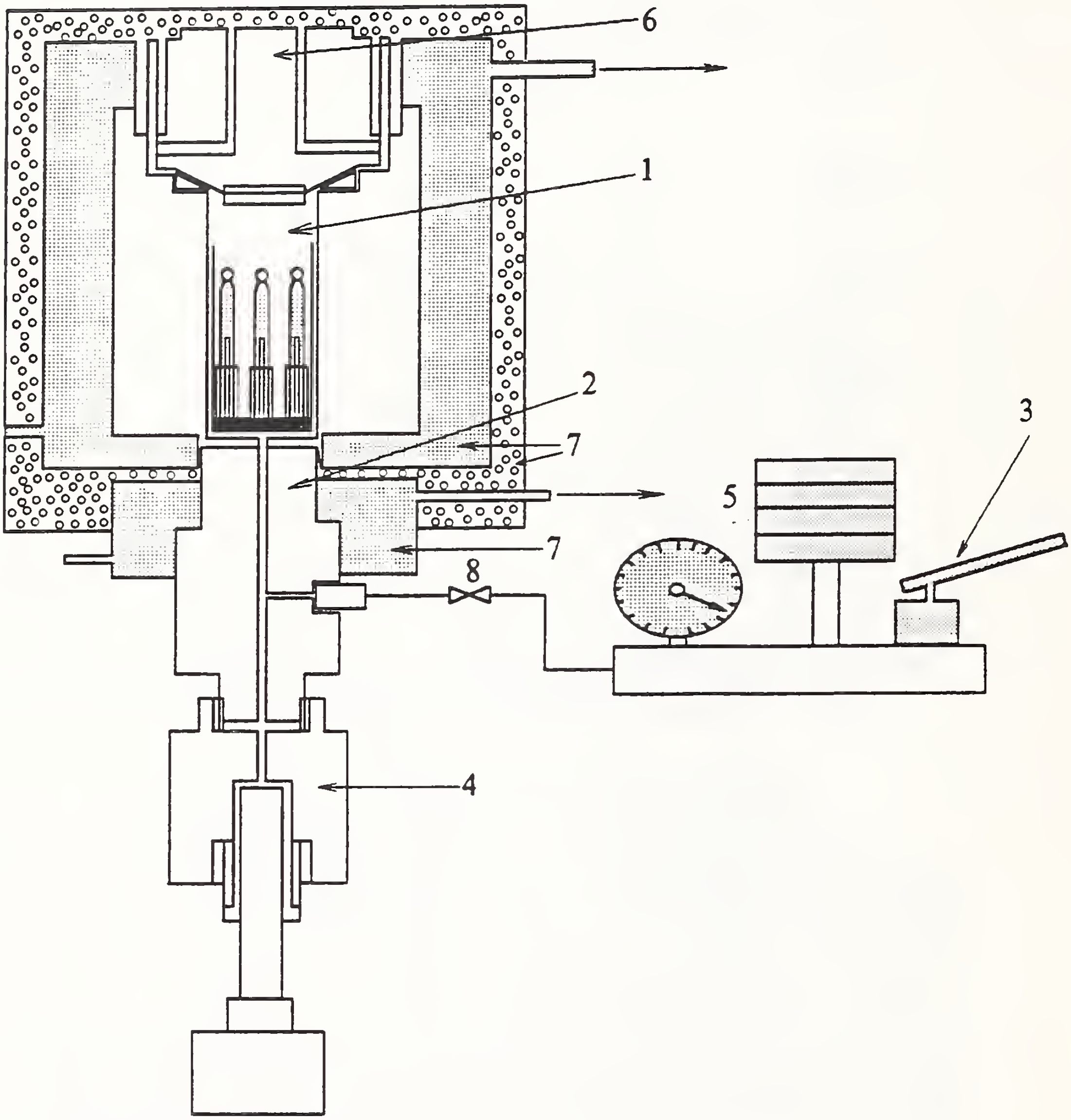


Fig. 3. Schematic diagram of the high-pressure installation for studying the compression of water - ammonia solutions.

1 - high-pressure chamber, 2 - cross brace, 3 - preliminary pressure system, 4 - multiplicator, 5 - piston manometers, 6- obturator, 7 - thermostatic control and heat-insulation, 8 - valves.

The procedure for the compression measurements was established by preliminary experiments with water. The time required for establishing equilibrium in the piezometer was determined and the absence of temperature gradients and fluctuations in the high-pressure (HP) chamber was proven.

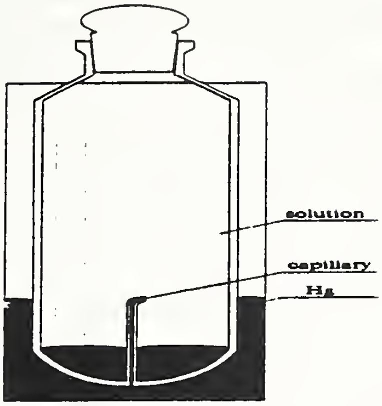
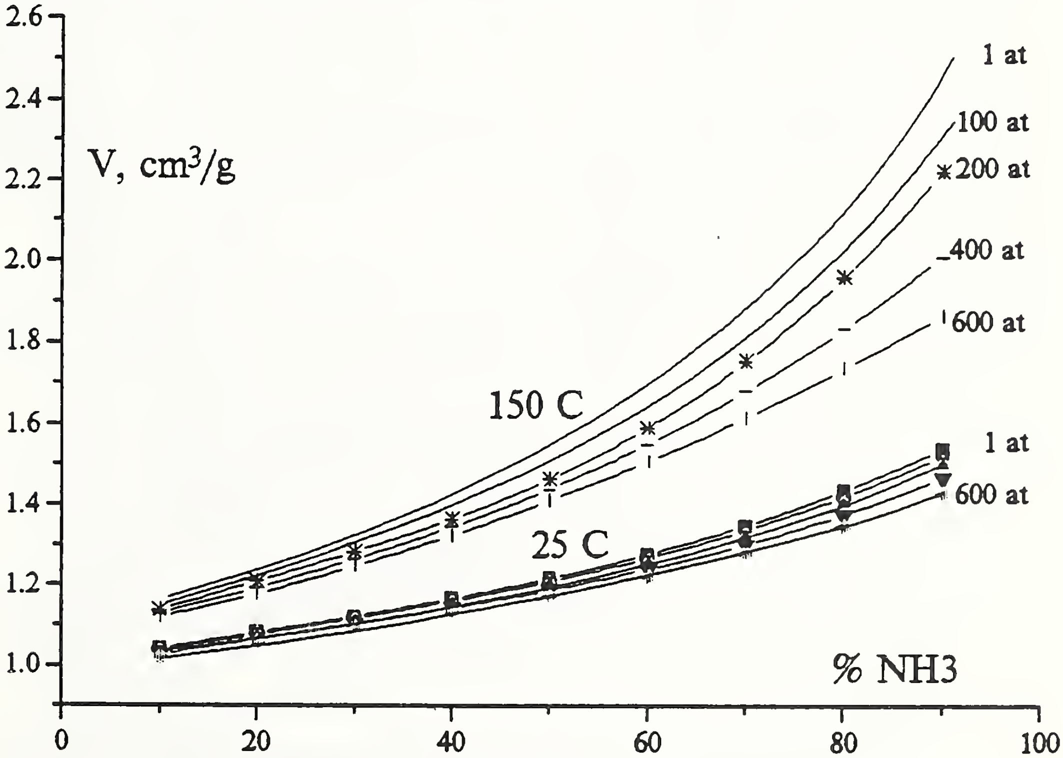


Fig. 4. Gibson piezometer.

The data on compression of ammonia-water mixtures were analyzed with the help of a special computer program. Smoothed curves of compression were obtained and the specific volumes for the NH_3-H_2O liquid solutions were calculated for temperatures up to 423K and pressures up to 600 atm. The specific volumes at the atmospheric pressure were taken from [3]. Examples of the data obtained are given in the Fig. 5.



Fif. 5. The dependence of the volume of liquid on the temperature, pressure and NH_3 content.

III. *Calorimetric study of ammonia-water solutions.*

The calorimetric experiments were carried out using an automated heat flux C-80 "Setaram" calorimeter (France). Processing of experimental data - filtering, base line subtraction, integration - was done with the use of an original Program Package "Experiment" developed in the Russian Scientific Center "Applied Chemistry".

For the heat of mixing investigation special mixing vessels with two chambers separated by a membrane were used. The pressure inside the vessels can reach 150-200 bar. Volumes of the upper and lower chambers are each equal to 1.2 cm^3. The membrane is made of a special nickel foil of high purity, 0.2mm. New vessels allowed us to work with pure ammonia in the lower cell up to 373K, and with 30-60% ammonia solutions up to 423K.

A predetermined amount of purified ammonia was placed in the lower chamber, cooled with liquid nitrogen. The chamber was closed with the membrane and the vessel was heated to ambient temperature. Then the corresponding quantity of water was added, the vessel was totally

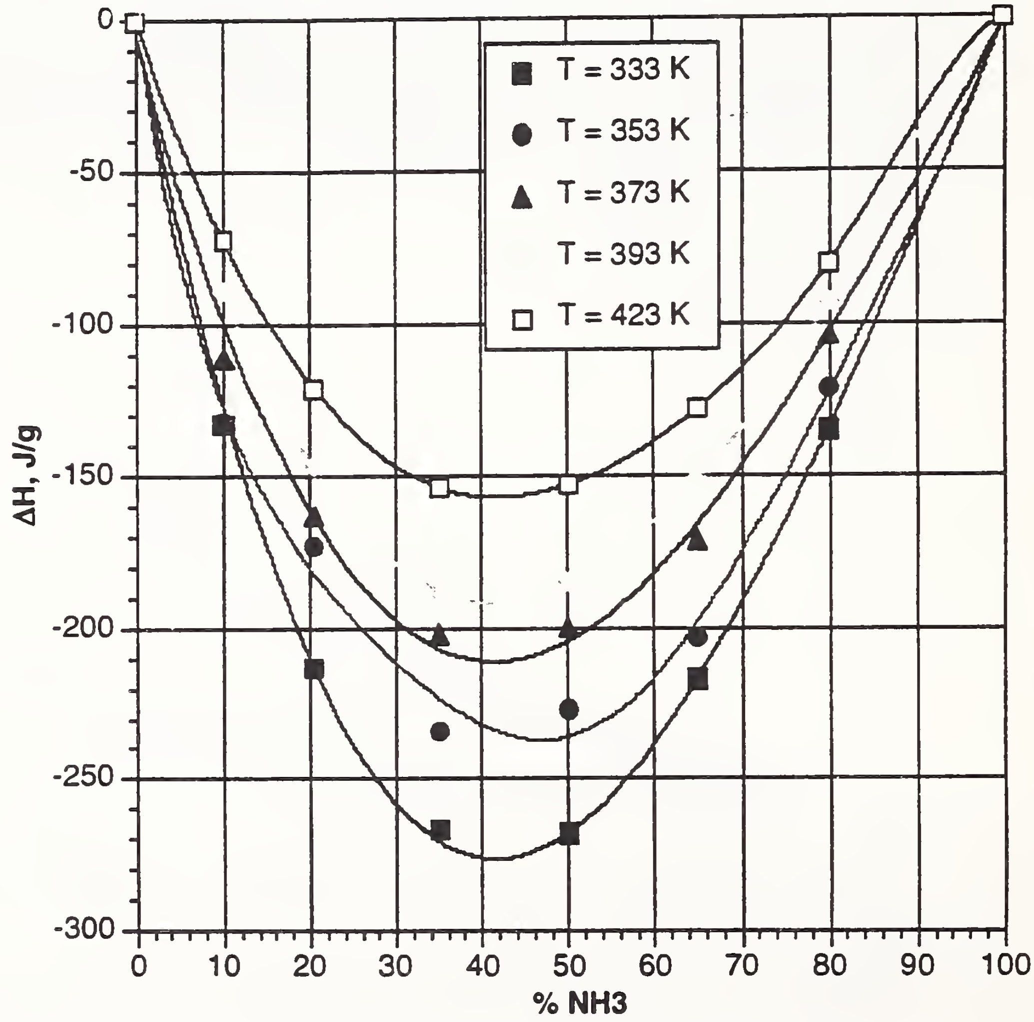


Fig. 6. Heats of mixing of liquid ammonia and water at different temperatures.

assembled and inserted into the calorimeter cell to reach thermal equilibrium. A membrane separates the two chambers and two liquids until the beginning of mixing. Mixing is performed by piercing the membrane with a rod which also serves as an initial stirrer. Then mixing is performed by revolving the calorimetric block. Experimental values of heat of mixing are given in Fig. 6.

At temperatures above 383K, the membrane could no longer seal pure ammonia vapor before reaching thermal equilibrium. For high-temperature tests, corresponding 62 and 38% ammonia solutions were prepared in the lower chamber, and the necessary quantity of water was introduced into the upper chamber. Assuming the similarity of heat effects of mixing at low and high temperatures, the corresponding values of heat effects were calculated.

The measurements of heat capacity were made in stainless-steel ampoules with aluminum joints similar to standard "Setaram" ampoule adapted to pressures up to 200 bars. The inner volume was 7.5 cm^3. Ammonia was placed in the cooled ampoule and diluted with water to get the necessary concentration. At temperatures close to the critical temperature for the corresponding concentration, not less than ~70-80% of the ampoule inner volume was filled with a liquid.

Experiments were performed in a linear heating mode, 0.5K/min, temperature range 293-563K. Base line with an empty ampoule was recorded under the same conditions. For comparison the heat capacity of H_2O was determined under the same conditions. The obtained data were

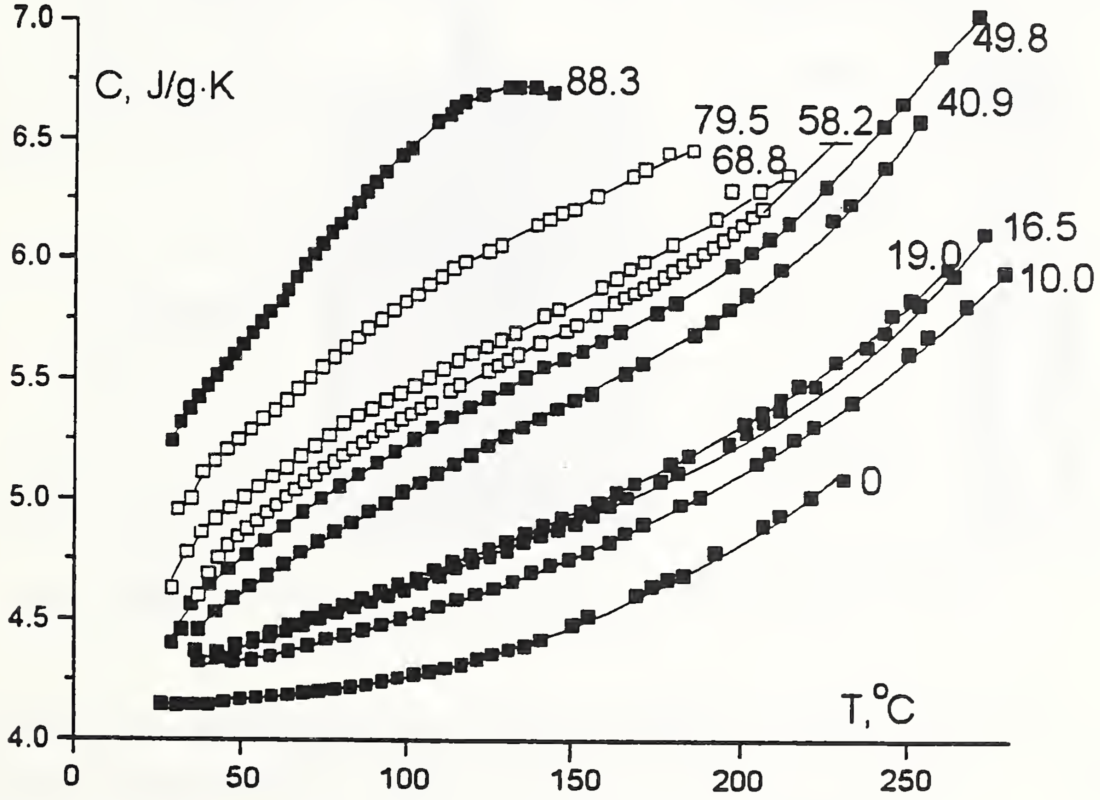


Fig.7. Temperature dependencies of heat capacities of ammonia solutions.

additionally verified by the experiments that were conducted at low heating rates 0.05K/min and by direct determination of the heat capacity at 303K. The correlation was good. For temperatures above 593K, the values obtained must be corrected for vaporization processes and the heat capacity of vapor. The experimental values of heat capacities are given in Fig. 7.

A new method of thermal conductivity measurement for liquids based on a heat flow calorimeter was used to investigate ammonia-water solutions. It can be applied to various solids and liquids or liquid solutions having a low conductivity in the range 0.1 - 1.0 W/m·K. For the system "NH_3 - H_2O" a method applying standard high-pressure vessels (see Fig. 8, $V = 8.5\ cm^3$) were developed. Water was used as a standard. The method of thermal conductivity measurement is based on the theory of a regular cooling mode developed by Kondratiev [4]. When a body of an arbitrary shape is heated with a constant temperature and heat exchange, a special mode of heating is established after a certain time interval. Temperature variation in any point of the body does not depend on the initial temperature distribution inside the body. The rate of heating is the same for any point of the body. At the end of the heating procedure the heat flow to the body was fixed and the thermal conductivity was calculated.

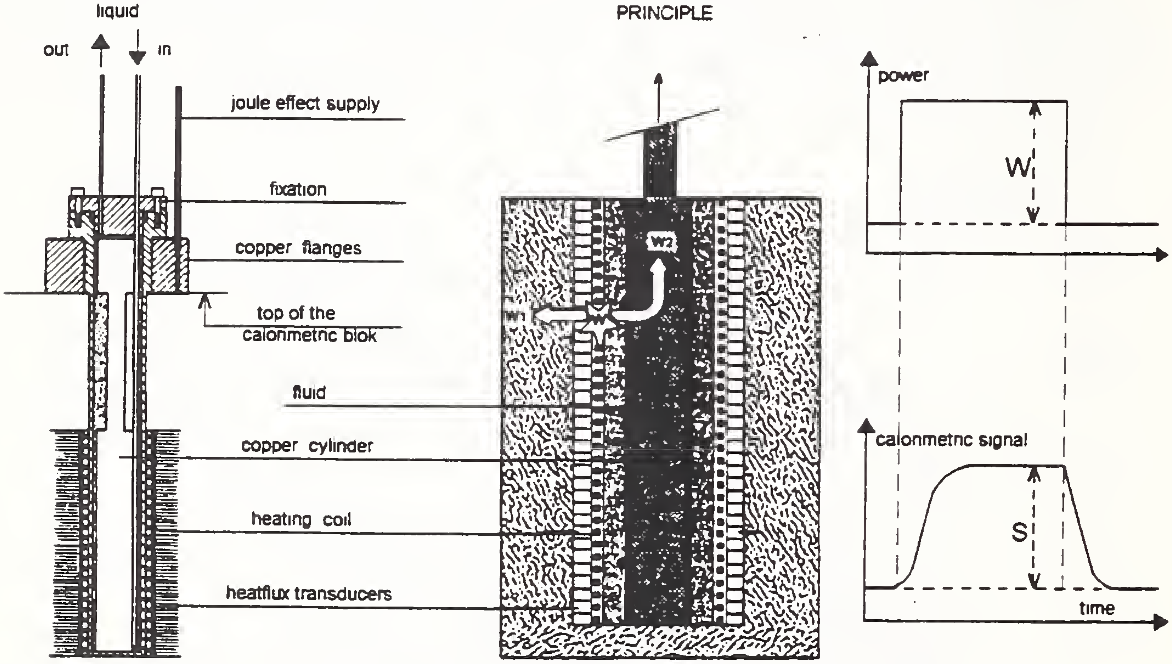


Fig. 8. Scheme of the vessel for thermal conductivity determination of the ammonia - water system.

Experiments to measure the thermal conductivity were run at temperatures up to 460K. The following ammonia solutions were studied: 20, 40-45, 58, 80%. The data obtained are shown in Fig. 9.

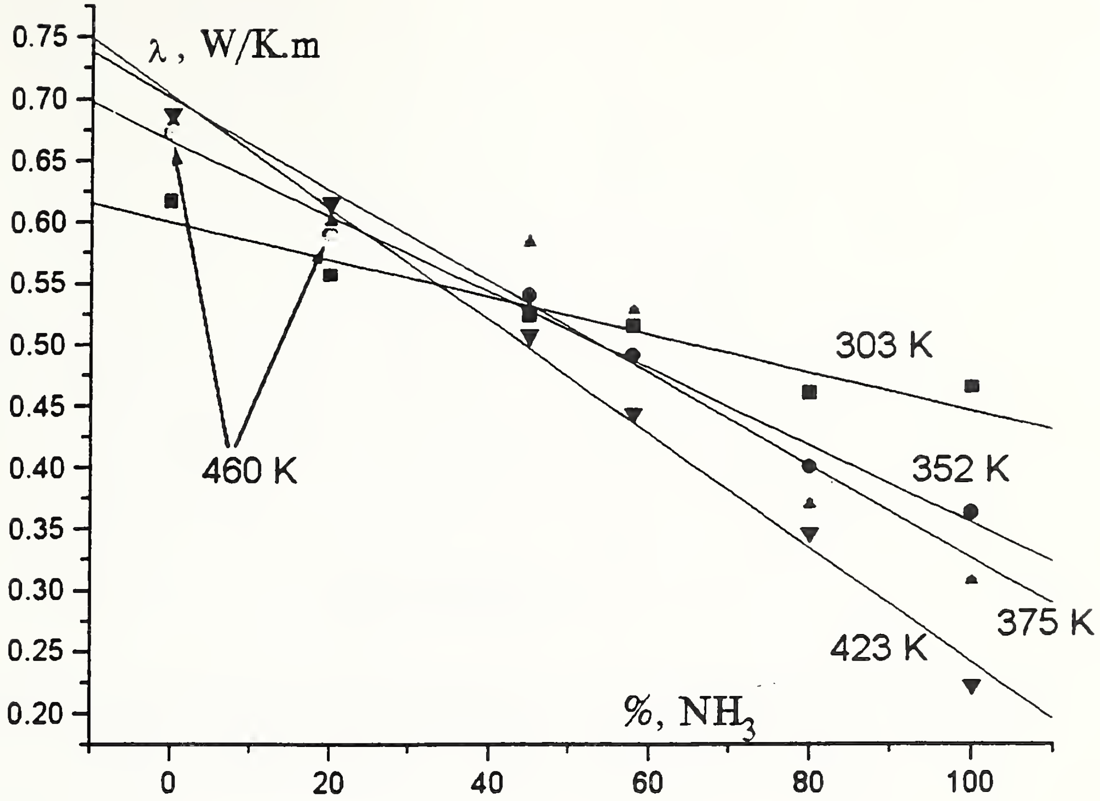


Fig.9. Thermal conductivity of ammonia - water solutions.

Conclusions.

The volumetric and some calorimetric properties of ammonia-water gases and liquid solutions was investigated. It was shown that the gases solutions are almost ideal in the wide range of temperatures and pressures.

Literature:

1. Kalina A.I. "Kalina Cycles and System for Direct-Fired Power Plants" AES. 1991. Vol.25/HTD. Vol.191.
2. Gibson R.E./ J.Am. Chem.Soc., 1937. V.59. p.1521.
3. Jenning B.H./ Trans.Amer.Soc.Heat. Refrig. and Air Condition Eng. 1971. V.77 Part.1 p.149-51.
4. Kondratiev, G.M., Regular Heat Processes GITTL, Moscow (1954)

APPENDIX F.

F. GABRIELLI: FLUID PROPERTIES REQUIREMENTS OF KALINA CYCLE FOR DIRECT COAL-FIRED PLANTS

Direct-Fired Kalina Cycle: Overview

- Goals: a 10%-20% improvement in net plant efficiency at a cost advantage of 10%
- Goals achieved mostly via structural improvements
- Kalina cycles represent a whole class of system designs
- Application - match the optimal Kalina system design to power plant constraints and requirements:
  - Utility cycles (>350 MW)
    - current Rankine efficiency = 37-41% (HHV net)
    - predicted Kalina efficiency = 45+% (HHV net)
  - Industrial cycles (e.g. 50 MW demo plant)
    - current Rankine efficiency = 30% (HHV net)
    - predicted Kalina efficiency = 38% (HHV net)

Properties Requirements

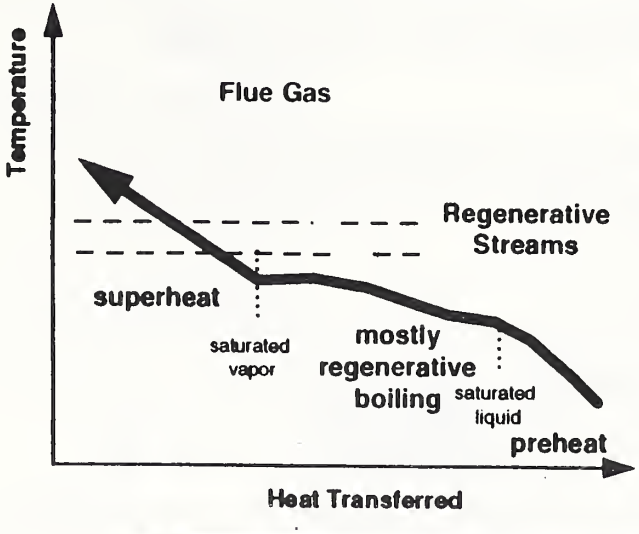
- *Heat Capacity*
- *Surface Tension*
- *Viscosity*
- *Thermal Conductivity*
- *Density*

Kalina Cycle: Inherent Advantages

Improved Heat Acquisition from Furnace

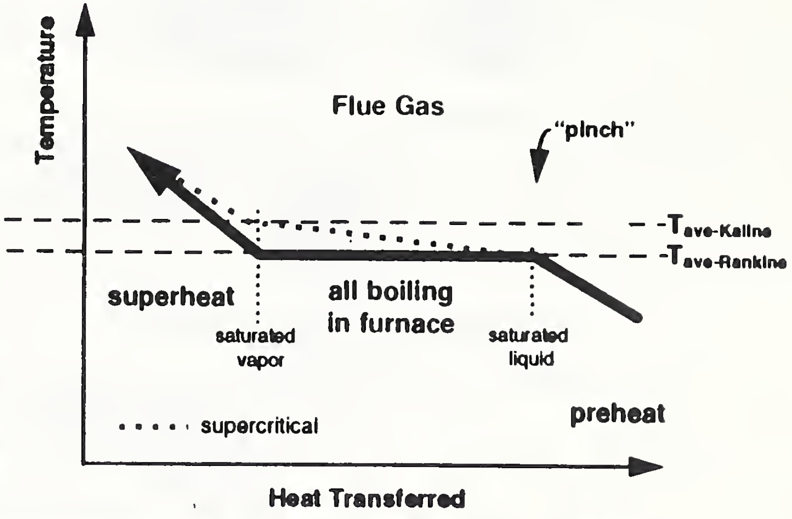
Kalina Heat Acquisition

minimal boiling occurs in furnace,
superheat matches flue gas profile well



Rankine Cycle Heat Acquisition

isothermal boiling causes temperature profile mismatches,
all boiling occurs in furnace even for supercritical cycle



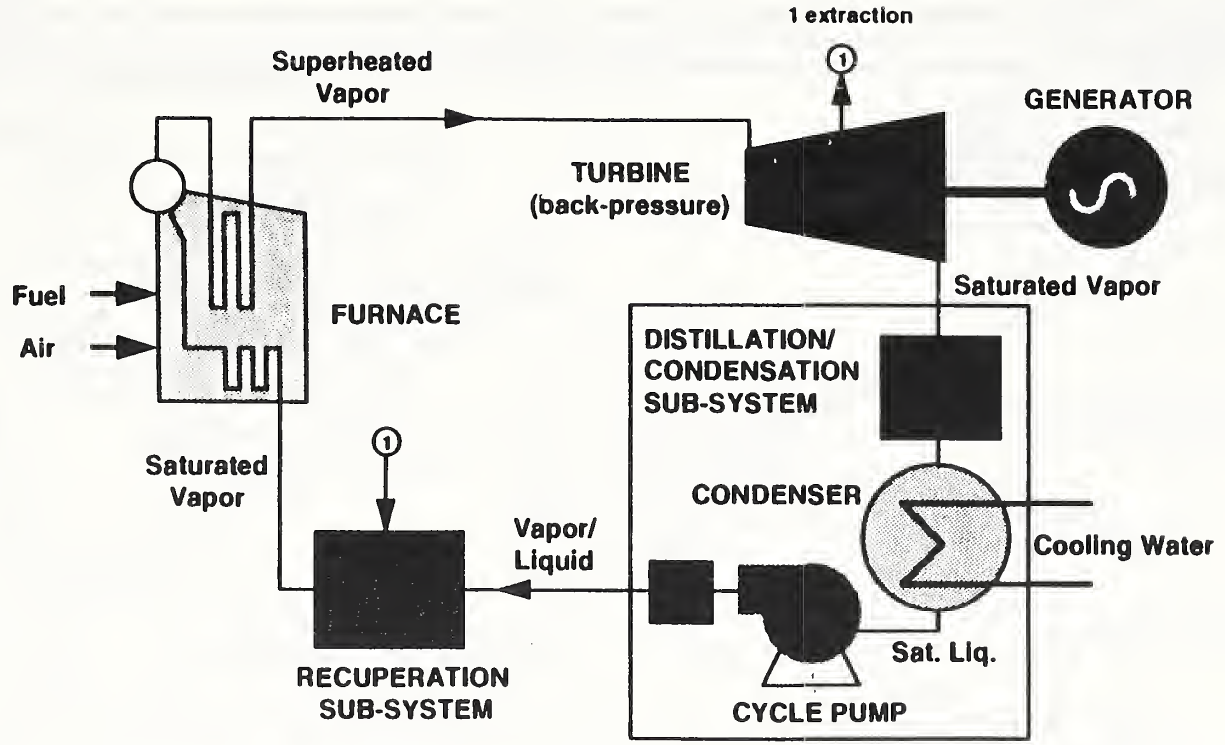
Higher average temperature of heat acquisition means improved cycle efficiency

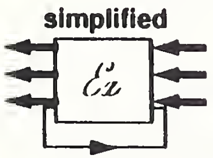
Fundamental Features & Benefits of Using an Ammonia-Water Mixture

- Variable temperature boiling and condensing
  - higher average temperature of heat acquisition
  - lower average temperature of heat rejection
- Thermo-physical properties can be manipulated via mixture concentration
  - to maximize degree of regenerative boiling
  - to optimize performance at off-design conditions
- Heat of mixing
  - to improve cycle recuperation
- Lower freezing temperature (winter peaking bonus)
- Aqueous ammonia is cheap, non-toxic
- Back-pressure turbine

Schematic: Kalina Cycle Power Plant

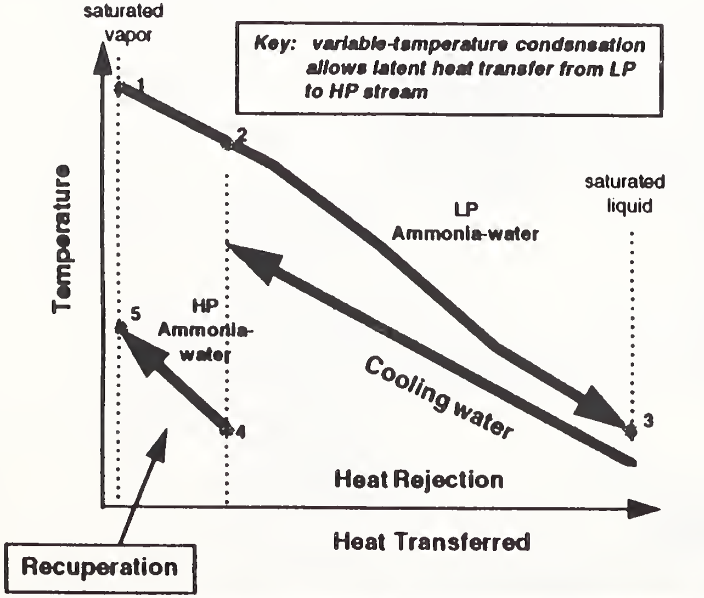
Simplified Direct-Fired



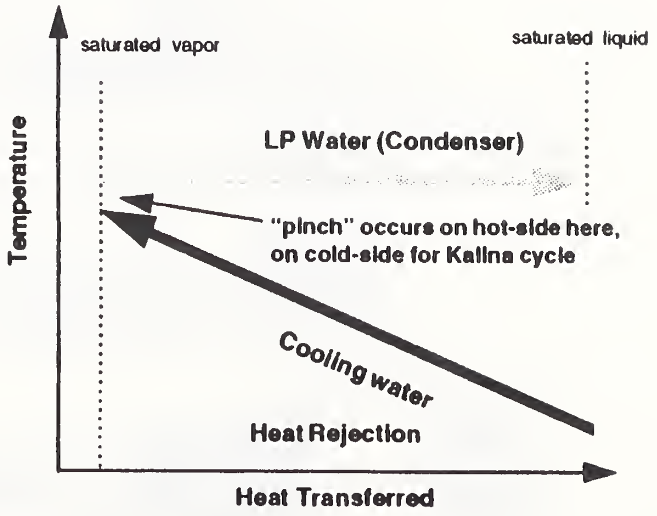


Kalina Cycle: Inherent Advantages

Improved Heat Rejection and Partial Recuperation of Latent Heat


Kalina Heat Rejection with Partial Recuperation

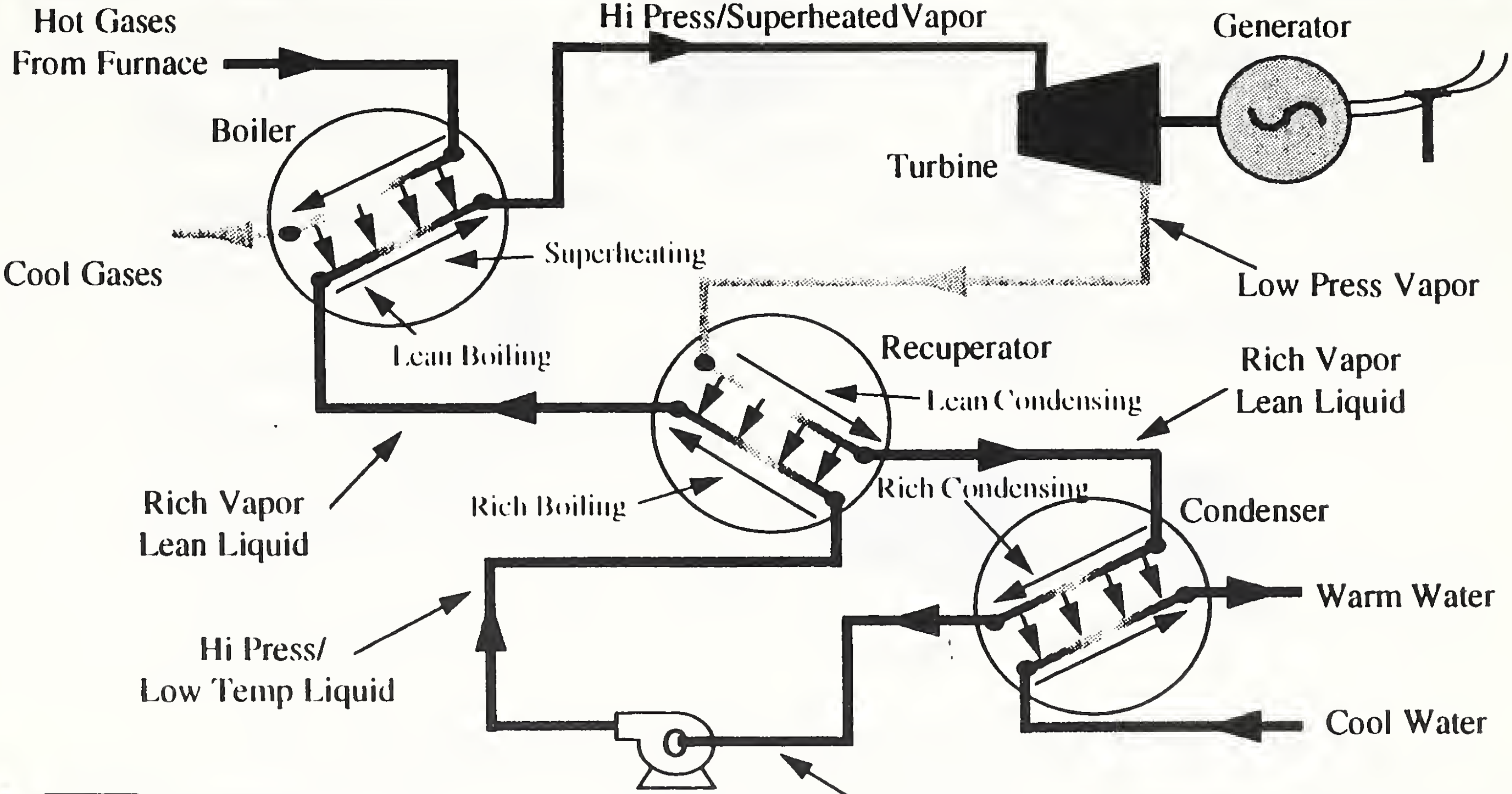
Key: variable-temperature condensation allows latent heat transfer from LP to HP stream


Rankine Heat Rejection

"pinch" occurs on hot-side here, on cold-side for Kalina cycle

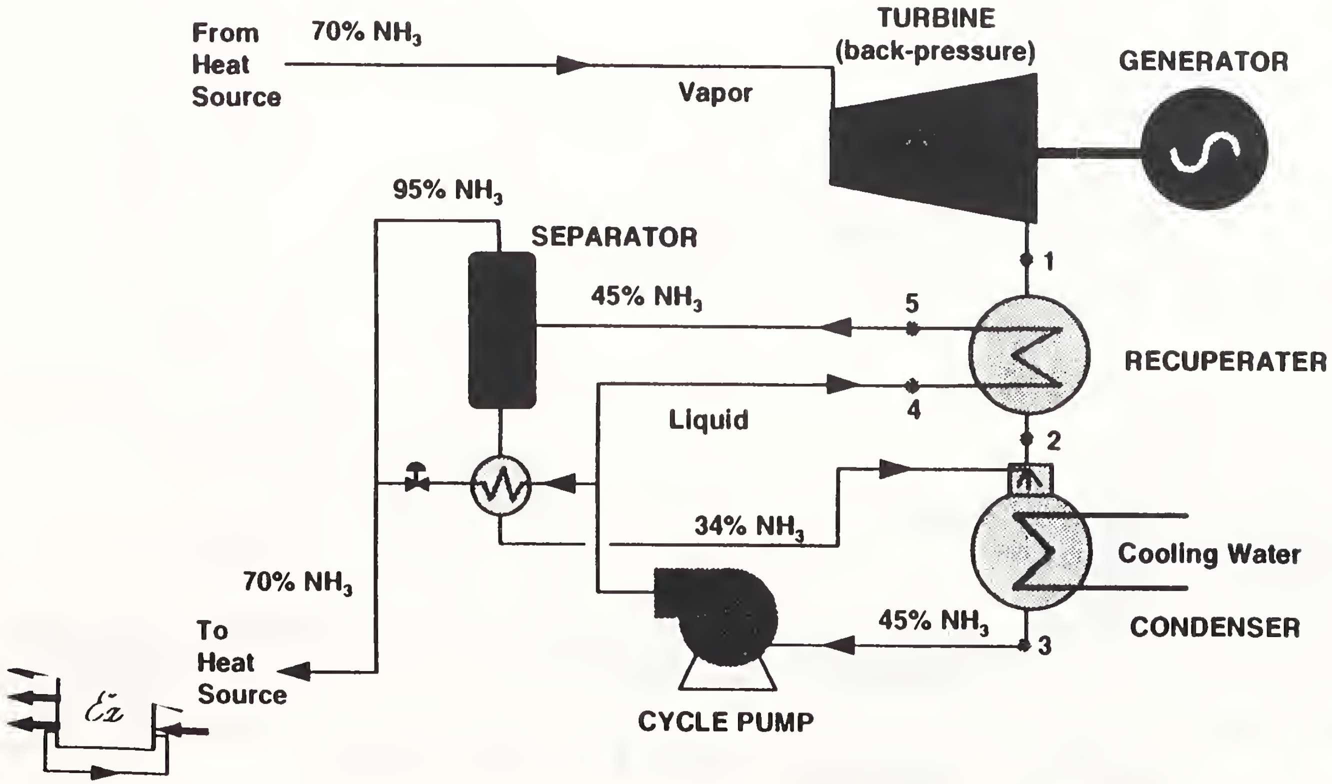
Less heat rejection at lower average temperature and more recuperation means improved cycle efficiency

Schematic
Kalina Cycle Power Plant



Kalina Cycle: Absorption-Condensation

Use Leaner Mixture to Help Reduce Turbine Back-Pressure

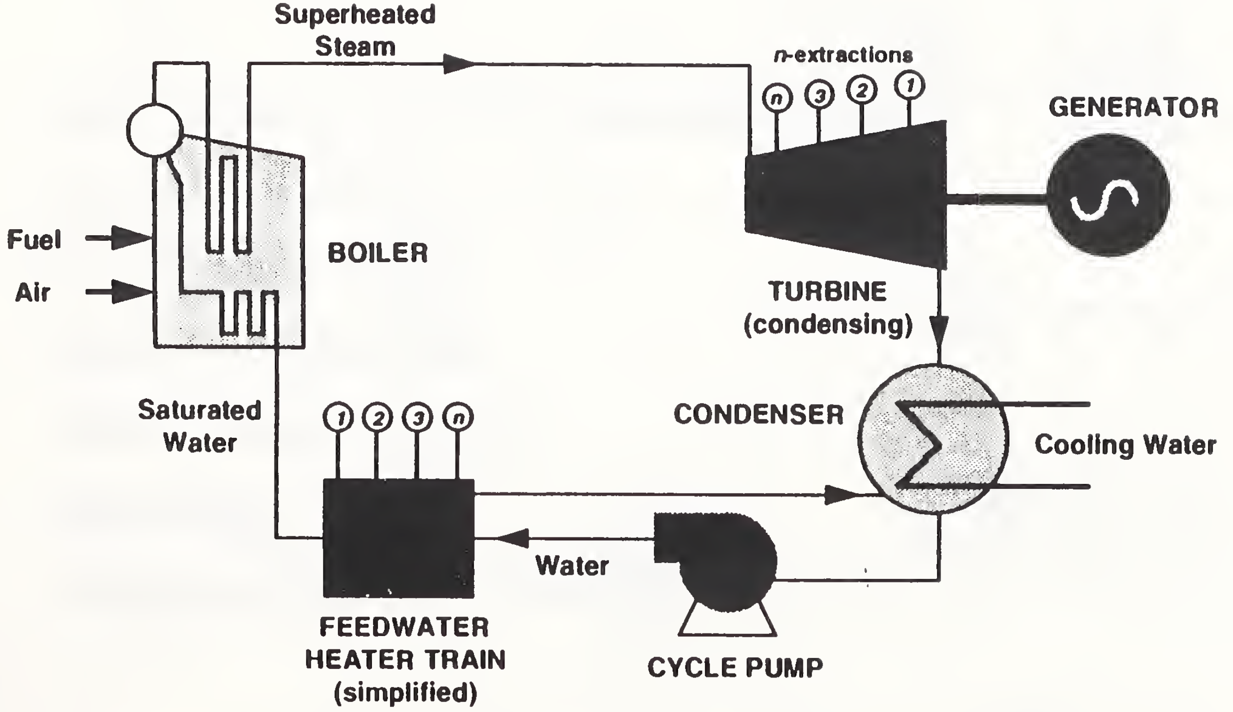


Technical Development Programs

- Thermodynamic properties
- Materials
- Cycle performance
- Heat exchangers
- Furnace design
- Vapor turbine
- Pilot plant testing (Canoga Park)

ABB

Schematic: Rankine Cycle Power Plant



APPENDIX G.

J. HAHN: FLUID PROPERTY NEEDS FOR GEOTHERMAL POWER CYCLES

Fluid Property Needs for Geothermal Power Cycles

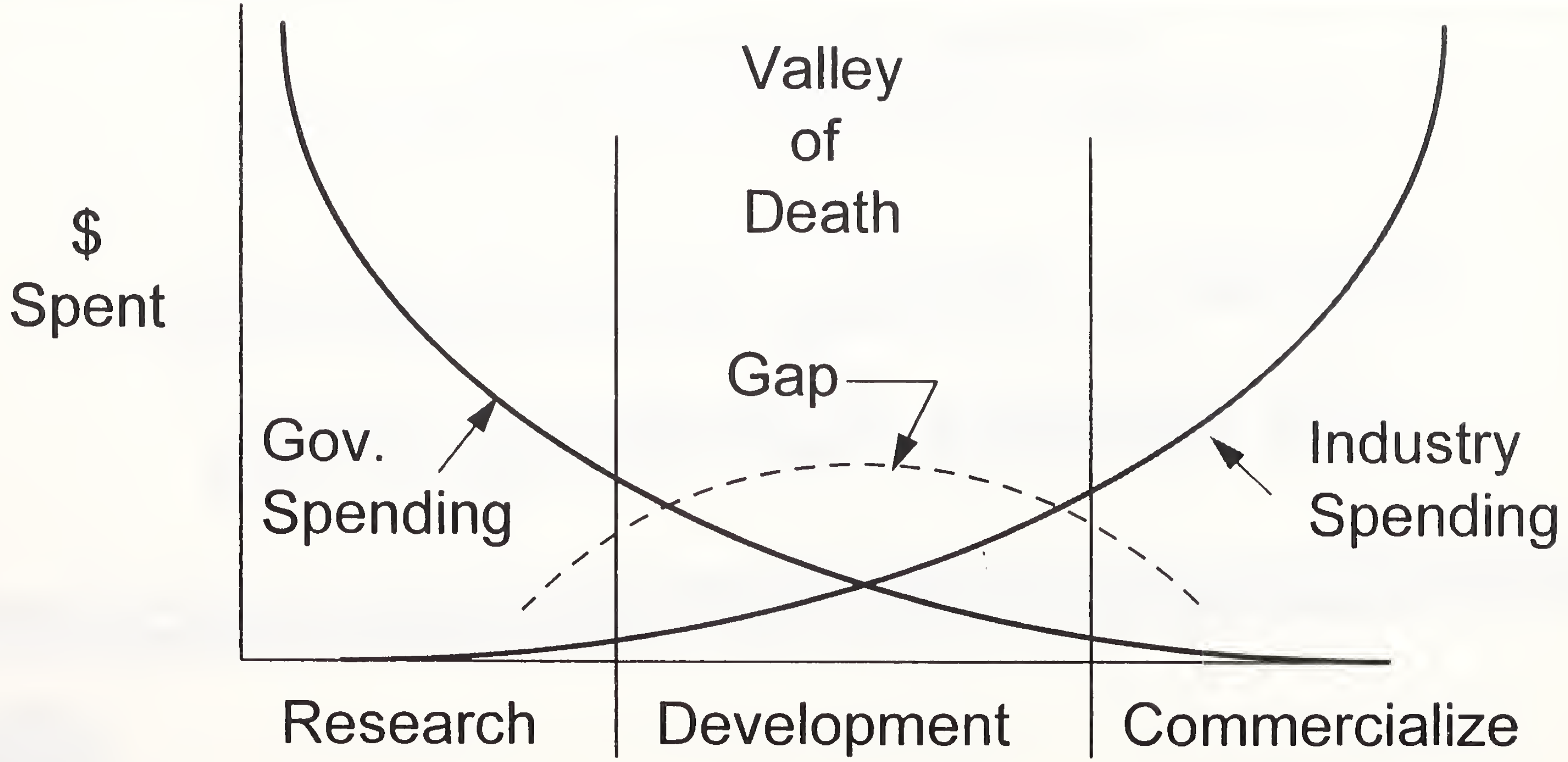
Workshop on Thermophysical Properties of
Ammonia/Water Mixtures

By Jeffrey L. Hahn

June 26, 1996

U.S. Dept of Energy, Golden Field Office

From Research to Commercialization



June 26, 1996

U.S. Dept of Energy, Golden Field Office

Purpose of Financial Assistance

- Reduce the financial risk
- Promote U.S. industry
- Re-invest the tax payers money

June 26, 1996

U.S. Dept of Energy, Golden Field Office

Selection of the Exergy Project

Solicitation - Demonstration of Economic Benefits of Improved Electrical Power Generating Systems for Geothermal Applications

- Exergy was selected through a competitive process
  - Kalina cycle is technically strong
  - Good candidate for commercialization

June 26, 1996

U.S. Dept of Energy, Golden Field Office

Commercialization Requires Proof

- Utilities and Power Plant Operators are very conservative
- New products require testing for operation and reliability
- The Kalina cycle power plant needs to be demonstrated

Geothermal Energy Conversion Program

Majority of Program involves Binary cycles where temperatures are below 350 F

- Most high temperature resources (> 350F) have been exploited
- There are more low temperature resources available

DOE's Research and Development program is working to improve economics through

- increasing cycle efficiency (Rankine)
- improve component efficiency, reliability and cost

Rankine Cycle Efficiency Improvements

Multipressure Boiler

- Not feasible in geothermal binary systems

Supercritical Cycle

- Standard practice in geothermal binary systems

Mixed Working Fluids

- Allows variable temperature boiling which provides a better match between the heat source temperature and the working fluid temperature in the boiler

Mixed Working Fluid

Ammonia/Water working fluid allows

- Use of a conventional steam turbine
- Turbine exhaust to partially evaporate the working fluid

Thermophysical properties will allow additional research in:

- Condenser design
- Mixture ratios

APPENDIX H.

A. ZALTASH: PROPERTY NEEDS FOR ABSORPTION SYSTEMS

Hi-Cool and GAX Programs
March 1, 1996

Ammonia-Water Property Databases

MEETING OBJECTIVE

- ► Arrive at a consensus regarding the most appropriate "benchmark" property database for ammonia/water
- ► "Benchmark" property database shall be used for simulations of preferred Hi-Cool cycles

Early Experimental Data:

Perman (1901); Mollier (1908); Wilson (1925); Wucherer (1932); Clifford and Hunter (1933); Pierre (1959); Macriss et al. (1964); Jennings (1965).

P-T-x-y, specific volume, liquid and vapor enthalpies in the saturated range.

Pressures: 10 -- 2500 kPa (1.45 -- 362 psia)
Temperatures: -71 -- 177°C (-96 -- 350 °F)

Early Correlations:

Jennings and Shannon (1938): Tables based on Wucherer's (1932) data

Scatchard et al. (1947): Tables based on Perman's (1901) and Wucherer's (1932) data

Macriss et al. (1964): Tables based on Scatchard et al. (1947) tables, adding Pierre's (1959) and own measurements

Jain and Gable (1971): Polynomial formulas based on Macriss et al. (1964) tables

Jennings (1981): Tables based on all the above data, referenced in ASHRAE

Early Correlations (Cont'd):

Schultz (1971): First thermodynamic correlation. Equation of state for the Gibbs free energy of liquid and vapor

Ziegler and Trepp (1984): Extension of the range of Schultz's (1971) work

Also proprietary correlation by Electrolux (Reistad, 1970)

Saturated range covered
Correlations extrapolated from measurements
Pressures: 1 -- 5000 kPa (0.145 -- 725 psia)
Temperatures: -73 -- 230 °C (-99 -- 446 °F)

Statement Characterizing the Early Correlations

"There is still no clear answer as to whether aqua-ammonia data should be presented in graphical or in tabular form. A graphical presentation can give a picture of the whole liquid-vapor spectrum of saturated water-ammonia but the numerical range required on one chart is so great that it is impossible to read values with suitable accuracy even when using a high-power reading glass. Moreover, determination of values of the vapor in equilibrium with the boiling liquid can only be found by graphical alignment and seldom can be read with sufficient accuracy for the purposes desired."

B. H. Jennings, Presidential Member ASHRAE, 1981

Recent Experimental Data:

Gillespie et al.(Wiltec) (1985) ; Guillevic et al. (1985); Rizvi and Heidemann (1987); Sassen et al (1990); Zimmermann (1991)

P-T-x-y, specific volume, liquid and vapor enthalpies in the saturated range, up to the critical region.

Pressures up to 22,000 kPa (2900 psia)
Temperatures up to 345 °C (653 °F)

Recent Correlations:

Ibrahim and Klein (1993): Extension of the range of Ziegler and Trepp's (1984) work, using the same Gibbs free energy method, to include the new data of Gillespie et al. (1985) at higher temperatures and pressures. Range covered includes saturated and superheated, pressures 20 to 11,000 kPa (2.9 to 1595 psia), temperatures -43°C to 327°C (-45°F to 621°F)

IIR Bulletin (1994): Tables based on extension of IGT Bulletin 34 by Macriss et al.(1964) plus new high-temperature data of Gillespie et al. (1985). Saturated range covered, pressures 4 to 19,100 kPa (0.6 to 2770 psia), temperatures -50°C to 316°C (- 58°F to 601°F)

Recent Correlations (Cont'd):

Peters (1995): Data correlation method based on calculated activity coefficients for VLE conditions from all the above experimental data plus that of Zimmermann (1991). Method provides P-T-x correlation for pressures 10 to 18,000 kPa (1.5 to 2610 psia), temperatures -50°C to 230°C (- 58°F to 446°F)

Patek and Klomfar (1995): "Simple functions for fast calculations" based on most of the above data (to be evaluated)

Hellmann and Grossman (1996): Correlation in functional form based on Ibrahim and Klein (1993) convenient for computer calculations; 20 to 11,000 kPa (2.9 to 1595 psia), -43°C to 327°C (-45°F to 621°F)

Characteristics of Recent Correlations

Based on old as well as new experimental data, obtained with improved, modern instrumentation

New data covers extended P and T range up to critical region

New data compared with and checked against old data

Correlations based on thermodynamic equations-of-state

Accurate calculations and plots using modern computers

Property-based software enables accurate cycle calculations

Differences Among Databases:

Simulation of the same GAX cycle under the same typical cooling conditions using different property data correlations shows significant differences:

Up to 5% in COP and capacity
Up to 9% in heat exchanged between absorber and generator
Up to 14% in rectifier heat duty
Also differences in calculated values of the weak and strong solutions and of the refrigerant

Main differences among various data sources and property correlations appears to be in the ammonia-rich vapor region

Criteria for evaluation of different property data sources:

(1) Origin of data, experimental method and type of instrumentation employed

(2) Range of correlation vs. range of measurements. Is there considerable extrapolation?

(3) Type of correlation: Thermodynamic vs. algebraic

(4) Is the superheated range covered? Most correlations cover only the saturated range

(5) Is software available? Accuracy? Is it highly iterative?

Property data sources employed by Hi-Cool Subcontractors

Data Source	Origin	Thermo-dynamic correlation?	Superh'td Range Covered?	Hi-Temp Range Covered?	Software Available?
IGT Bulletin 34	1964	No	No	No	0
Electrolux	1970	No	No	No	0*
Jennings	1981	No	No	No	1
Ibrahim & Klein	1993	Yes	Yes	Yes	2
IIR Bulletin	1994	Yes	No	Yes	0

* Proprietary. Easily Programmable

APPENDIX I.

KALINA CYCLE APPLICATION TO GAS TURBINE COMBINED CYCLES; R. BJORGE ET AL.

Kalina Cycle Application to Gas Turbine Combined Cycles

Robert W. Bjorge
Manager – Gas Turbine/Combined Cycle Programs

James C. Corman
General Manger – Power Generation Systems

Raub W. Smith
Manager – Combined Cycle Systems Technologies

GE Power Systems

Power-Gen Europe '96
Budapest, Hungary
June 1996

ABSTRACT

Gas turbine-based combined-cycle power plants have gained broad acceptance worldwide due to their favorable economics, high efficiency and excellent environmental performance. Combined-cycle performance improvements based on 9FA gas turbines have demonstrated net efficiencies greater than 55%. The introduction of the steam-cooled STAG 109H combined-cycle system, with its 60% net plant efficiency capability, is the latest step in this trend. These plants typically use high-efficiency steam bottoming cycles, with the current state-of-the-art being a three-pressure reheat cycle. The Kalina Cycle, using a mixture of ammonia and water as the working fluid, promises additional improvements in combined-cycle efficiency through dramatic changes in the bottoming cycle. These changes make possible non-isothermal heat acquisition and heat rejection, as well as internal heat recuperation, which reduce losses of thermodynamic availability (exergy).

This paper presents results of studies on the application of the Kalina Cycle to gas turbine-based combined cycles, including system design and performance characteristics, and compares the Kalina Cycle's performance and economics with those of a state-of-the-art conventional steam bottoming cycle. Several variants of the Kalina Cycle overall system design and the Distillation Condensation Subsystem (DCSS), which replaces the condenser as the heat rejection and recuperation system of the Kalina Cycle, were studied. Results show that the Kalina Cycle can increase the net bottoming cycle power output of a STAG 207FA system by approximately 13%, with no increase in fuel consumption, when compared with a three-pressure reheat Rankine bottoming cycle. This corresponds to an increase in overall combined-cycle efficiency of approximately 2.5 percentage points, a significant improvement over state-of-the-art systems with steam bottoming cycles. GE and Exergy, Inc. have agreed to pursue the commercialization of Kalina Cycles for combined-cycle applications on a worldwide exclusive license basis. Plans and objectives for the next phase in this process, a commercial-scale demonstration project, are reviewed.

INTRODUCTION

The worldwide market for gas turbine combined-cycle power generation equipment has expanded significantly in recent years. The availability of clean, plentiful natural gas fuel supplies has caused a significant shift to combined cycles as a preferred power generation technology. This trend has also been accelerated by ongoing improvements in combined-cycle system efficiency. Combined-cycle plants, using 7FA and 9FA gas turbines and conventional steam bottoming cycles, are operating today with net efficiencies over 55%. GE's H technology combined-cycle systems, including the STAG 109H designed for 50 Hz markets, make possible power plants using steam bottoming cycles with net efficiencies of 60% [1]. Forecasts indicate that gas turbine combined-cycle power generation will continue to be the system of choice, with more than 260 gigawatts of combined-cycle capacity projected to be ordered worldwide in the next 10 years.

Improvements in combined-cycle efficiency to date have been paced primarily by gas turbine advances. This was facilitated by the transfer of advanced materials and cooling technology from aircraft engine applications to large heavy-duty gas turbines, and the resulting ability to increase firing temperatures. Compressor technology has also advanced, leading to units with increased airflow and pressure ratio capability. These advances in gas turbine technology have improved both the fuel efficiency and economies of scale of combined-cycle systems.

Along with gas turbine technology advances, significant improvements have been made in conventional steam bottoming cycle system technology. These include:

- Multiple pressure level heat recovery steam generators

- Reheat steam cycles
- Fuel gas preheating
- 3D steam turbine aerodynamic design of vanes and exhaust hoods
- Integrated steam-cooled gas turbine/combined-cycle systems – "H" technology

The application of the Kalina Cycle makes possible another major step in overall combined-cycle system efficiency, ranging from approximately 2.5 percentage points with the large F and H technology gas turbines to approximately 4 points with low exhaust temperature aeroderivative gas turbines such as the LM6000, when compared with high-efficiency steam bottoming cycles typically applied today.

Simplified schematics of conventional steam and Kalina Cycle mixed working fluid combined-cycle systems are shown in Figure 1. In conventional combined-cycle systems, the steam bottoming cycle uses the gas turbine exhaust energy to produce steam to be expanded in a steam turbine and then condensed. In a Kalina Cycle system, the gas turbine exhaust energy is used to vaporize an ammonia-water (or other) working fluid mixture, which is then expanded through a vapor turbine and absorbed and condensed after the injection of an ammonia-lean stream.

The key features of the Kalina Cycle which improve its combined-cycle efficiency are its ability to exchange energy from the topping cycle to the bottoming cycle in a non-isothermal manner and to reject heat from the bottoming cycle to the heat sink in a similar non-isothermal manner. Figure 2 shows a comparison of the HRSG exhaust gas and bottoming cycle working fluid temperature profiles for single-pressure non-reheat steam and Kalina bottoming cycle systems. Temperature differences between the exhaust gas and the bottoming cycle working fluid create losses in thermodynamic availability, or exergy, and reduce the power generation potential of the system. The Kalina Cycle significantly reduces these losses. The distillation-condensation subsystem (DCSS) similarly reduces losses in the heat rejection portion of the cycle.

The development of the Kalina Cycle moved from theory to practice with Exergy's successful operation of a 3 MW unit at Canoga Park in California (Figure 3). In addition to fulfilling all performance expectations, the Canoga Park pilot plant has confirmed excellent system operability characteristics, comparable with those expected of a conventional steam combined-cycle system [2, 3].

THERMODYNAMIC COMPARISON – RANKINE vs KALINA

Rankine Cycles

The conventional steam bottoming cycles applied today in combined-cycle systems are known as steam Rankine cycles. Exergy[1] losses in steam Rankine bottoming cycles are commonly reduced by generating steam at multiple pressure levels and by the addition of reheat. Figure 4 shows the heat recovery exergy profiles for single- and two-pressure non-reheat and three-pressure reheat steam systems for a STAG 207FA. These plots are derived from the heat recovery temperature profiles by weighting the temperatures based on the Carnot efficiency at each temperature relative to a common sink temperature.

Exergy losses in the heat recovery steam generator (HRSG) are proportional to the area between the exhaust gas and steam temperature profiles. Exergy losses due to the discharge of exhaust gas from the HRSG are a function of stack temperature. The power outputs of these cycles are proportional

---

[1] Exergy – A measure of how much power could be extracted from a heat source (such as gas turbine exhaust) at Carnot efficiency. Exergetic efficiency is a figure of merit for a cycle relative to its maximum theoretical efficiency (i.e., 100% exergetic efficiency = Carnot efficiency).

tional to the exergy recovered in the HRSG and made available to the steam turbine. Employing multiple pressure levels makes it possible to more closely match the exhaust gas temperature profile in the HRSG, thereby reducing exergy losses. As additional pressure levels and/or reheat (or even supercritical cycle designs) are employed, the performance benefits become incrementally smaller, while cost and complexity increase [4]. The two-pressure non-reheat and three- pressure reheat bottoming cycles are most frequently seen today in large combined-cycle installations – the latter being applied when fuel costs demand the most efficient power generation systems available.

The key reason that multiple steam generation pressure levels must be employed to improve steam Rankine bottoming cycle efficiency is the limitation imposed by the properties of the working fluid. The highest exergetic efficiency attained for steam Rankine cycles in combined-cycle applications is about 70%.

Kalina Cycles

The ideal HRSG heat exchanger configuration in which the exhaust gas and bottoming cycle working fluid temperature profiles are parallel cannot be achieved with a single component working fluid such as water, because all evaporation must take place at constant temperature. The Kalina Cycle systems reduce exergy losses by tailoring the working fluid properties as required at each point within the cycle. This goal is achieved by using a mixture of two fluids and by varying the mixture composition. Although several fluids are available for this purpose, the mixture of ammonia and water has emerged as the most versatile, economic and commercially proven mixture.

Shown in Figure 5 is a heat recovery exergy plot for the Kalina Cycle system of Figure 1 as applied to a STAG 207FA. This plot illustrates the non-isothermal evaporation of the ammonia-water mixture. This provides direct benefits in both decreased exergy losses and increased bottoming cycle output. This is the same Kalina Cycle system arrangement as was demonstrated at Canoga Park.

Although significant improvements can be achieved, as shown in Figure 5, regions of high exergy loss are still present. Two additional improvements are employed in the more advanced Kalina Cycle shown in Figure 6 [5]. These are the addition of reheat and the use of a regenerative evaporator to accomplish a portion of the evaporative duty outside the heat recovery vapor generator (HRVG). These improvements make it possible to achieve significantly higher cycle efficiencies than are achievable using three-pressure reheat steam Rankine bottoming cycles.

The improvements in the Kalina Cycle configuration of Figure 6 address the consequences of the non-linear ammonia-water mixture temperature profile in the HRVG. The steeper slope of the ammonia-water mixture in the superheat sections of the HRVG can be flattened out and made more parallel to the exhaust gas by increasing the working fluid flow in this portion of the boiler. This is partially realized by the addition of reheat to the cycle. This adds about 4% to the Kalina bottoming cycle output. The regenerative boiler contributes further to the reduction of cycle exergy losses. Diverting a fraction of preheated (but still subcooled) working fluid from the HRVG improves the temperature match for evaporation in the HRVG. The diverted flow is routed to a regenerative evaporator which boils this fraction of the working fluid prior to re-admission to the HRVG for superheating. The net result is increased evaporation of working fluid, which further reduces superheater and economizer exergy losses. By properly balancing the flows, and selecting the reheat and regenerative boiler operating pressures and working fluid composition, it is possible to achieve very nearly optimum (i.e. parallel) heat transfer profiles throughout the heat recovery system. Shown in Figure 7 is the heat recovery exergy profile for the Kalina Cycle system of Figure 6.

The Kalina Cycle system of Figure 6 achieves optimum performance with a working fluid composition through the heat recovery boiler and turbines of 80% to 85% ammonia and 15% to 20% water. The temperature necessary to directly condense the working fluid would be -6 C (22 F) at the conditions existing at the exhaust of the LP turbine, which is clearly impractical. Instead, the DCSS, shown in Figure 8, is used to condense and regenerate the working fluid in three stages. This process involves partial condensation and subsequent dilution of the vapor turbine exhaust to a fully condensible composition. The lean (basic) solution from the first (low-pressure) condenser is pumped to a higher pressure, heated regeneratively against the condensing turbine exhaust and separated into ammonia rich vapor and the lean liquid necessary to dilute and condense the turbine exhaust. Two additional distillation condensation steps are necessary to regenerate the original working fluid composition as a liquid suitable for return to the HRVG for heating. The use of an ammonia-water mixture allows selection of a working fluid composition which results in a LP turbine exhaust pressure above atmospheric at all operating conditions. This reduces the size (and attendant cost) of the low-pressure turbine and simplifies other aspects of the system.

PERFORMANCE

The Kalina Cycle can be applied as a bottoming cycle with the full range of GE gas turbines. Performance has been estimated using GE turbine efficiency correlations and heat balance software developed by Exergy. The Kalina Cycle results were weighed against high-efficiency GE steam Rankine cycle systems for comparability and accuracy.

Comparisons were made for a number of combined-cycle configurations, ranging from a single LM6000 to the largest F technology units. The greatest expected efficiency improvement – approximately 4 percentage points – comes with the aeroderivative LM6000, which is typically applied with a two-pressure non-reheat cycle due to its low gas turbine exhaust temperature. The efficiency improvement with the 7FA and 9FA-based combined cycles is approximately 2.5 percentage points compared with a high-efficiency three pressure reheat cycle.

Table 1 shows the estimated performance of the STAG 207FA Kalina Cycle system of Figure 7, compared with the two most common conventional steam Rankine cycle systems (two-pressure non-reheat and three-pressure reheat). In addition to its higher net design efficiency (58.46% vs. 55.89%), the Kalina Cycle produces an additional 23.6 MW of net power output compared with the optimized three-pressure reheat Rankine cycle system. This increase in output is obtained at the cost of increased HRVG (vs HRSG) surface area, as shown in Table 1, plus the addition of the DCSS in lieu of a condenser. HRSG/HRVG characteristics are also shown in Table 1.

Comparable efficiency improvements, and scaled-up output improvements, would be expected with a STAG 109FA. Estimates of these values are shown in Table 2. (These performance comparisons are based on a wet cooling tower application, with an ambient air temperature of 15 C (59 F) and with other boundary conditions, auxiliary loads and component design efficiency correlations kept the same. Expected efficiency gains with direct seawater cooling would be approximately one-half point lower, as the opportunity to cross-optimize the DCSS and cooling tower is not available.)

Exergy losses in the STAG 207FA three-pressure reheat Rankine bottoming cycle and the Kalina Cycle system of Figure 6 were computed using the heat balance calculations supporting the performance estimates shown in Table 1. The resulting comparison is shown in Figure 9. The reduction in exergy losses of 23.6 MW with the Kalina Cycle system translates directly into the increased net power output shown in Table 1.

It is evident from Figure 9 that the exergy losses in the heat recovery process are greatly reduced in the Kalina cycle. However, the exergy losses in the turbine expansion process are also significantly reduced. To understand why, it is important to note the difference between turbine exergetical efficiency and isentropic expansion efficiency.

The exergetical efficiency of a turbine considers only losses due to exergy destruction in the turbine, while the isentropic efficiency of a turbine considers both exergy destruction in the turbine and the exergy contained in the turbine exhaust stream. If the turbine exhaust exergy is not utilized or recuperated by downstream equipment, then its availability to do work is in fact lost and the exergetical efficiency of the turbine in such a system equals its isentropic efficiency. For example, the high-pressure turbine in a reheat Rankine cycle has a higher exergetical efficiency than isentropic efficiency because an increase in its exhaust exergy reduces the reheater heat duty, thereby increasing the exergy available for steam generation in the HRSG. However, unconverted energy from the intermediate/low pressure (reheat) turbine is irreversibly lost in the condenser of a Rankine cycle.

In the Kalina Cycle, not only the high-pressure turbine but all of the turbines receive the benefit of downstream recuperation. The high-pressure turbine is followed by the reheater (as in the Rankine cycle), the intermediate-pressure (reheat) turbine is followed by the regenerative evaporator, and the low-pressure turbine is followed by the DCSS (a recuperative subsystem).

ECONOMIC CHARACTERISTICS

An economic evaluation of the Kalina Cycle vs. the conventional steam Rankine cycle involves an assessment of the three principal elements of life-cycle cost: capital cost, fuel cost and operation and maintenance costs. Evaluations to date have focused primarily on the largest two, that is, capital cost and fuel cost. Operation and maintenance costs have been assumed constant. While the Kalina Cycle uses ammonia and has additional heat exchanger equipment, it also has a simpler HRVG and vapor turbine, no need for water treatment facilities and no vacuum systems. The net effect may actually be to reduce operation and maintenance costs of Kalina Cycle plants below those of conventional plants.

Figure 10 shows the results of an economic evaluation of the STAG 207FA Kalina Cycle system. The economic benefit of improved efficiency for the Kalina Cycle (in $/kW) is plotted vs. operating hours per year for three values of fuel cost [in $/MMBtu ($/GJ)]. The following additional economic assumptions were used in the analysis:

Discount rate	10%
Number of years	20
Fixed charge rate	18%
Fuel cost escalation	4%

As Figure 10 demonstrates, the improvement in combined-cycle efficiency alone over an economic evaluation period of only 20 years can be translated into an equivalent total combined-cycle plant capital cost value in the $30/kW to $90/kW range.

Efficiency is not the only factor, however. When the value of the additional power output is also considered, the value is even further enhanced. Shown in Figure 11 is the total value in incremental $/kW of the increased output and efficiency of the Kalina Cycle above the Rankine cycle for a range of operating hours and fuel price scenarios. The benefit is the sum of the value of the incremental power output (modeled here at a typical value of $500/kW) together with the value of efficiency, since the incremental power output is produced with no incremental operating cost.

The capital cost of a Kalina Cycle combined-cycle plant using a given gas turbine will be higher than that of the comparable Rankine cycle plant, due to the increased equipment required by the Kalina Cycle. However, this cost can be more than offset by the value of the Kalina Cycle's increased output and efficiency. For example, assume that the incremental cost of the STAG 207FA Kalina Cycle system is $1100/kW for its incremental output of 23.6 MW above a three-pressure reheat Rankine cycle system. With a fuel cost of $4/MMBtu ($4.22/GJ) and 4% escalation, the Kalina Cycle would be the economic choice when operation longer than 3500 hours per year is anticipated. The sensitivity of the selection of a Kalina Cycle vs Rankine cycle system to the Kalina Cycle's incremental output, efficiency and cost, as well as fuel costs, can be readily assessed.

KEY TECHNOLOGIES

Technology areas important to the application of the Kalina Cycle include heat exchanger design, materials compatibility, working fluid properties and system operability and safety.

The nearly ideal heat exchange relationship attained in the Kalina Cycle creates an increased incentive to minimize heat exchanger temperature differences. A conventional Rankine bottoming cycle reaches a point of diminishing returns as HRSG surface is increased due to the evaporator pinch points. In contrast, the Kalina bottoming cycle rewards increases in heat exchanger surface area with a nearly linear reduction of exergy losses and, hence, increased power output. This thermodynamic characteristic of the cycle, in combination with the heat exchangers necessary in the DCSS, creates a strong relationship between heat exchanger sizing and system economics.

Heat transfer testing has been performed at the Kalina Cycle pilot plant facility at Canoga Park to reduce uncertainty in this area. The data has now been analyzed to provide an understanding of the heat transfer characteristics of the NH_3/H_2O working fluid in all regimes.

Materials compatibility in the NH_3/H_2O working fluid is another area of primary interest. Results to date from the pilot plant have not shown any nitriding of turbine or HRVG materials. Further testing will be undertaken to confirm this finding and identify optimal materials for use throughout the cycle. This is a straightforward materials qualification and material selection process and is not seen as a technical barrier for the cycle. In the low temperature areas, such as the DCSS, carbon steel will be used. This is consistent with over a century of ammonia absorption refrigeration experience. Certain materials are clearly not appropriate for use with the NH_3/H_2O working fluid. These include copper anywhere in the cycle. Also, materials catalytic with respect to ammonia decomposition in high temperature regions such as hastelloy, low nickel iron alloys, and alloys with cobalt would not be employed.

A related issue is the rate of ammonia decomposition. Data from the pilot plant show very low rates of ammonia decomposition at a working fluid composition of 70% NH_3 and 30% H_2O. The higher operating temperatures and richer working fluid composition of a commercial plant will increase the decomposition rate somewhat, but not to a level that adversely impacts performance (due to buildup of non-condensibles) or economics (as related to ammonia makeup needs).

Proper design, operation and maintenance of Kalina Cycle power plants from a safety standpoint is particularly important due to the use of the ammonia-water working fluid mixture [6]. Fortunately, there is an extensive experience database to draw on from the process industries, including ammonia synthesis plants, ammonia absorption refrigeration systems and handling and distribution of ammonia as a fertilizer and feedstock. Power plants have used ammonia for decades to control working fluid pH, and more recently for boiler and gas turbine emission control systems and gas turbine inlet air chillers.

Ammonia, though classified as a hazardous substance, has a number of favorable characteristics. Due to its strong, distinctive odor, the presence of ammonia is easily detected at well below harmful concentrations. Though potentially flammable, ammonia is very difficult to ignite. Ammonia is rendered harmless when diluted sufficiently with water. Pure or anhydrous ammonia is gaseous at atmospheric pressure and is lighter than air. If released to the environment, it readily combines with water and carbon dioxide to form non-harmful compounds.

Industry experience has resulted in a maturation of standards responsible for plant safety. These standards have a proven track record in ensuring safe and environmentally responsible plant design, operation and maintenance.

COMMERCIALIZATION OBJECTIVES

Market evaluations show the greatest potential for Kalina Cycle combined-cycle systems to be in those applications which today demand the most efficient plants available. A number of combined-cycle plants have been built to date and others are underway in this market segment using F technology gas turbine units with high-efficiency steam bottoming cycles.

GE has a worldwide exclusive licensing agreement with Exergy, Inc. to develop and market the Kalina Cycle technology for combined-cycle applications. GE is presently in the process of identifying a site for a commercial-scale plant to demonstrate the technology. The demonstration plant is being targeted at the 40-140 megawatt (combined cycle) size range, and its objective will be to confirm the life-cycle cost, performance and operational characteristics of the Kalina Cycle technology, and to provide a further foundation for commercialization.

In parallel with the demonstration plant efforts, GE and Exergy are actively exploring additional opportunities for commercial projects with Kalina Cycle combined-cycle systems where high efficiency is of particular importance.

CONCLUSIONS

The Kalina Cycle has been shown to have attractive potential as a bottoming cycle in gas turbine-based combined-cycle applications, in terms of both higher efficiency and reduced operating cost compared with conventional steam cycles. Technology developments and commercialization initiatives are underway with the objective of exploiting this potential as a key element in enhancing the position of combined cycles as the most efficient and cost-effective power generation system available today.

ACKNOWLEDGMENTS

The authors wish to thank Exergy, Inc., and especially Dr. Alexander Kalina, for his continuing support of our efforts, Mr. Robert Fisk of GE Power Systems for his contribution to the economic evaluation, Mr. Bijan Davari of GE Power Systems for his assistance with the exergy analysis, and Prof. Philippe Mathieu for his comments and suggestions.

REFERENCES

[1] Tomlinson, L. and C. Maslak, "Advanced Technology Combined Cycle," Power-Gen Americas '95, Anaheim, pp. 277-300.

[2] Marston, C., "Development of the Adjustable Proportion Fluid Mixture Cycle," Mechanical Engineering, September 1992, pp. 76-81.

[3] Leibowitz, H., "Operating Experience on the 3 MW Kalina Cycle Demonstration Plant," Proceedings of the American Power Conference, Chicago, 1993.

[4] Dechamps, P., Magain, D. and Ph. Mathieu, "Advanced Combined Cycle Alternatives with Advanced Gas Turbines," ASME Cogen-Turbo Expo '93, Bournemouth.

[5] Kalina, A., Leibowitz, H., Markus, D. and R. Pelletier, "Further Technical Aspects and Economics of a Utility-Size Kalina Bottoming Cycle," ASME Gas Turbine and Aeroengine Congress, Orlando, 1991.

[6] Mlcak, H.A., "Understanding the Kalina Cycle Fundamentals - The Users Perspective," Proceedings of the American Power Conference, Chicago, 1995.

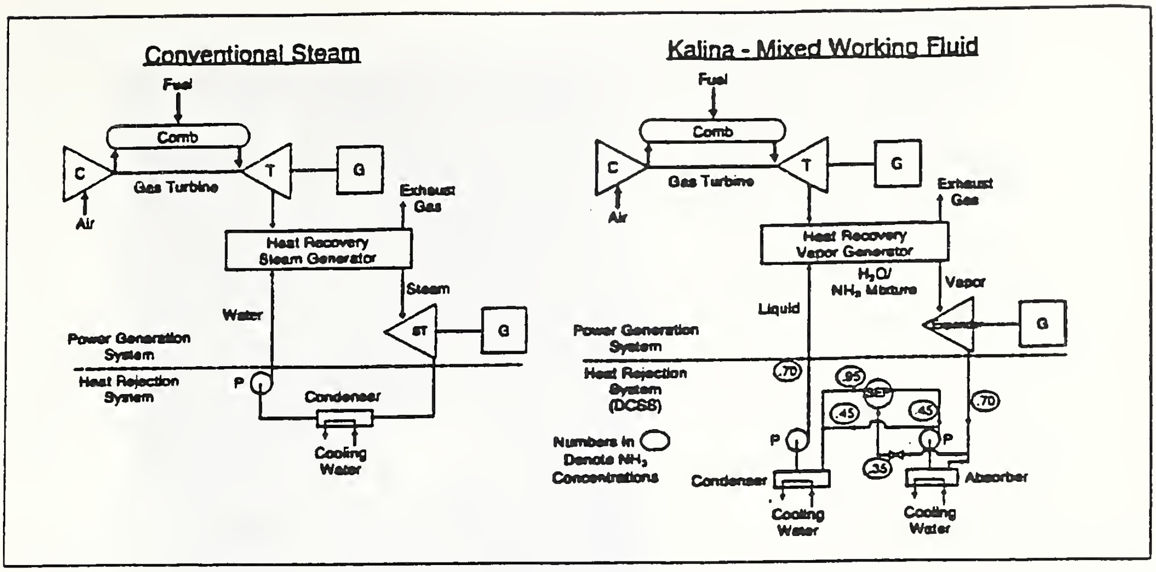


Figure 1. Conventional Steam and Kalina Combined-Cycle Systems

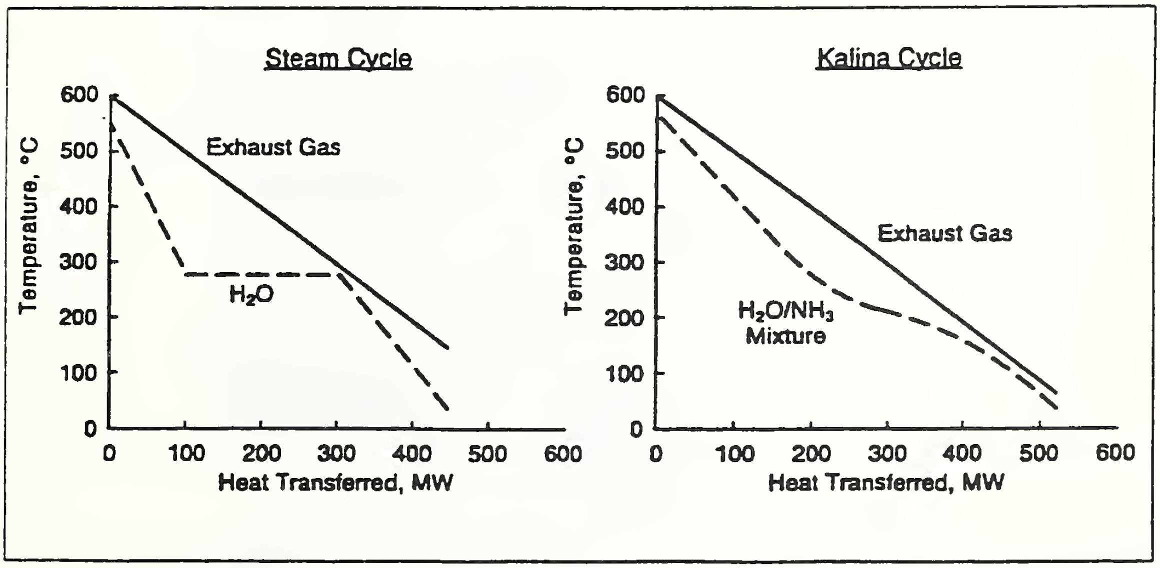
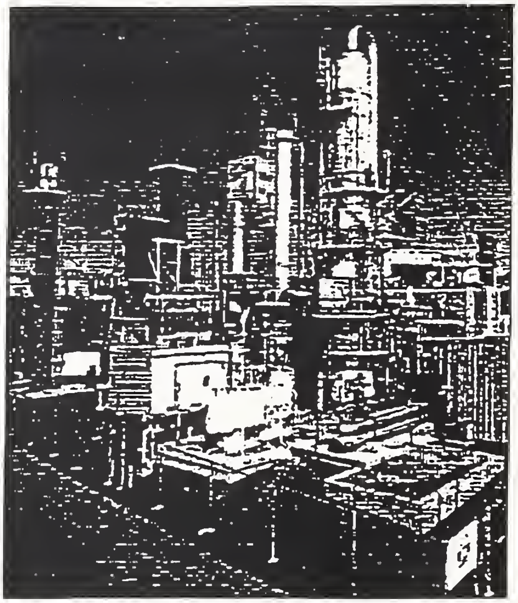
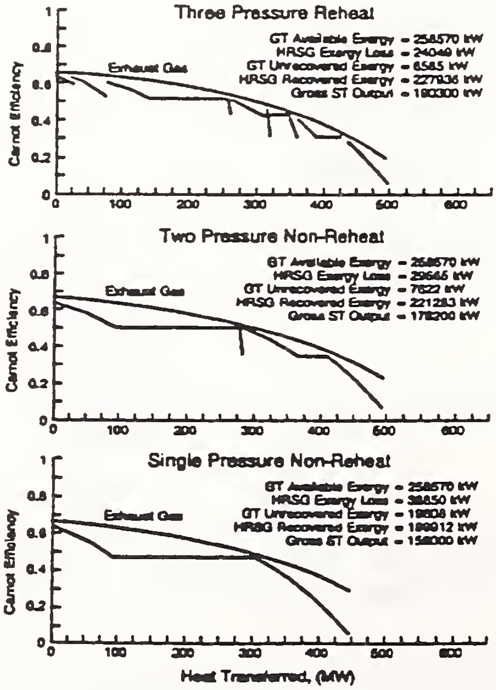


Figure 2. HRSG Temperature Profiles – Conventional Steam Cycle and Kalina Cycle



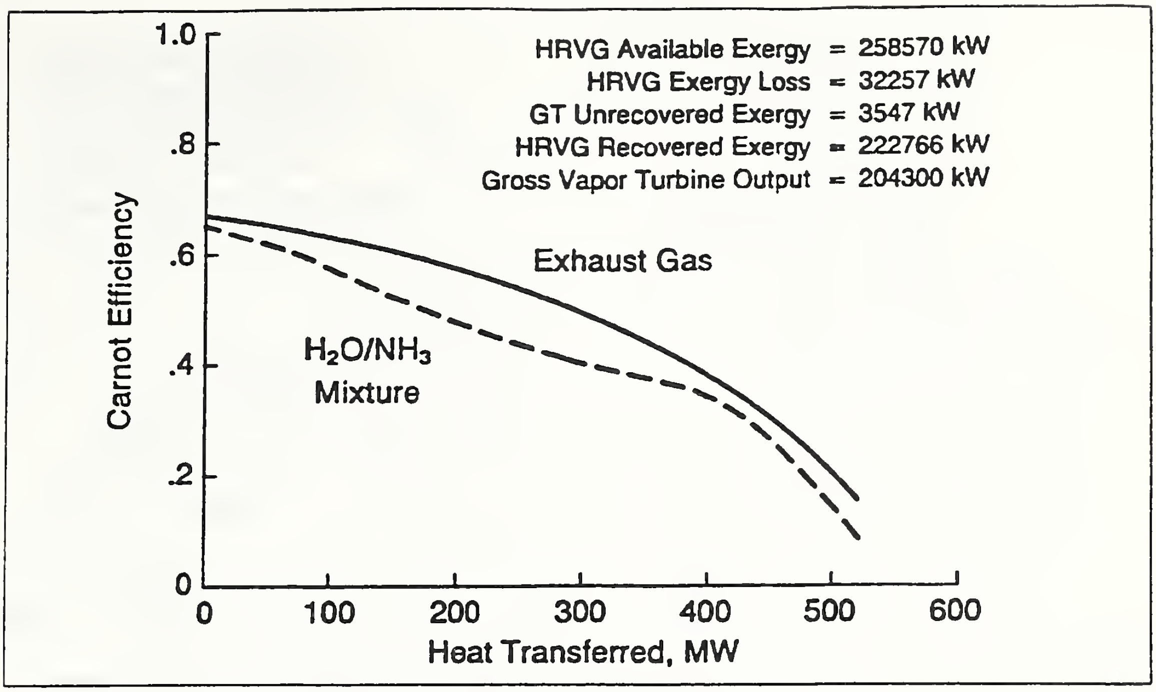
GT24403

Figure 3. Exergy Pilot Plant at Canoga Park



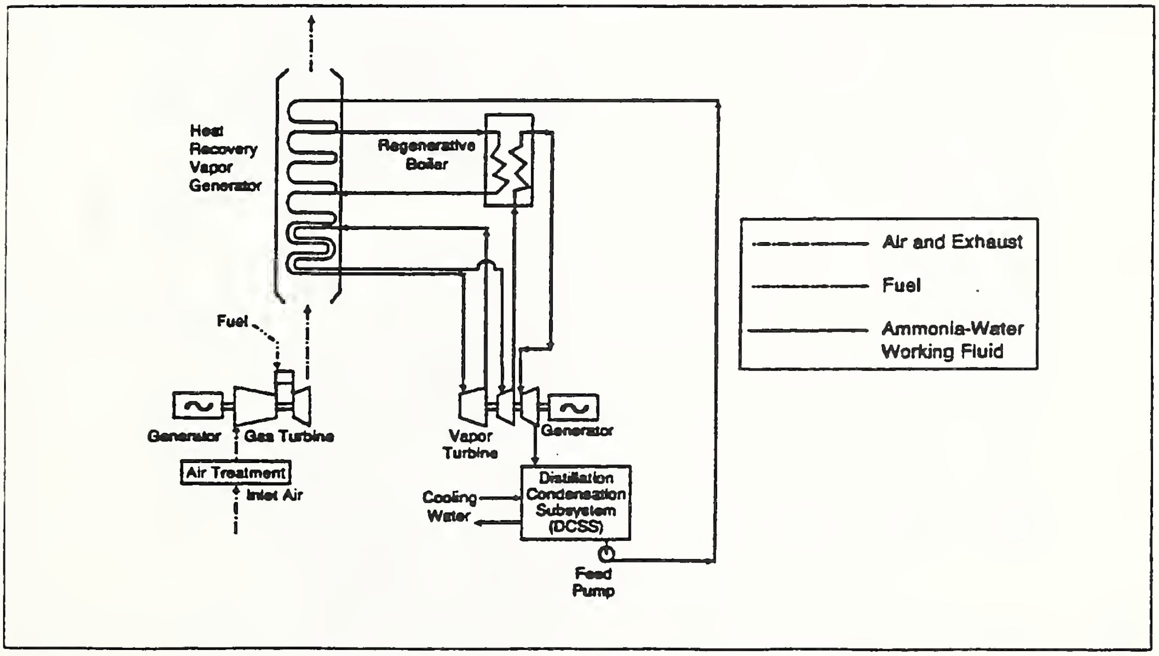
GT24411A

Figure 4. Rankine Bottoming Cycle Heat Recovery Exergy Profiles (STAG 207FA)



GT24412A

Figure 5. Kalina System 1 – Heat Recovery Exergy Profile



GT24432

Figure 6. Advanced Kalina Combined Cycle

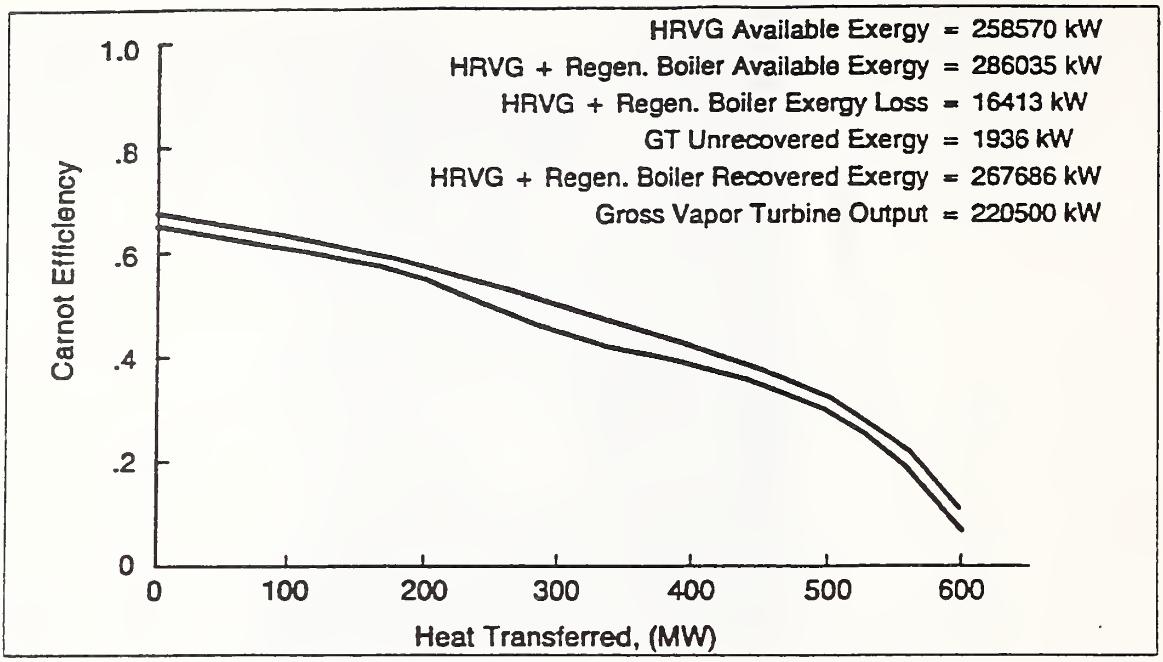


Figure 7. Kalina System 6 – Heat Recovery Exergy Profile

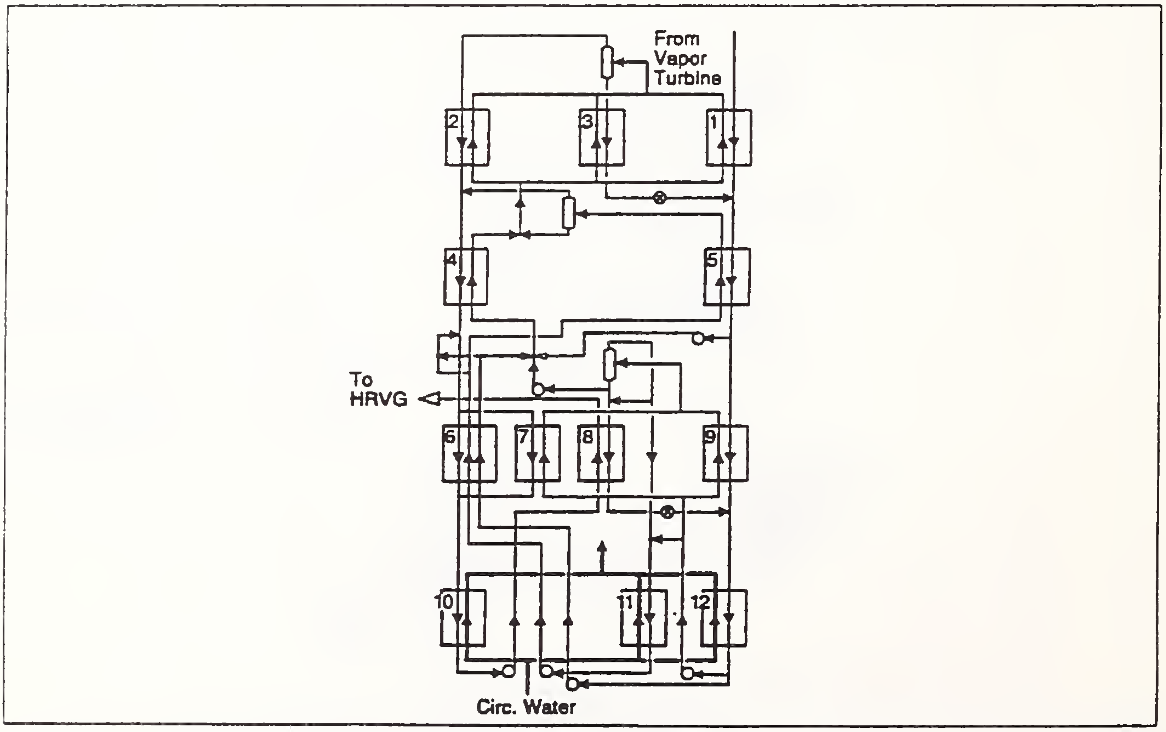


Figure 8. Kalina Cycle, Distillation Condensation Subsystem 4g

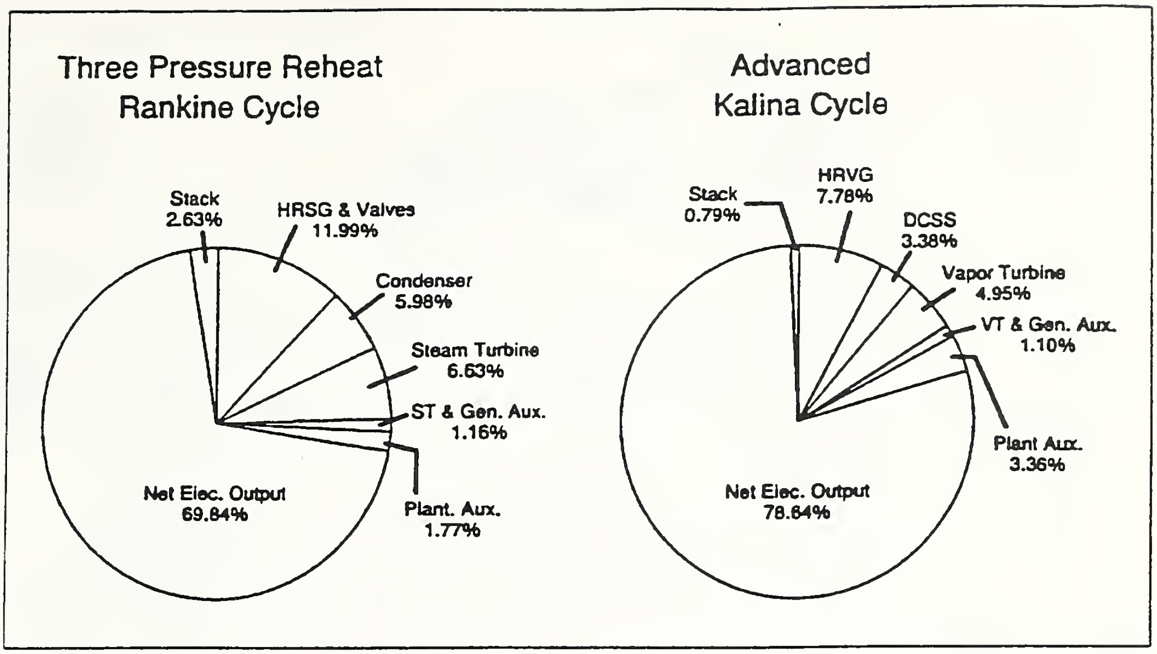


Figure 9. Bottoming Cycle Exergy Loss Analysis

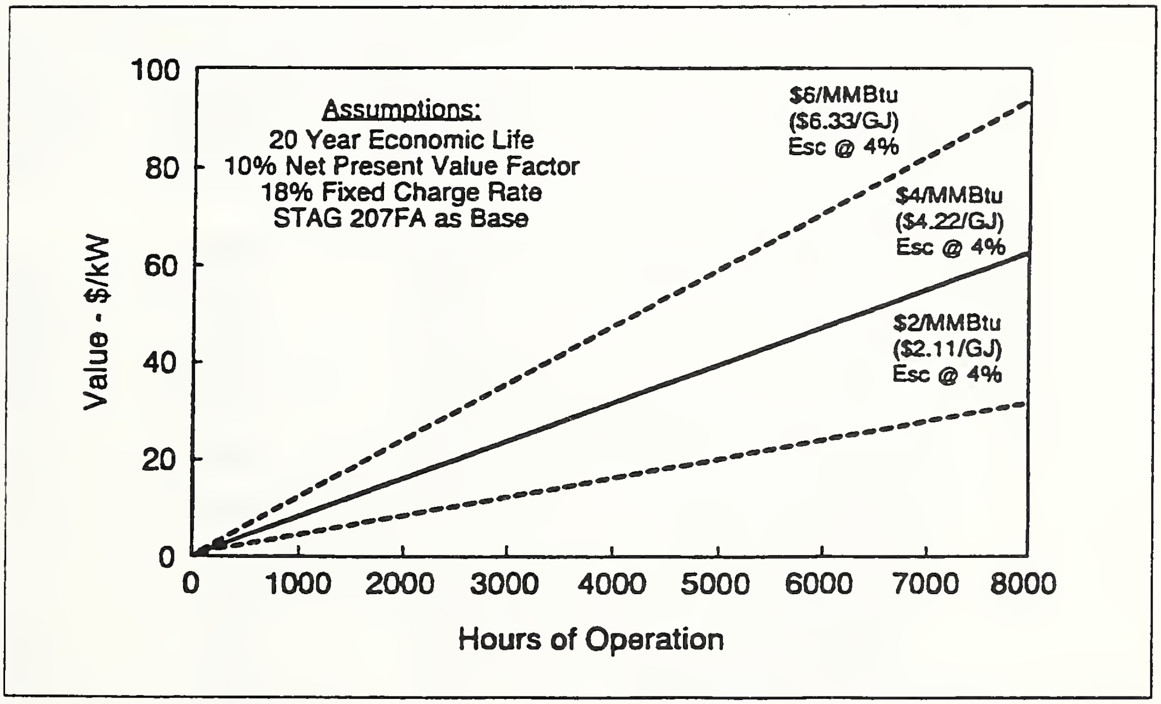


Figure 10. Value of Kalina Cycle Efficiency Advantage

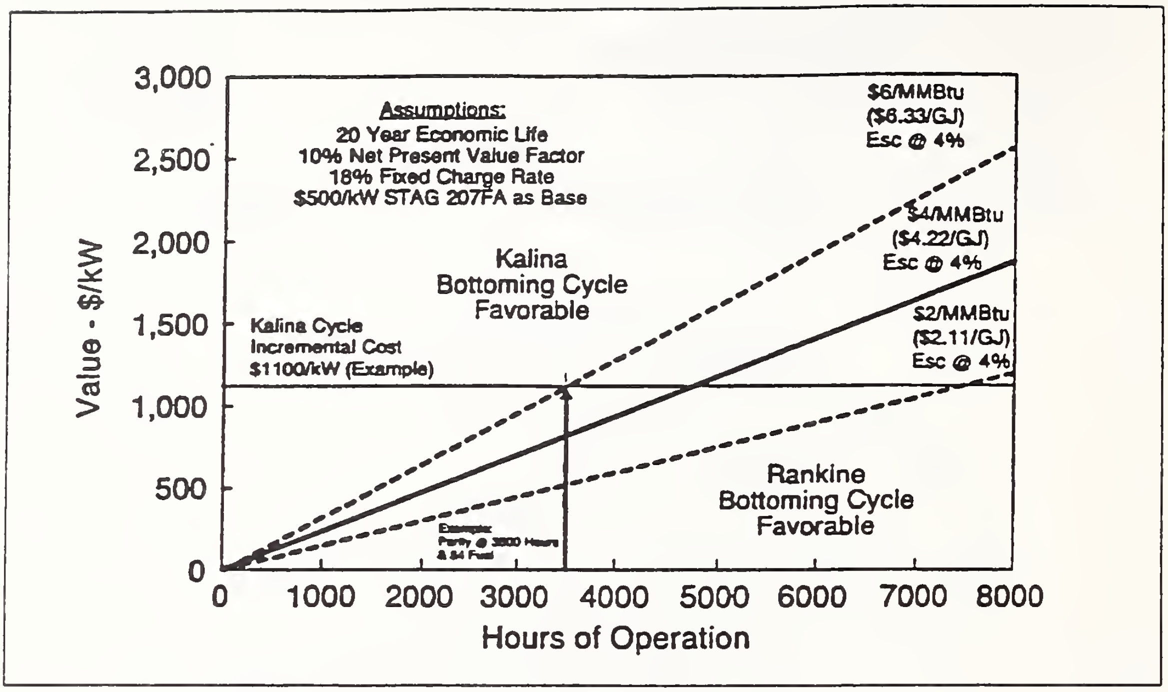


Figure 11. Combined Value of Kalina Cycle Output and Efficiency

	Rankine		Kalina
	Two-Pressure Non-Reheat	Three-Pressure Reheat	System 6/ DCSS 4g
Heat Cons., GJ/hr (LHV)	3294.7	3294.7	3294.7
Power, MW			
Gas Turbine	329.4	329.4	329.4
Steam/Vapor Turbine	178.2	190.3	220.5
Gross	507.6	519.7	549.9
Auxiliaries	7.4	8.8	15.4
Net	500.2	510.9	534.5
Net Heat Rate, kJ/kWh (LHV)	6587	6449	6164
Net Efficiency, % (LHV)	54.65	55.82	58.40
HRSG/HRVG Basis			
Pinch, C	8.3	8.3	10
Subcooling, C	5.6	5.6	NA
Approach, C	31.7	31.7	31.7
Relative Surface Area	1.0	1.14	1.83

GT24438A

Table 1. STAG 207FA Performance Comparison (ISO)

	Rankine		Kalina
	Two-Pressure Non-Reheat	Three-Pressure Reheat	System 6/ DCSS 4g
Heat Cons., GJ/hr (LHV)	2344.9	2344.9	2344.9
Power, MW			
Gas Turbine	231.8	231.8	231.8
Steam/Vapor Turbine	128.4	137.1	158.8
Gross	360.2	368.9	390.6
Auxiliaries	5.4	6.4	11.1
Net	354.8	362.5	379.5
Net Heat Rate, kJ/kWh (LHV)	6609	6469	6178
Net Efficiency, % (LHV)	54.47	55.65	58.27

GT25415

Table 2. Estimated STAG 109FA Performance Comparison (ISO)

APPENDIX J.

D. FRIEND: STATUS OF DATA AND MODELS FOR AMMONIA/WATER MIXTURES

Status of Data and Models for Ammonia-Water Mixtures

Daniel G. Friend

National Institute of Standards and Technology
Physical and Chemical Properties Division
Boulder, Colorado

Collaborators:

Jim Rainwater, Reiner Tillner-Roth (Hannover), Marcia Huber, Amy Olson, Adam Nowarski (Krakow), Jim Wardell, Sergei Kiselev (Moscow)

Workshop on *Thermophysical Properties of Ammonia/Water Mixtures*

Boulder, Co June 26,1996

Components of NH_3-H_2O Project

- Bibliographic effort
- Data evaluation
- Selected experimental data acquisition
- Model development
- Optimization

DATA EVALUATION and STANDARD REFERENCE DATA

- Fluid purity / mixture composition
- Experimental technique
- Independent variables: uncertainty and traceability to standards
- Calibrations & model-dependent corrections
- Availability of raw data
- Uncertainty of experimental data:
    - experimentalist's assessment
    - precision by replication
    - intercomparisons with other data sets
- Bibliographic research
    - worldwide archival literature
    - theses
    - laboratory records / personal contacts
- Theoretical components
    - multiple properties

Bibliographic Efforts on Ammonia-Water Mixtures

NBS Special Publication 718 (1986)
by B.R. Staples *et al.*

Absorption Fluids Data Survey: Final Report on Worldwide Data (1988, 1989)by R.A. Macriss et al. (ORNL, Institute of Gas Technology)

Standard Thermophysical Properties of the Ammonia Water Binary Fluid (1995) by D.G. Friend, A.L. Olson, and A. Nowarski (Proc. 12th ICPWS)

Survey and Assessment of Available Measurements of Thermodynamic Properties of the Mixture (Water + Ammonia) (1996) by R. Tillner-Roth and D.G. Friend (to be published)

NIST

Ammonia-Water Property Compilations and Computer Programs

- *Thermodynamic properties -- saturated liquid and vapor of ammonia-water mixtures* by Scatchard *et al.*, J. ASRE(1947).
- *Physical and Thermodynamic Properties of Ammonia-Water Mixtures* by R.A. Macriss *et al.*, IGT Research Bulletin No. 34 (1964).
- **ASHRAE Handbook** (1993)
  Research Project No. 271-RP (TC 8.3); Data Reference: B.H. Jennings (1965).
- *Thermodynamics of Aqueous Solutions Containing Volatile Weak Electrolytes* by Edwards et al.; AIChE J (1978).
- *Equations of State for the System Ammonia-Water for Use with Computers* by S.C.G. Schultz; dissertation (1971) and IIR (1971).
- "Tables from Fluor Engineers" in **Ammonia Absorption Refrigeration in Industrial Processes** by M. Bogart (1981).
- *Equation of State for Ammonia-Water Mixtures* by Ziegler and Trepp; IJR (1984).

NIST

Ammonia-Water Property Compilations and Computer Programs (2)

- *Thermodynamic Properties of Water-Ammonia Mixtures: Theoretical Implementation for Use in Power Cycle Analysis* by El-Sayed and Tribus; ASME Trans.(1985); Exergy (1994).
- *Thermodynamic Properties of Ammonia-Water Mixtures* by Park and Sonntag; ASHRAE Trans. (1991).
- *An Effective Approach to the VLE of the Ammonia-Water System* by Nowarski and Styrylska; ENSEC (1993).
- *Thermodynamic Properties of Ammonia-Water Mixtures* by Ibrahim and Klein; ASHRAE Trans. (1993).
- *Equation of State for the NH_3-H_2O System* by Duan, Moller, and Weare; J. Sol. Chem. (1996).
- *A Helmholtz Free Energy Formulation of the Thermodynamic Properties of the Mixture (Water+Ammonia)* by Tillner-Roth; to be submitted (1996).

NIST

Pure Fluid Formulations

Water:

- NBS/NRC Steam Tables (1984)
  (Haar, Gallagher, and Kell)
- IAPWS ('95): Formulation for General and Scientific Use (Pruß and Wagner)

Ammonia:

- *Thermodynamic Properties of Ammonia* (Haar and Gallagher, JPCRD 7, 635, 1978)
- *An Assessment of the Current Status of the Thermophysical Properties of Ammonia* (Penoncello and Haugk, CATS Rpt. 94-5,1994)
- *Eine neue Fundamentalgleichung fuer Ammoniak* (Tillner-Roth, Harms-Watzenberg, and Baehr, Proc. 20th DKV (Heidelberg) p. 167, 1993).

NIST

Fixed Point Properties of H_2O and NH_3

- Water:

$T_c \approx 647.082$ K

$P_c \approx 22.055$ MPa

$\rho_c \approx 17.87$ mol·dm^{-3}

- Ammonia:

$T_c \approx 405.37$ K

$P_c \approx 11.333$ MPa

$\rho_c \approx 13.80$ mol·dm^{-3}

Experimental Data Summary

- About 5700 points, 50 references
- 1016 PTx (Bubble Points)
- 1324 PTxy
- 226 PTy (Dew Points)
- 63 Txy
- 9 $P\rho$
- 324 $\rho_{\sigma L}$
- 2022 $P\rho Tx$
- 321 $H_{\sigma L}$, H_{mix}, ΔH
- 98 C_p
- 288 T_t, P_t

TABLE 1. Summary of experimental data for {water+ammonia}

Source	Year	N	Range of data		
			T/K	p/MPa	x(NH_3)
			(p, T, x)-data (bubble point measurements)		
Carius [3]	1856	6	273 - 298	0.1	0.26 - 0.39
Foote [9]	1921	17	283 - 303	0.05 - 0.2	0.29 - 0.53
Guillevic *et al.* [12]	1985	13	403 - 503	1.3 - 7.1	0.07 - 0.7
Gillespie *et al.* [11]	1987	173	313 - 588	0.01 - 20.8	0.008 - 0.99
Jennings [20]	1965	72	297 - 490	0.05 - 3.7	0.10 - 0.79
Mittasch *et al.* [25]	1926	51	273 - 334	0.01 - 0.9	0.21 - 0.52
Mollier [26]	1908	35	274 - 393	0.1 - 0.9	0.12 - 0.52
Perman [29]	1901	77	273 - 334	0.002 - 0.24	0.04 - 0.34
Pierre[a] [32]	1959	(173)	233 - 513	0.004 - 4.8	0.05 - 0.41
Postma [34]	1920	202	196 - 480	0.001 - 17.8	0.127 - 1.0
Rizvi and Heidemann [37]	1987	36	304 - 618	0.02 - 21.9	0.007 - 0.88
Roscoe and Dittmar [38]	1859	34	273 - 327	0.002 - 0.26	0.07 - 0.69
Sassen *et al.* [40]	1990	111	389 - 613	1.3 - 21.5	0.189 - 0.8
Sims [41]	1861	16	273 - 373	0.002 - 0.28	0.06 - 0.52
			(p, T, x, y)-data		
Clifford and Hunter [5]	1933	57	333 - 420	0.02 - 1.6	0.016 - 0.26
Gillespie *et al.* [11]	1987	46	313 - 588	0.15 - 20.7	0.03 - 0.93
Guillevic *et al.* [12]	1985	5	403 - 503	4.4 - 5.7	0.09 - 0.64
Harms-Watzenberg [14]	1995	46	308 - 573	0.26 - 18.2	0.08 - 0.9
Hoshino *et al.* [16]	1975	21	240 - 363	0.101325	0.025 - 0.975
Inomata *et al.* [18]	1988	7	332	0.16 - 2.1	0.20 - 0.84
Iseli [19]	1985	44	354 - 493	3.6 - 16.1	0.47 - 0.89
Müller *et al.* [27]	1988	40	373 - 473	0.19 - 3.1	0.04 - 0.32
Neuhausen and Patrick [28]	1921	31	273 - 313	0.1 - 0.5	0.25 - 0.66
Perman [30]	1903	42	273 - 333	0.002 - 0.08	0.03 - 0.23
Polak and Lu [33]	1975	23	363 - 420	0.1 - 0.44	0.001 - 0.04
Rizvi and Heidemann [37]	1987	285	303 - 618	0.03 - 22.5	0.01 - 0.99
Smolen *et al.* [42]	1991	198	293 - 413	0.01 - 3.1	0.04 - 0.96
Wilson [48]	1925	47	273 - 363	0.003 - 1.14	0.09 - 0.85
Wucherer[b] [50]	1932	(432)	223 - 483	0.01 - 2	0.05 - 0.9

[a]: smoothed data

[b]: these data were constructed from smoothed data (see appendix A)

TABLE 1. – continued –

Source	Year	N	Range of data		
			T/K	p/MPa	x(NH_3)
(p, T, y)-data (dew-point measurements)[c]					
Guillevic *et al.* [12]	1985	21	403 - 503	0.8 - 6.7	0.195 - 0.974
Neuhausen and Patrick [28]	1921	28	273 - 313	0.14 - 0.53	>0.972
Macriss *et al.* [24]	1964	16	333 - 390	1.5 - 3.6	> 0.966
Postma [34]	1920	17	433 - 508	10 - 16	0.74 - 0.932
Rizvi and Heidemann [37]	1987	11	345 - 618	0.9 - 19.3	0.08 - 0.993
Sassen *et al.* [40]	1990	133	373 - 453	0.1 - 9.7	0.2 - 0.9
(T, x, y)-data					
Dvorak and Boublik [6]	1963	15	363.15	-	$x < 0.03$, $y < 0.3$
Hales and Drewes [13]	1979	30	276 - 297	-	$x < 0.001$
Jones [21]	1963	18	420 - 600	-	$x < 0.001$
Partial pressures					
Hougen [17]	1925	9	287 - 300	-	0.01 - 0.18
Saturated liquid densities					
Gillespie *et al.* [11]	1985	14	313 - 519	-	0.17 - 0.71
Harms-Watzenberg [14]	1995	60	243 - 413	-	0.1 - 0.9
Jennings [20]	1965	77	297 - 490	-	0.1 - 0.79
King *et al.* [23]	1930	28	293.15	-	0.005 - 0.98
Mittasch *et al.* [25]	1926	86	273 - 333	-	0.21 - 0.52
Wachsmuth [47]	1878	59	285	-	0.02 - 0.39
$(p, \overline{V}, T, x)$-data					
Carius [3]	1856	9	323 - 523	0.1	0.01 - 0.32
Ellerwald [7]	1981	323	323 - 523	0.04 - 8.3	0.08 - 0.97
Harms-Watzenberg [14]	1995	1208	243 - 413	0.8 - 38	0.1 - 0.9
Harms-Watzenberg [14]	1995	276	373 - 498	0.02 - 4.8	0.25 - 0.75
Neuhausen and Patrick [28]	1921	31	273 - 313	0.1 - 0.5	0.25 - 0.67
Staudt [43]	1984	175	298 - 403	2 - 20	0.1 - 0.9

[c]: mole fractions in column 6 are vapor mole fractions

TABLE 1. – continued –

Source	Year	N	Range of data		
			T/K	p/MPa	x(NH_3)
		Saturated liquid enthalpy			
Zinner[a] [51]	1934	(146)	203 - 453	–	0.1 - 0.9
		Enthalpy of mixing			
Baud and Gay [1]	1909	23	285	0.1	0.18 - 0.80
Staudt [43]	1984	92	298 - 373	5 - 12	0.09 - 0.93
		Enthalpy differences			
Macriss *et al.* [24]	1964	60	500 - 297	1.4 - 5.2	0.05 - 0.39
		Isobaric heat capacity			
Chan and Giauque [4]	1964	15	183 - 288	0.1	0.333
Hildenbrand and Giauque [15]	1953	60	197 - 290	0.1	0.5 - 0.67
Wrewsky and Kaigorodoff [49]	1924	23	275 - 334	0.1	0.01 - 0.40

[a] smoothed data

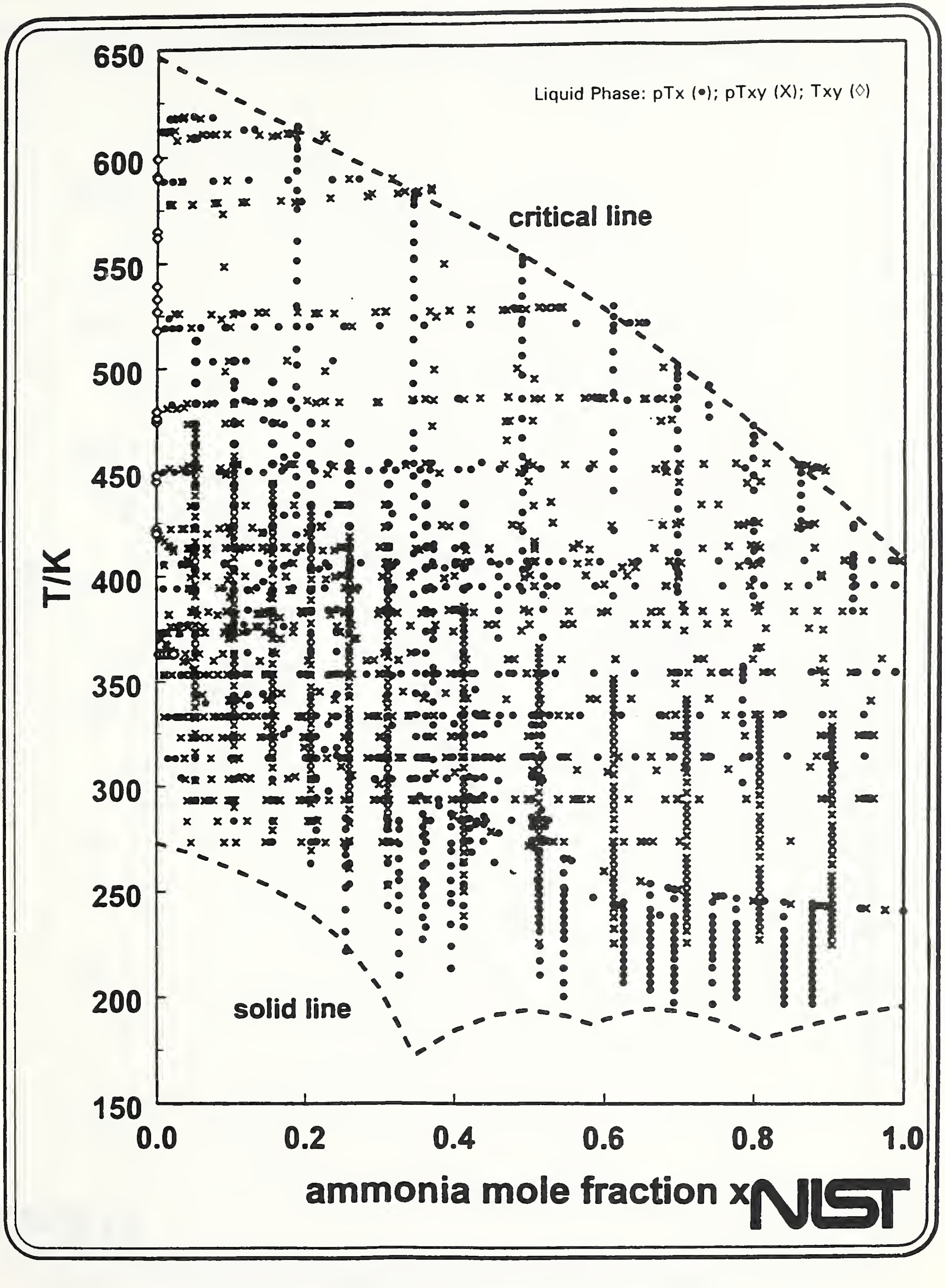
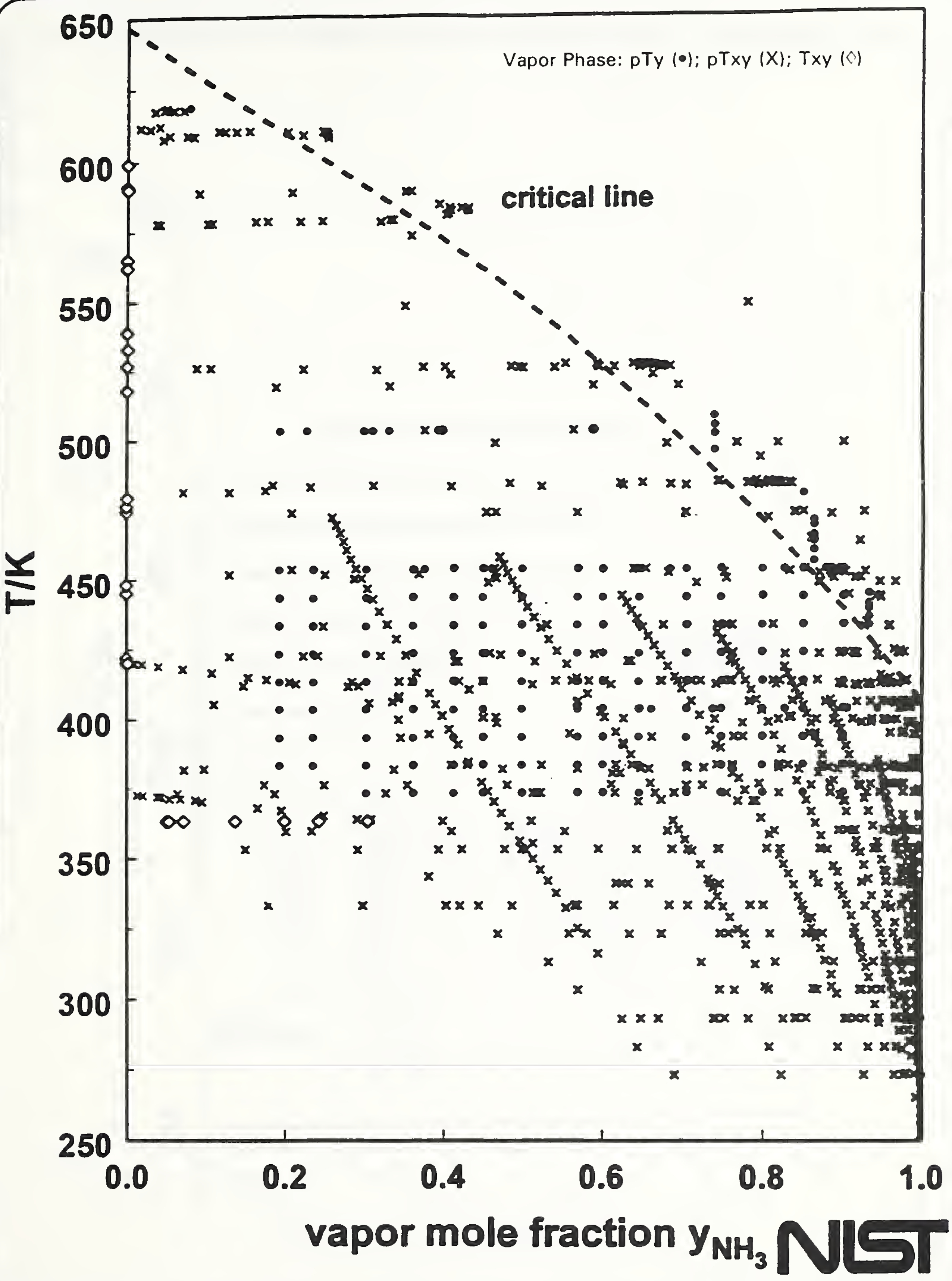
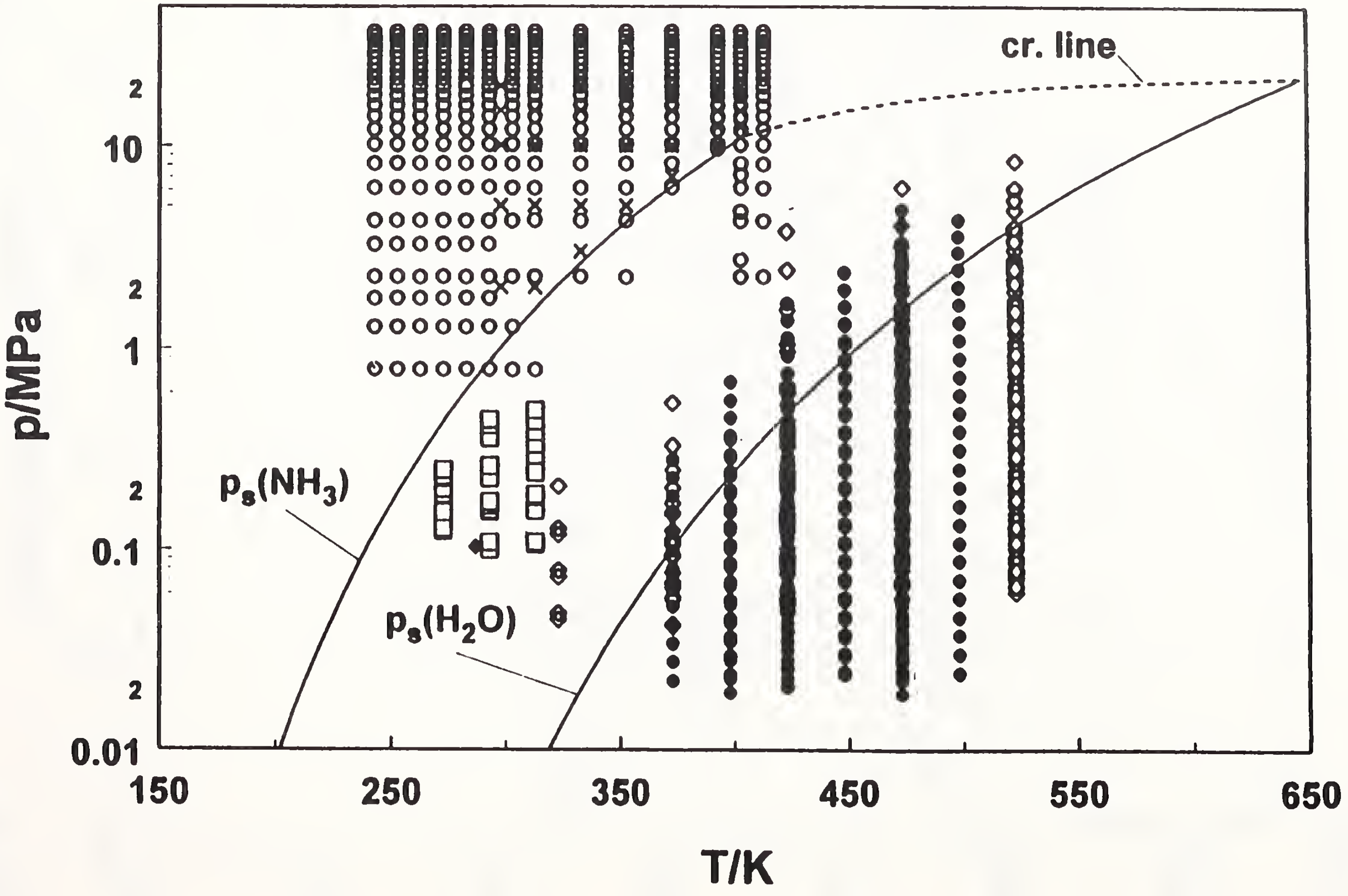

Liquid Phase: pTx (•); pTxy (X); Txy (◊)
critical line
solid line
T/K
650
600
550
500
450
400
350
300
250
200
150
0.0
0.2
0.4
0.6
0.8
1.0
ammonia mole fraction x

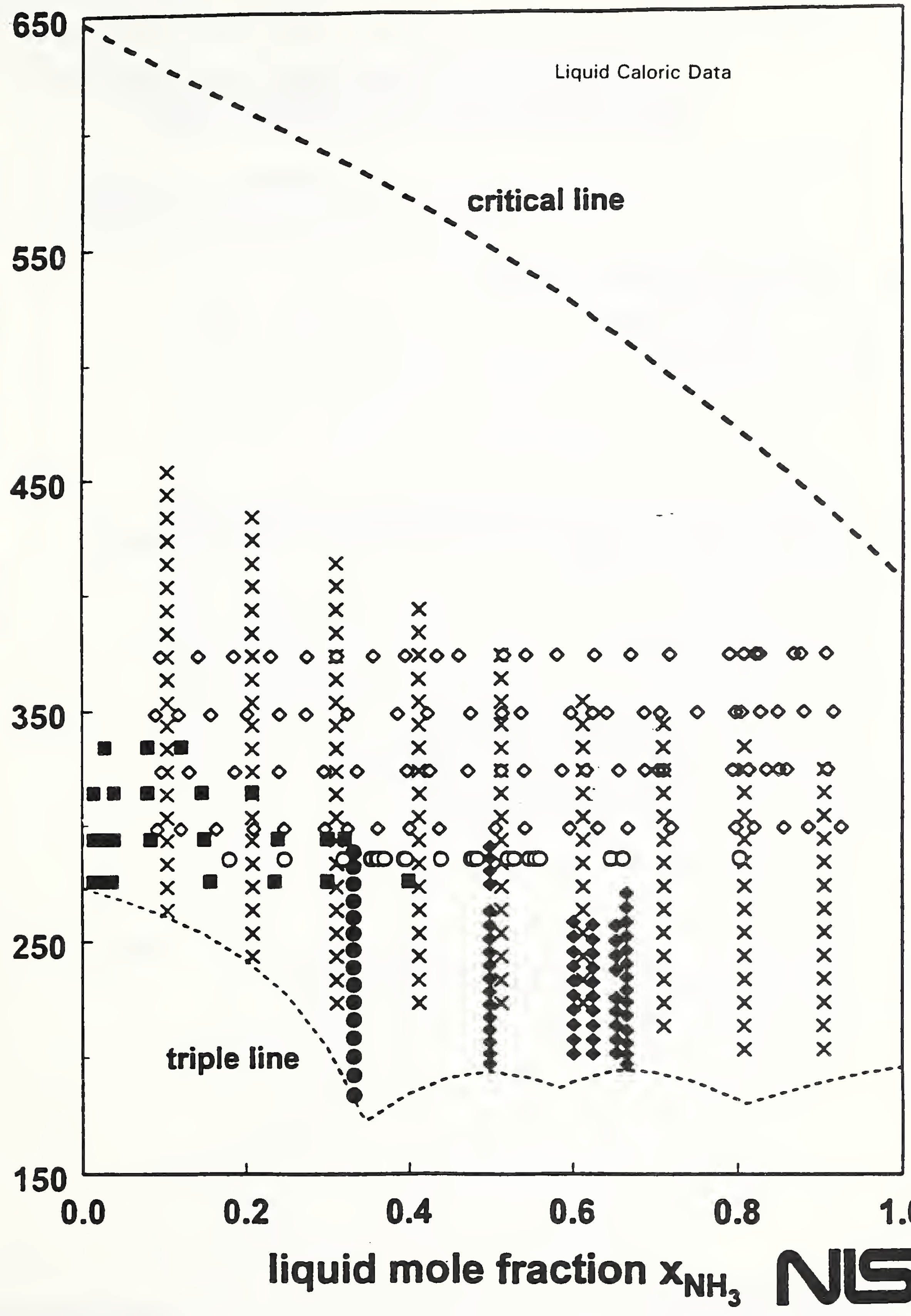
TABLE 2. Summary of experimental data for the triple line of {water+ammonia}

Source	Year	N	Composition range $x(NH_3)$
		Triple temperature	
Baume and Tykociner [2]	1914	13	0.04 - 0.58
Elliot [8]	1924	35	0.37 - 1.0
Postma [34]	1920	39	0.04 - 1.0
Pickering [31]	1891	67	0.01 - 0.31
Rupert [39]	1910	86	0.007 - 0.99
		Triple pressures	
Postma [34]	1920	48	0.04 - 1.0


Vapor Phase: pTy (•); pTxy (X); Txy (◊)
critical line
T/K
650
600
550
500
450
400
350
300
250
0.0
0.2
0.4
0.6
0.8
1.0
vapor mole fraction y_{NH_3}



Density Data


Liquid Caloric Data
critical line
triple line
650
550
450
350
250
150
T/K
0.0
0.2
0.4
0.6
0.8
1.0
liquid mole fraction x_{NH_3}

Approaches to Modelling

- Critical Region Theory
  - Rainwater
  - Kiselev

- Extended Corresponding States Approach (One-fluid model)
  - Huber
  - Nowarski
  - Friend
    - predictive version
    - "exact " shape factors
    - optimized model

- Two-fluid Helmholtz Energy Model
  - Tillner-Roth

NIST

Universal Critical Behavior

Scaling Theory
Renormalization Group

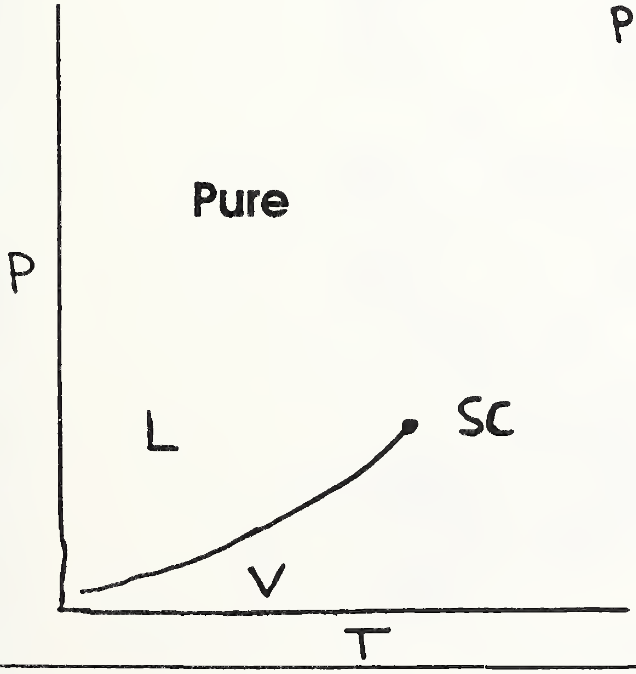
$$t = (T - T_c)/ T_c$$

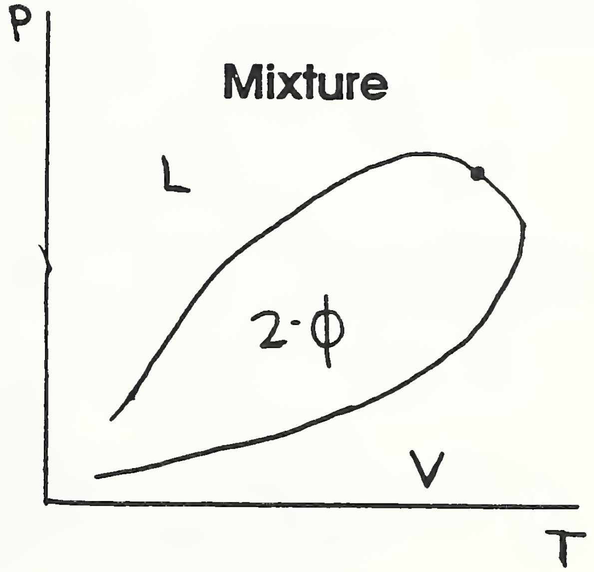
$$\rho = \rho_c(1 \pm C_1 t^\beta + C_2 t + \dots) \qquad \beta = 0.325$$

$$C_v = C_{vo}\ t^{-\alpha} \qquad \alpha = 0.110$$

Mixtures

$$B = 1/RT$$
$$\nu_1 = \mu_1/RT$$
$$\zeta = (K_1(B)\ e^{\nu 1})\{K_2(B)\ e^{\nu 2} + K_1(B)\ e^{\nu 1}\}$$





Binary Mixture Critical Lines

Gibbs free energy conditions:

$$\frac{\partial^2 G}{\partial x^2}\Big|_{P,T} = 0$$

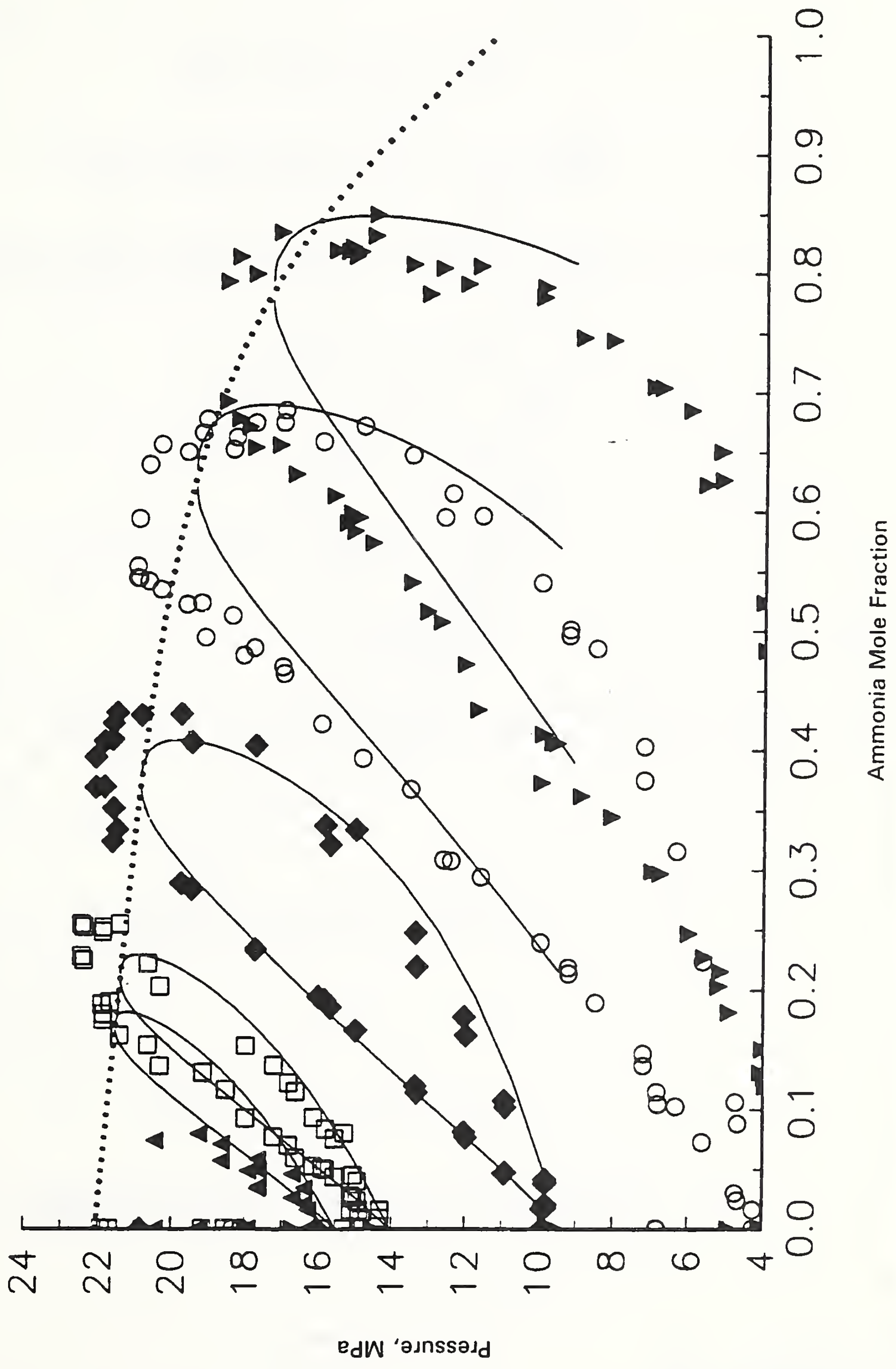
$$\frac{\partial^3 G}{\partial x^3}\Big|_{P,T} = 0$$

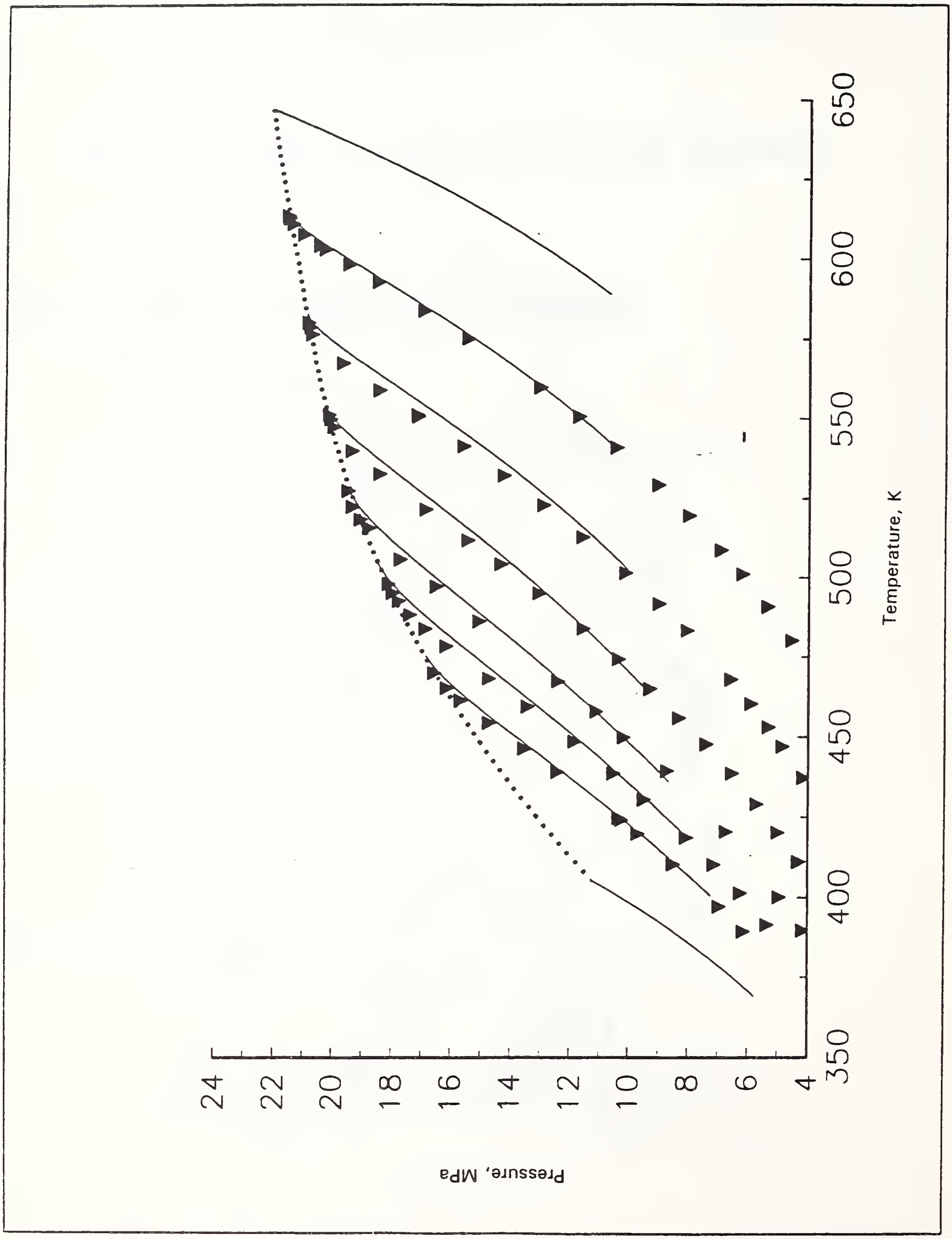
where

$$G = A + PV$$

We can write

$$\frac{\partial^2 G}{\partial x^2}\Big|_{p,T} = A_{xx} - \frac{A_{Vx}^2}{A_{VV}}$$


Pressure, MPa
24
22
20
18
16
14
12
10
8
6
4
Ammonia Mole Fraction
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


Pressure, MPa
24
22
20
18
16
14
12
10
8
6
4
350
400
450
500
550
600
650
Temperature, K

Helmholtz Energy Formulations

$$A(\rho,T,x) = U - TS$$

$$dA = P/\rho^2\, d\rho - S\, dT + \Sigma\mu_i\, dN_i$$

Canonical Ensemble: $A = -kT\, \mathit{ln}\, Q(N_i,\rho,T)$

$$P = \rho^2\, \partial A/\partial\rho|_{T,x}$$

$$S = -\,\partial A/\partial T|_{\rho,x}$$

$$H = A - T\, \partial A/\partial T|_{\rho,x} + P/\rho$$

$$C_v = -T\ \ \partial^2 A/\partial T^2|_{\rho,x}$$

$$C_p = -T\ \ \partial^2 A/\partial T^2|_{\rho,x} + T\, [\partial^2 A/\partial T\partial\rho|_x]^2/\, [\, \partial^2 A/\partial\rho^2|_{T,x}]$$

Vapor-Liquid Equilibria

$$T_L = T_v$$

$$P(\rho_L,T,x) = P(\rho_v,T,y)$$

$$\partial A(\rho_L,T,x)/\partial x|_{\rho,T} = \partial A(\rho_v,T,y)/\partial y|_{\rho,T}$$

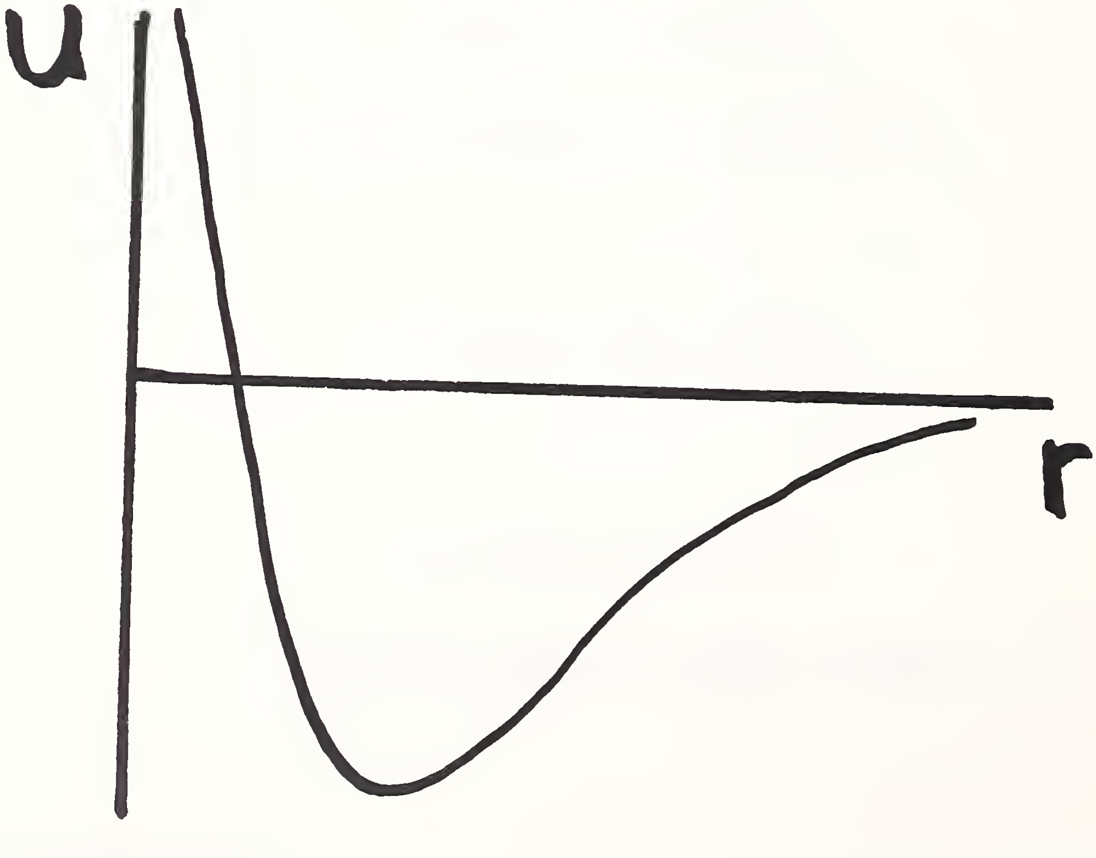
NIST

CORRESPONDING STATES (1)

Conformal Potentials
e.g. Lennard-Jones 12-6

$$U(r) = 4\varepsilon\,(\,(\sigma/r)^{12} - (\sigma/r)^{6}\,)$$

Rigorous Statistical Mechanics
- Partition function
- Full thermodynamic surface



CORRESPONDING STATES (2)

$$A^r(\rho,T) = (P_c / P_{c0}) (\rho_{c0}/\rho_c)$$

$$\times \quad A^r_0 (\rho (\rho_c / \rho_{c0}), T (T_c / T_{c0}))$$

Critical temperature

Critical pressure

Critical density

Critical compressibility factor

Acentric factor

Dipole moment

Radius of gyration

Hard-sphere diameter

Pure Fluids:
$f(T,\rho)$; $h(T,\rho)$

- Correlated shape factors
  SUPERTRAPP (SRD 4)
- Exact shape factors
  NIST14 (DDMIX)

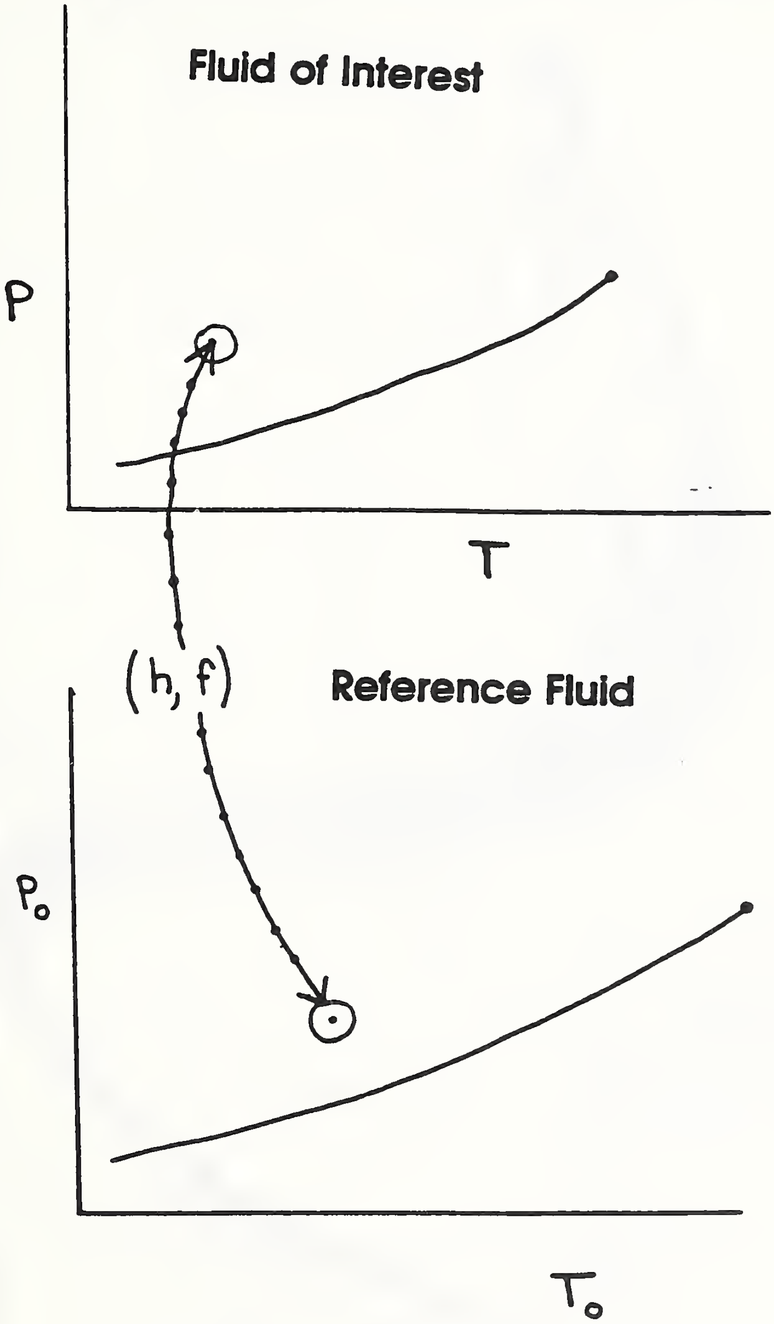
Given P, T
There exists f & h s.t.

$$a_o^r(\rho_o(P_o, T_o); T_o) = a^r(\rho(P, T); T)$$

$$Z_o^r(\rho_o(P_o, T_o); T_o) = Z^r(\rho(P, T); T)$$

$$P_o = P(h/f) \quad T_o = T/f$$

Corresponding States (3)
Extended Corresponding States

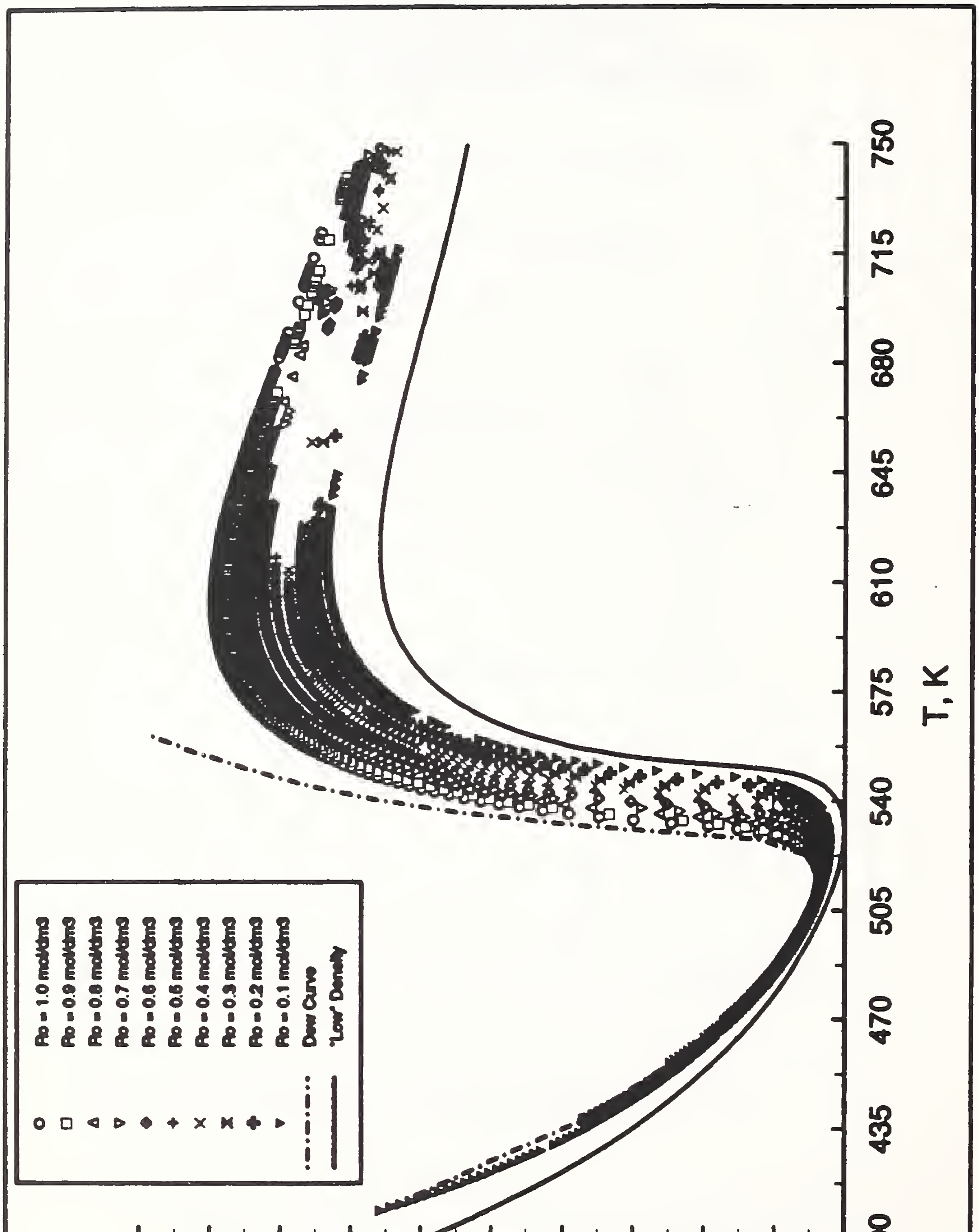


Fluid of Interest

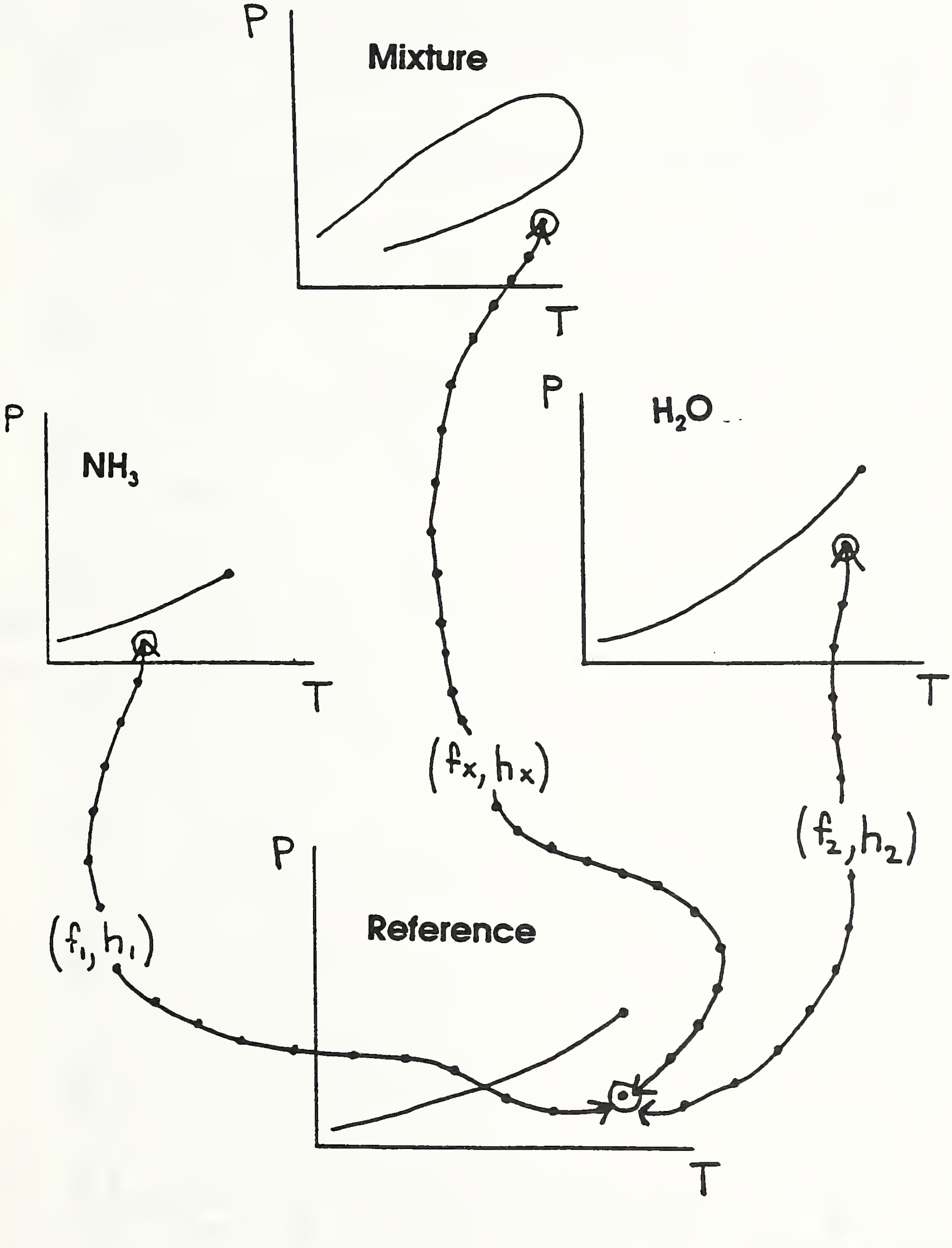
Reference Fluid

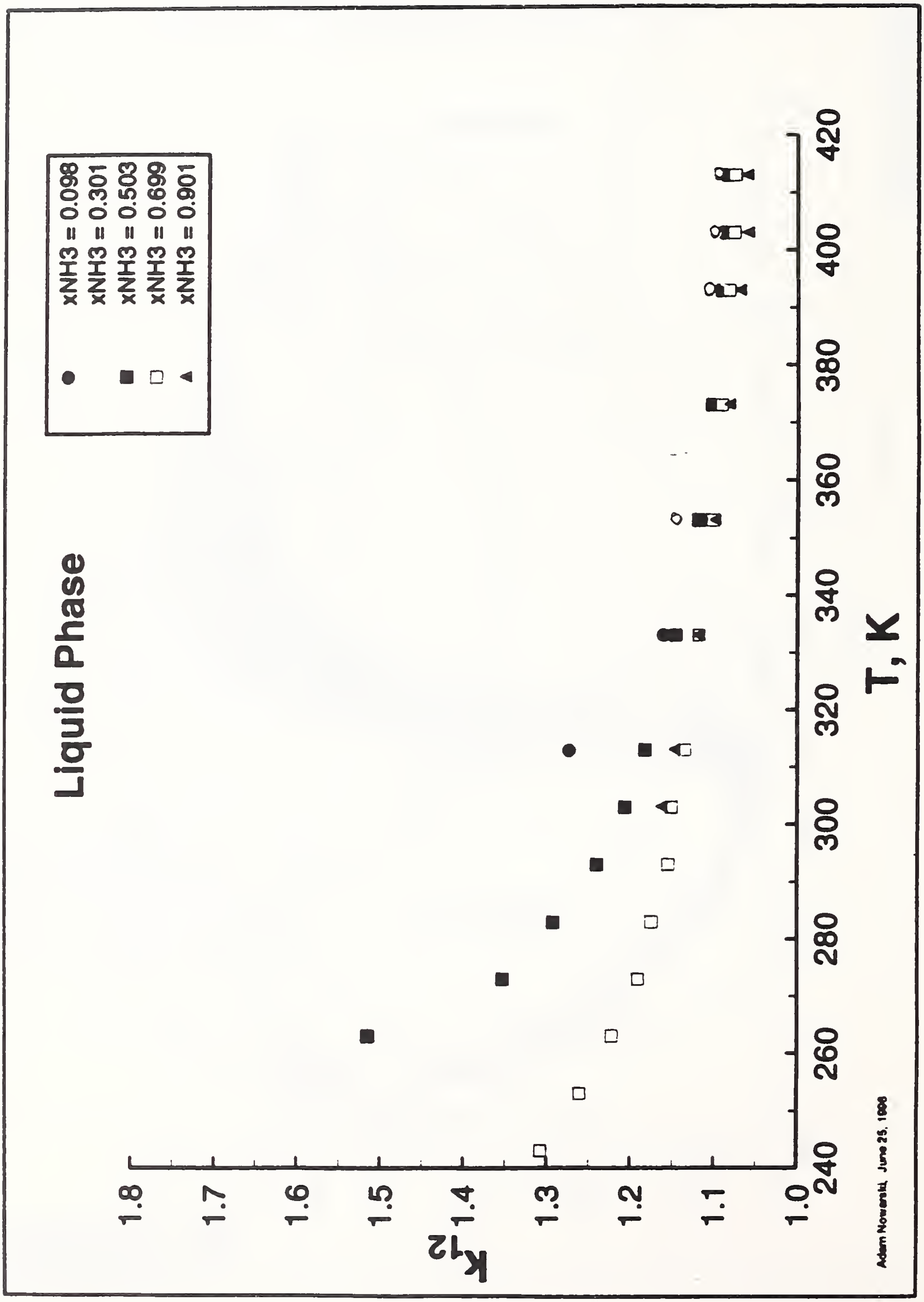
$P_o = P\, h/f$

$T_o = T/f$


Ro = 1.0 mol/dm3
Ro = 0.9 mol/dm3
Ro = 0.8 mol/dm3
Ro = 0.7 mol/dm3
Ro = 0.6 mol/dm3
Ro = 0.5 mol/dm3
Ro = 0.4 mol/dm3
Ro = 0.3 mol/dm3
Ro = 0.2 mol/dm3
Ro = 0.1 mol/dm3
Dew Curve
"Low" Density
h2
0.450
0.415
0.380
0.345
0.310
0.275
0.240
0.205
0.170
0.135
0.100
400
435
470
505
540
575
610
645
680
715
750
T, K

Mixtures: f(T,ρ,x); h(T,ρ,x)




Liquid Phase
K_{12}
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
T, K
240
260
280
300
320
340
360
380
400
420
● xNH3 = 0.098
■ xNH3 = 0.301
□ xNH3 = 0.503
▲ xNH3 = 0.699
xNH3 = 0.901
Adam Nowarski, June 25, 1996

Two-Fluid Helmholtz Energy Model

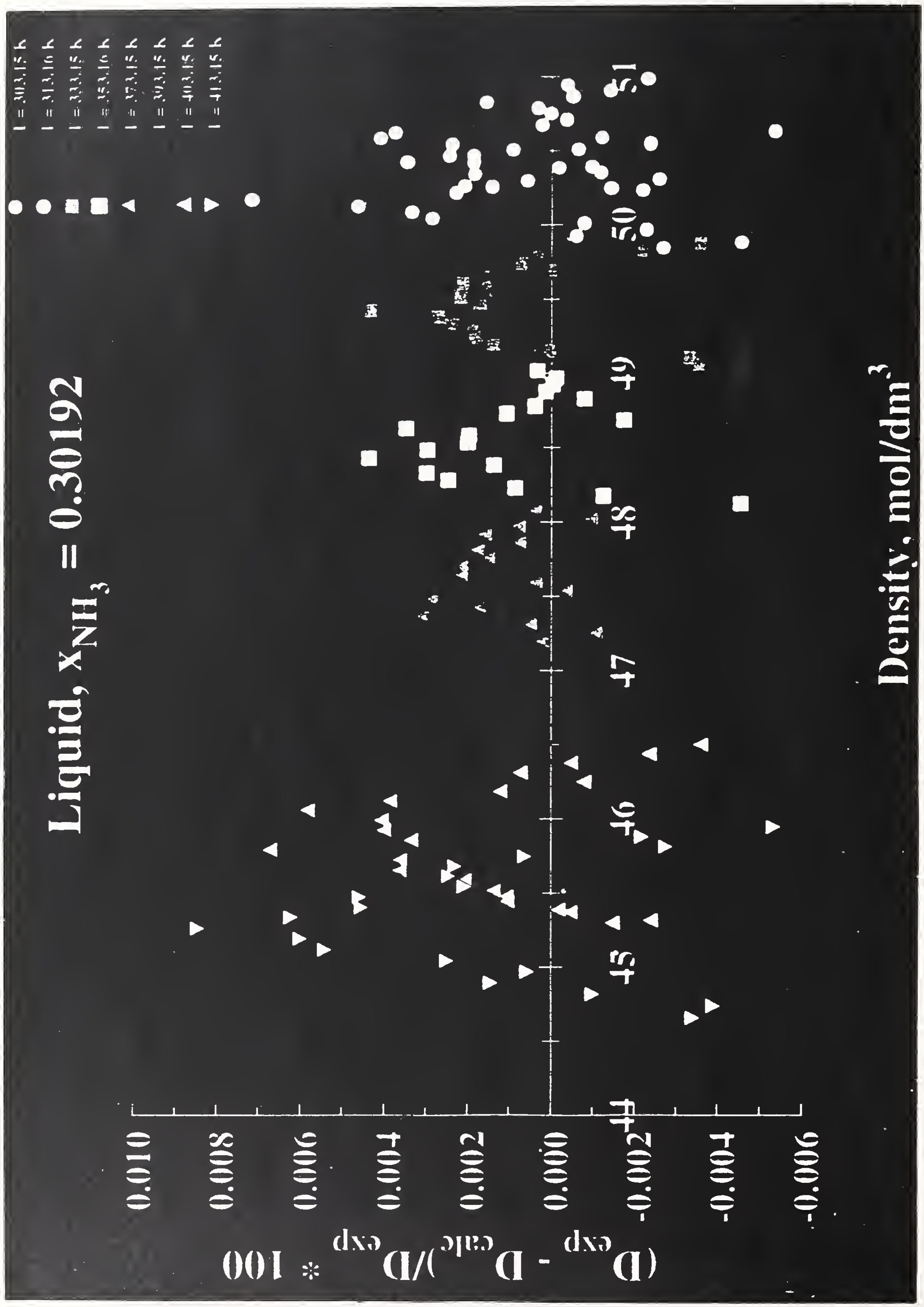
- Tillner-Roth: JPCRD to be submitted;
  thesis--University of Hannover (1993)
- Lemon: thesis--University of Idaho (1996)

$$\frac{A^r(\rho^*, T^*, x)}{RT} = x\frac{A_1^r(\rho^*, T^*)}{RT} + (1-x)\frac{A_2^r(\rho^*, T^*)}{RT} + \frac{A^E(\rho^*, T^*)}{RT}$$

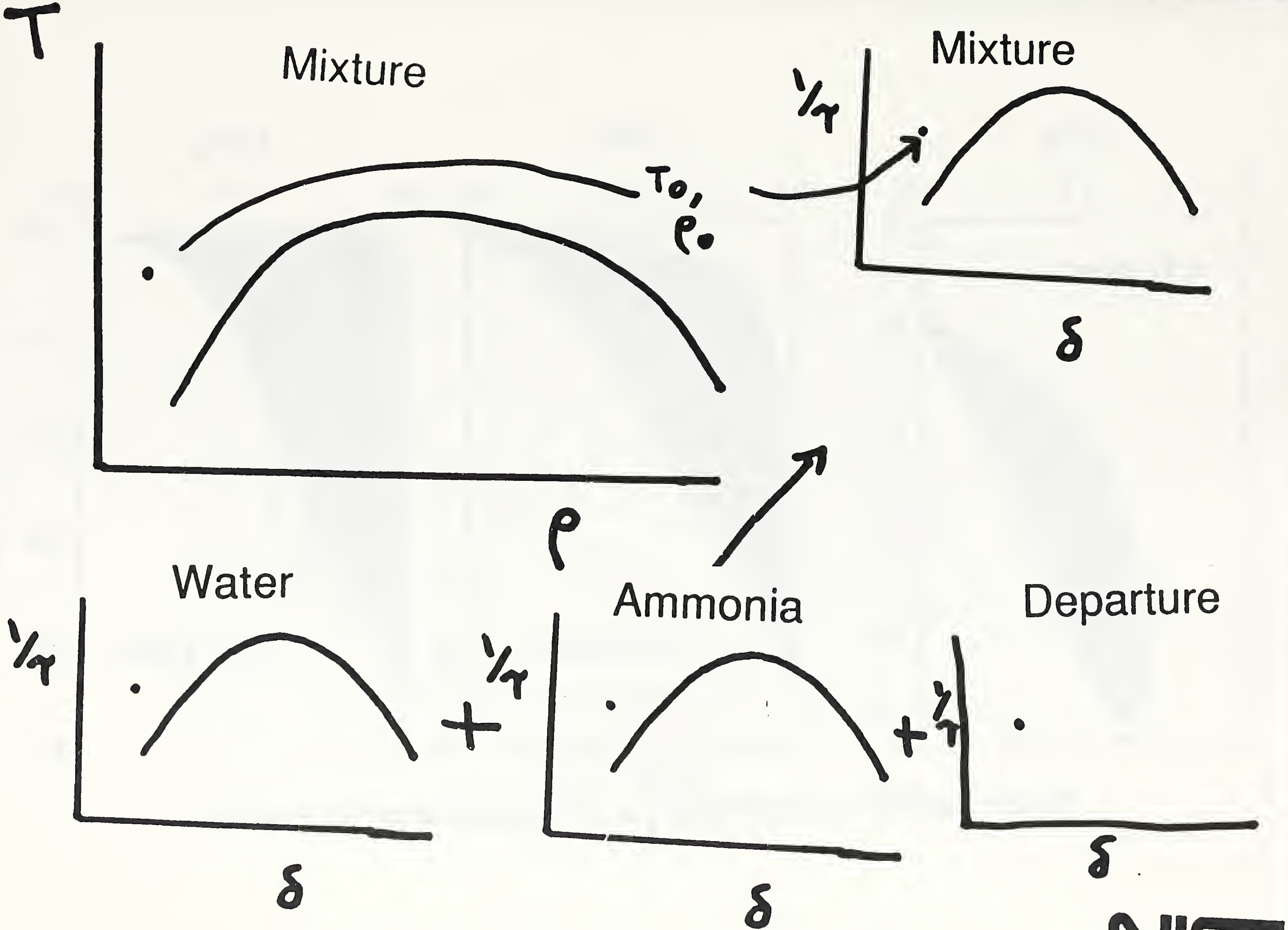
$$\rho^* = \frac{\rho}{\rho_0(x)} \quad , \quad T^* = \frac{T_0(x)}{T}$$

$$T_0(x) = (1-x)^2 T_{c1} + x^2 T_{c2} + x(1-x^{\alpha})(1-k)[T_{c1} + T_{c2}]$$

$$A^E = \sum_{i=1}^{14} a_i x^{f_i} \exp(-\rho^{*^{e_i}}) \rho^{*^{t_i}} T^{*^{d_i}}$$



Adam Nowarski Mar. 22, 1996



Mixture

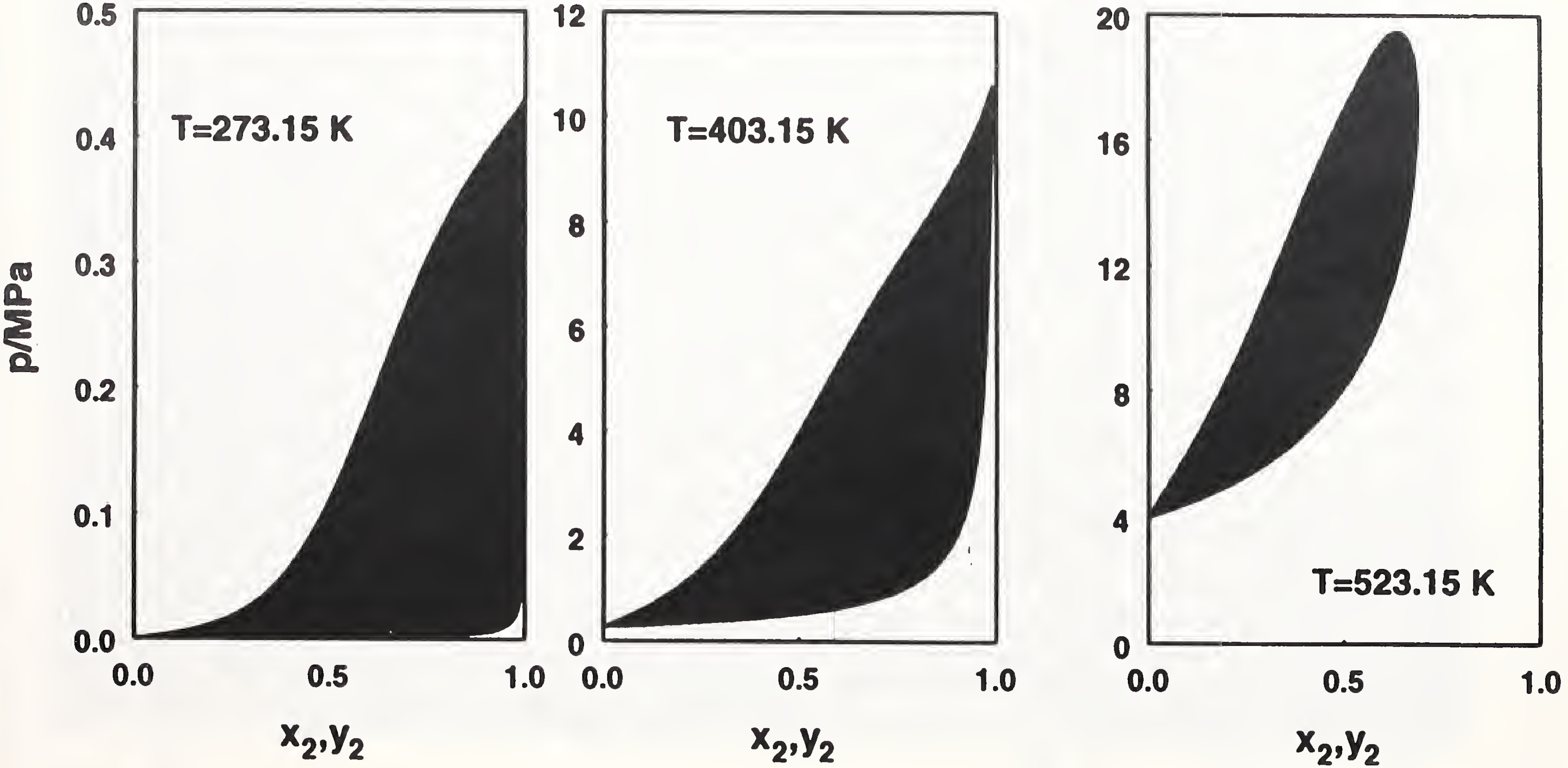
Mixture

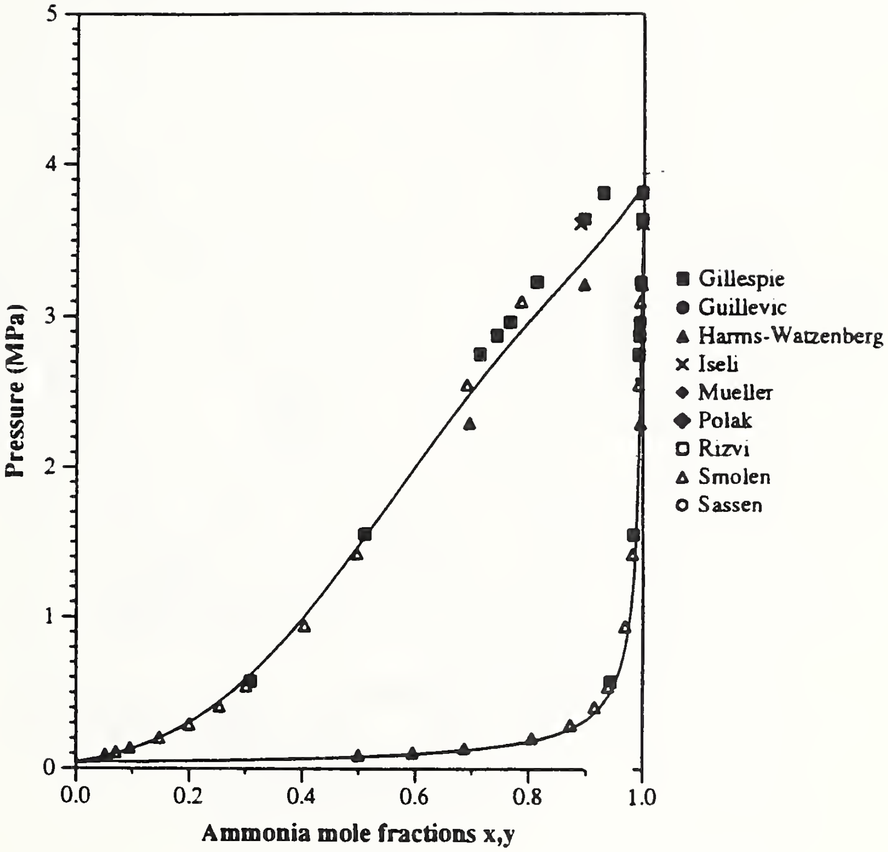
Water

Ammonia

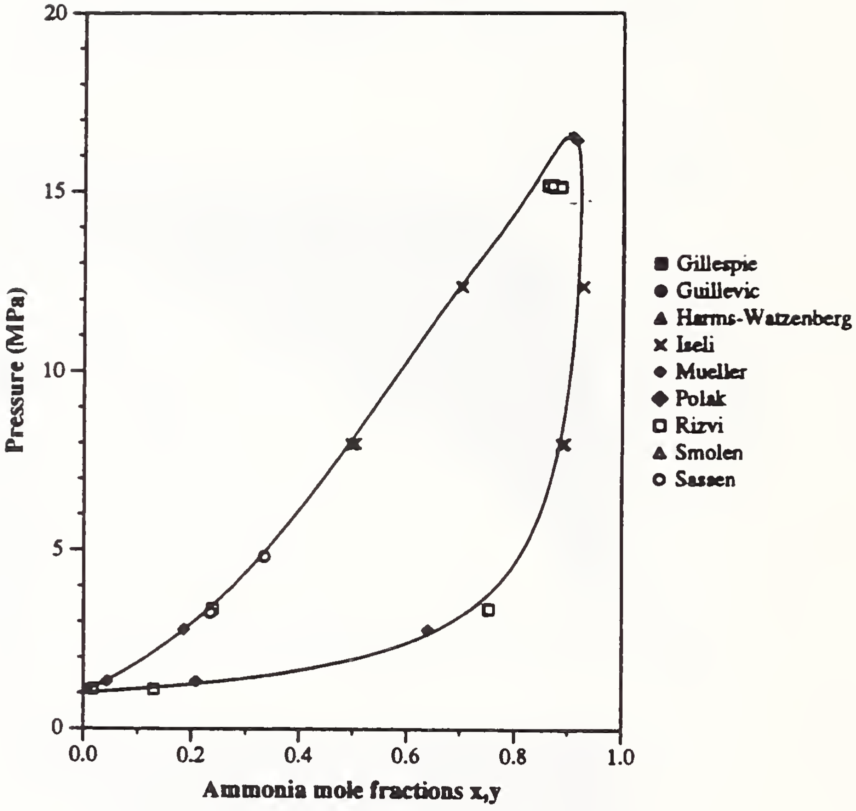
Departure

Vapor-liquid-equilibrium of {water(1) + ammonia(2)}

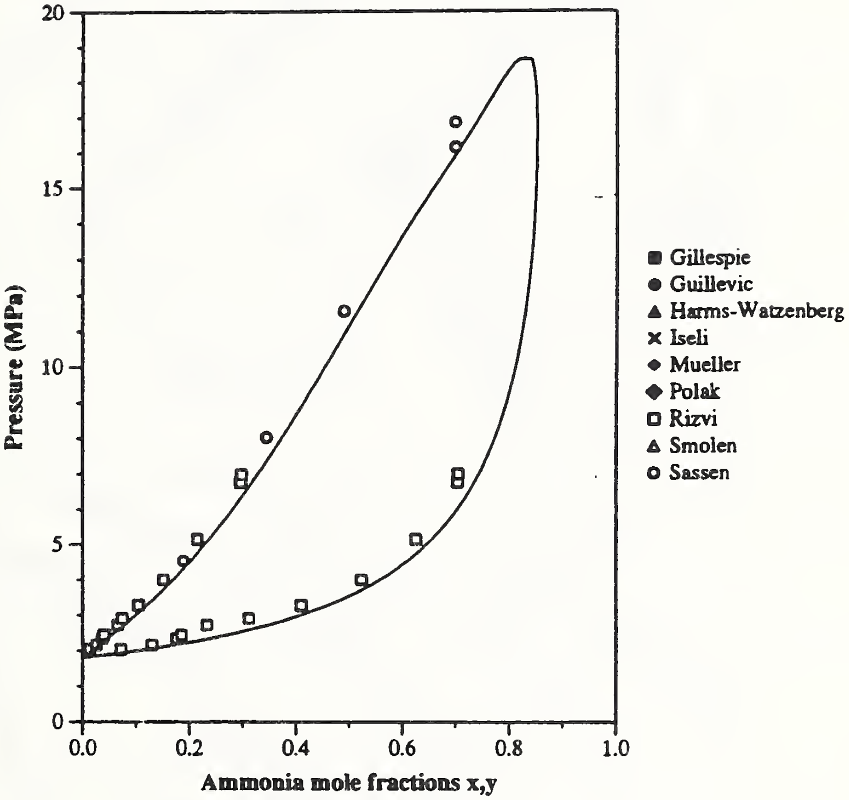



5
4
3
2
1
0
Pressure (MPa)
0.0
0.2
0.4
0.6
0.8
1.0
Ammonia mole fractions x,y
■ Gillespie
● Guillevic
▲ Harms-Watzenberg
× Iseli
◆ Mueller
◆ Polak
□ Rizvi
△ Smolen
○ Sassen

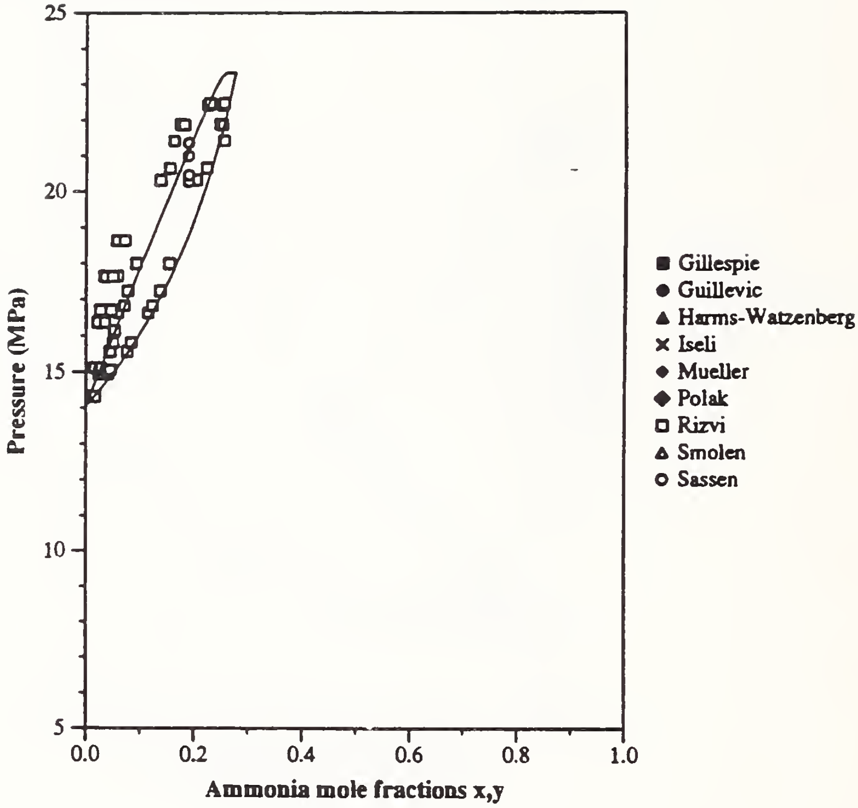
T=350.00 K


20
15
10
5
0
Pressure (MPa)
0.0
0.2
0.4
0.6
0.8
1.0
Ammonia mole fractions x,y
■ Gillespie
● Guillevic
▲ Harms-Watzenberg
× Iseli
● Mueller
◆ Polak
□ Rizvi
△ Smolen
○ Sassen

T=453.15 K

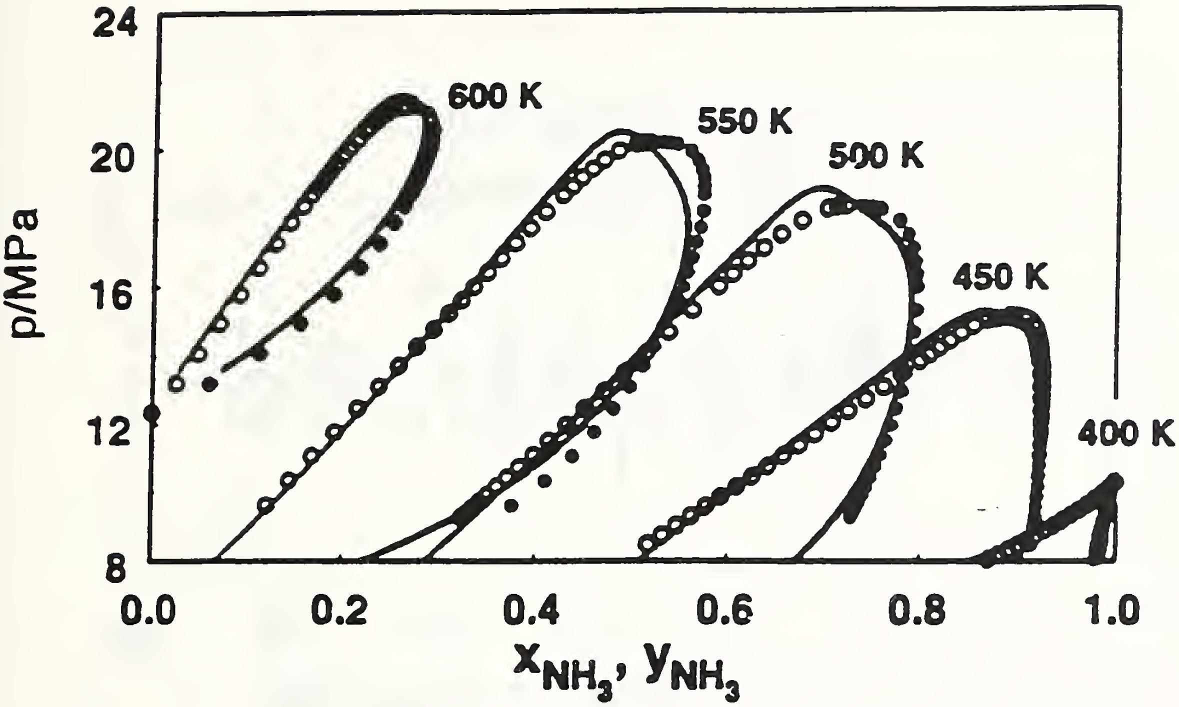

20
15
10
5
0
Pressure (MPa)
0.0
0.2
0.4
0.6
0.8
1.0
Ammonia mole fractions x,y
■ Gillespie
● Guillevic
▲ Harms-Watzenberg
× Iseli
◆ Mueller
◆ Polak
□ Rizvi
△ Smolen
○ Sassen

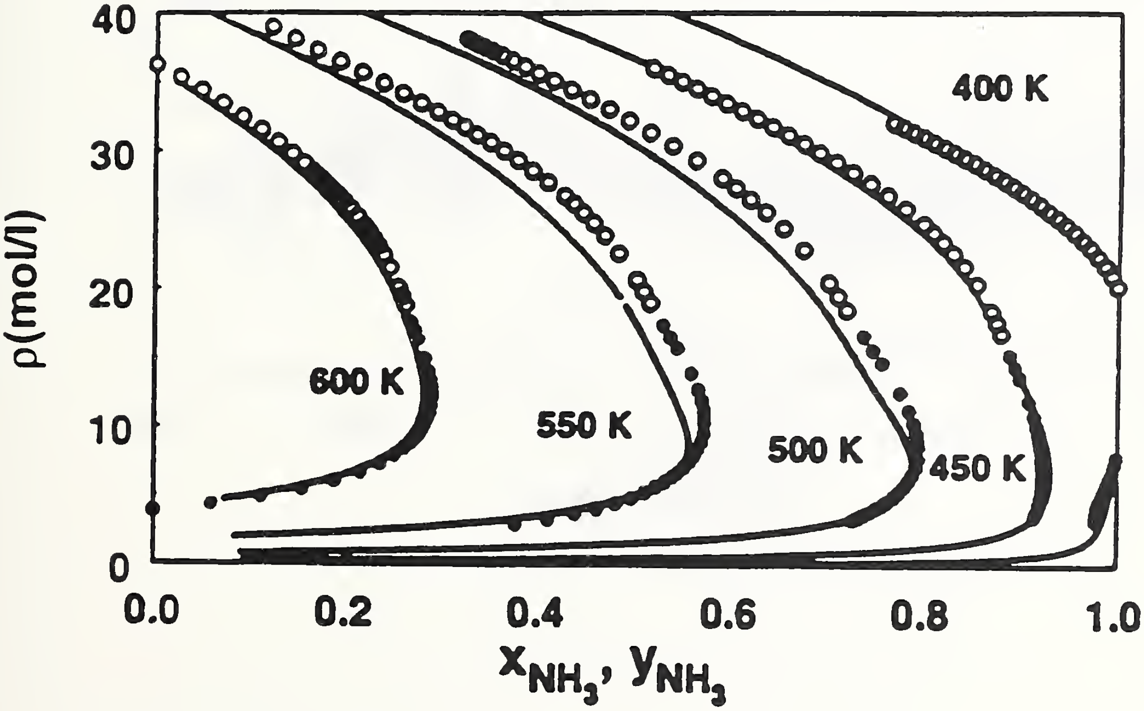
T=480.15 K


25
20
15
10
5
Pressure (MPa)
0.0
0.2
0.4
0.6
0.8
1.0
Ammonia mole fractions x,y
■ Gillespie
● Guillevic
▲ Harms-Watzenberg
× Iseli
◆ Mueller
◆ Polak
□ Rizvi
△ Smolen
○ Sassen

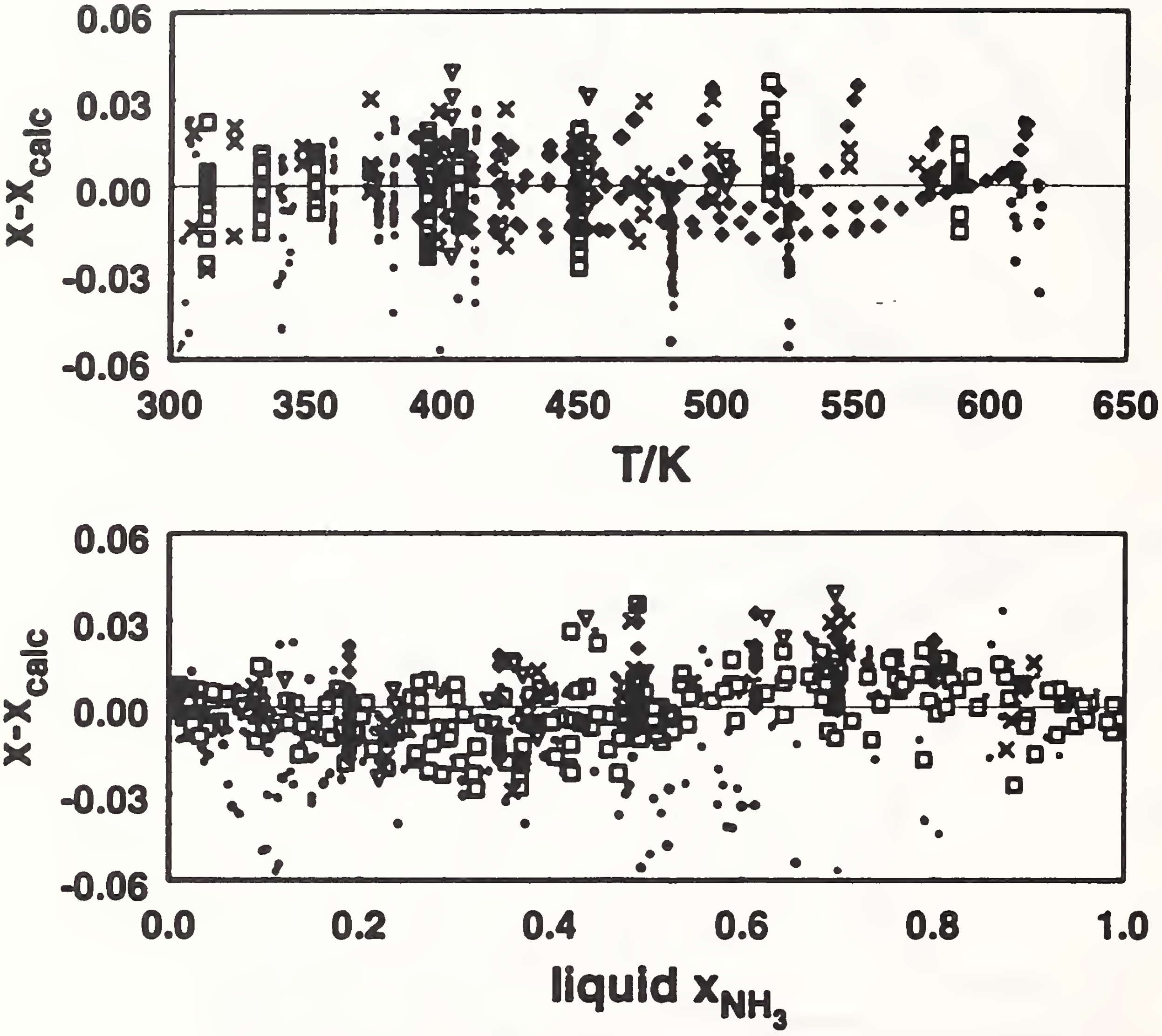
T=610.15 K

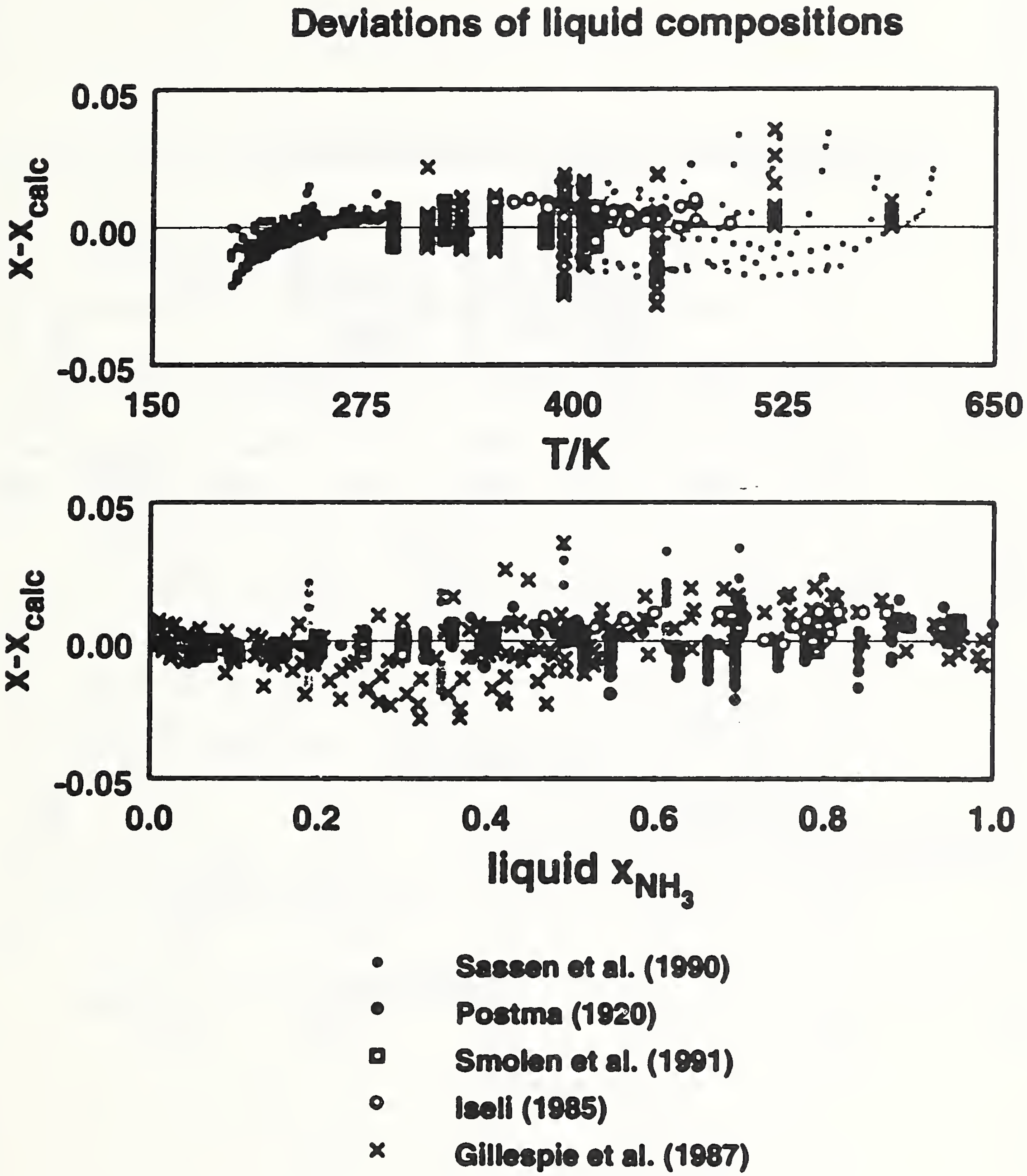
The critical region

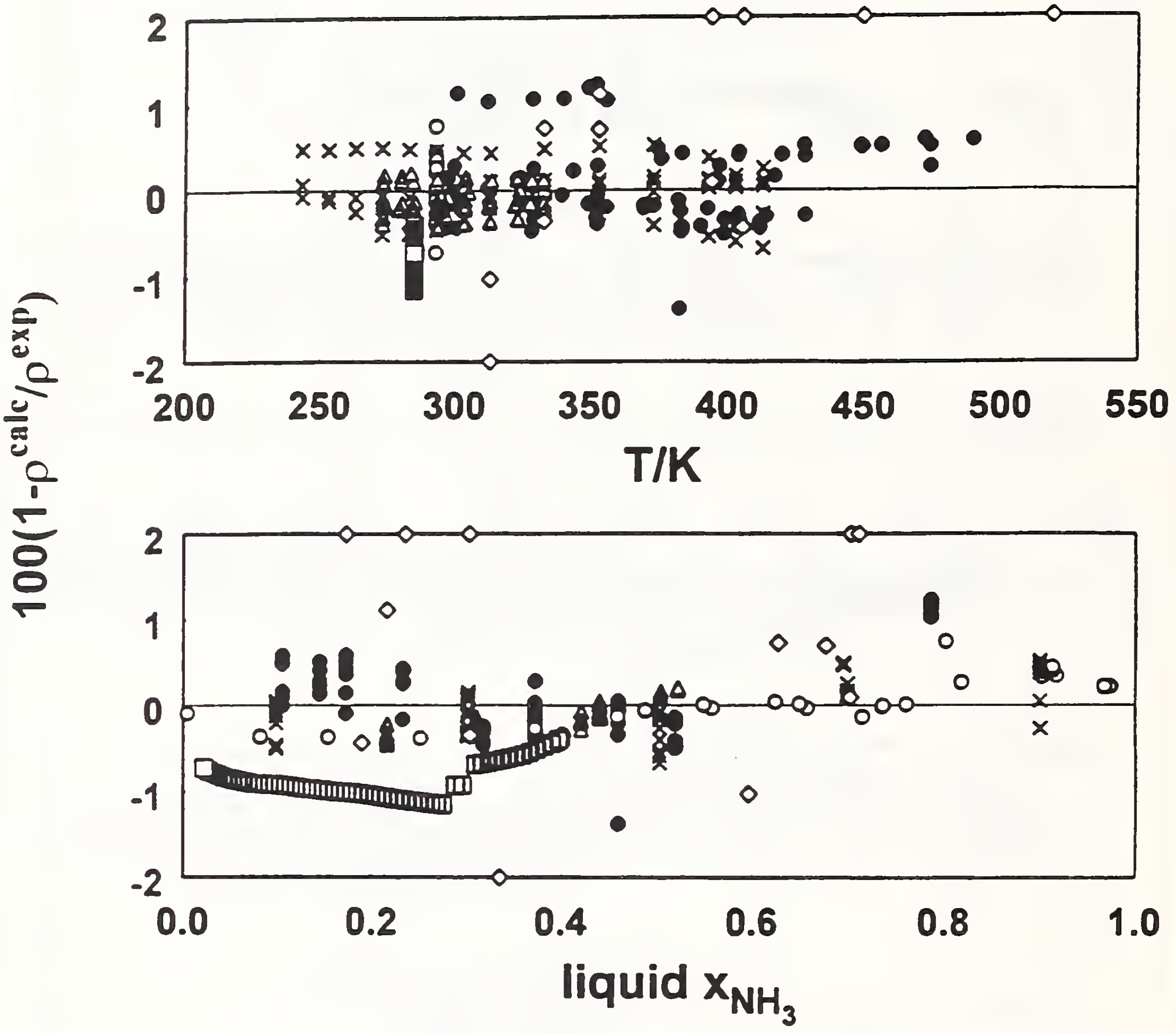


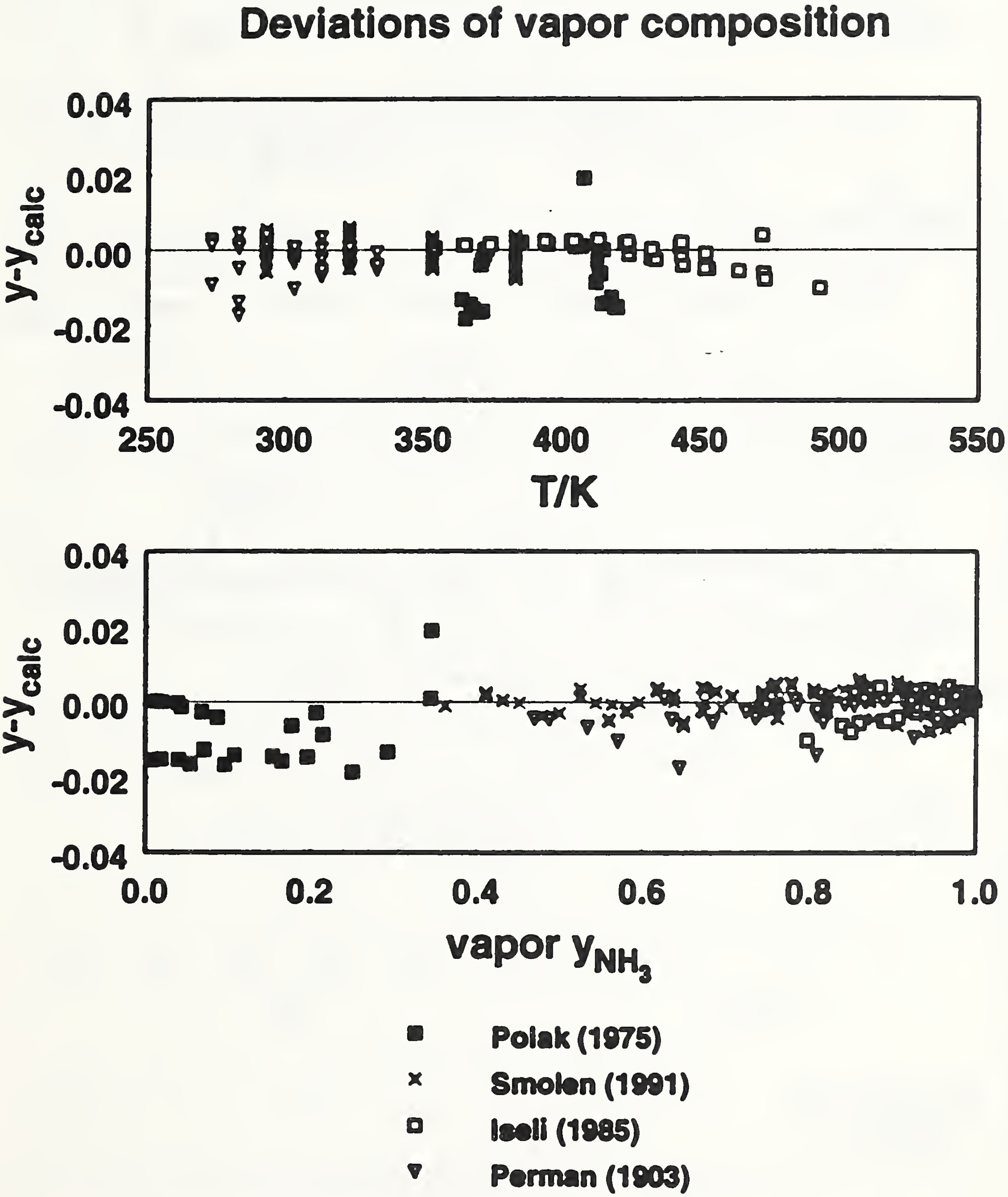


Deviations of liquid composition




Deviations of liquid compositions
0.05
0.00
-0.05
$X-X_{calc}$
150
275
400
525
650
T/K
0.05
0.00
-0.05
$X-X_{calc}$
0.0
0.2
0.4
0.6
0.8
1.0
liquid x_{NH_3}
• Sassen et al. (1990)
● Postma (1920)
▣ Smolen et al. (1991)
○ Iseli (1985)
× Gillespie et al. (1987)


2
1
0
-1
-2
200
250
300
350
400
450
500
550
T/K
100(1-ρ^calc/ρ^exp)
2
1
0
-1
-2
0.0
0.2
0.4
0.6
0.8
1.0
liquid x_NH3


Deviations of vapor composition
0.04
0.02
0.00
-0.02
-0.04
$y-y_{calc}$
250
300
350
400
450
500
550
T/K
0.04
0.02
0.00
-0.02
-0.04
$y-y_{calc}$
0.0
0.2
0.4
0.6
0.8
1.0
vapor y_{NH_3}
■ Polak (1975)
× Smolen (1991)
□ Iseli (1985)
▽ Perman (1903)

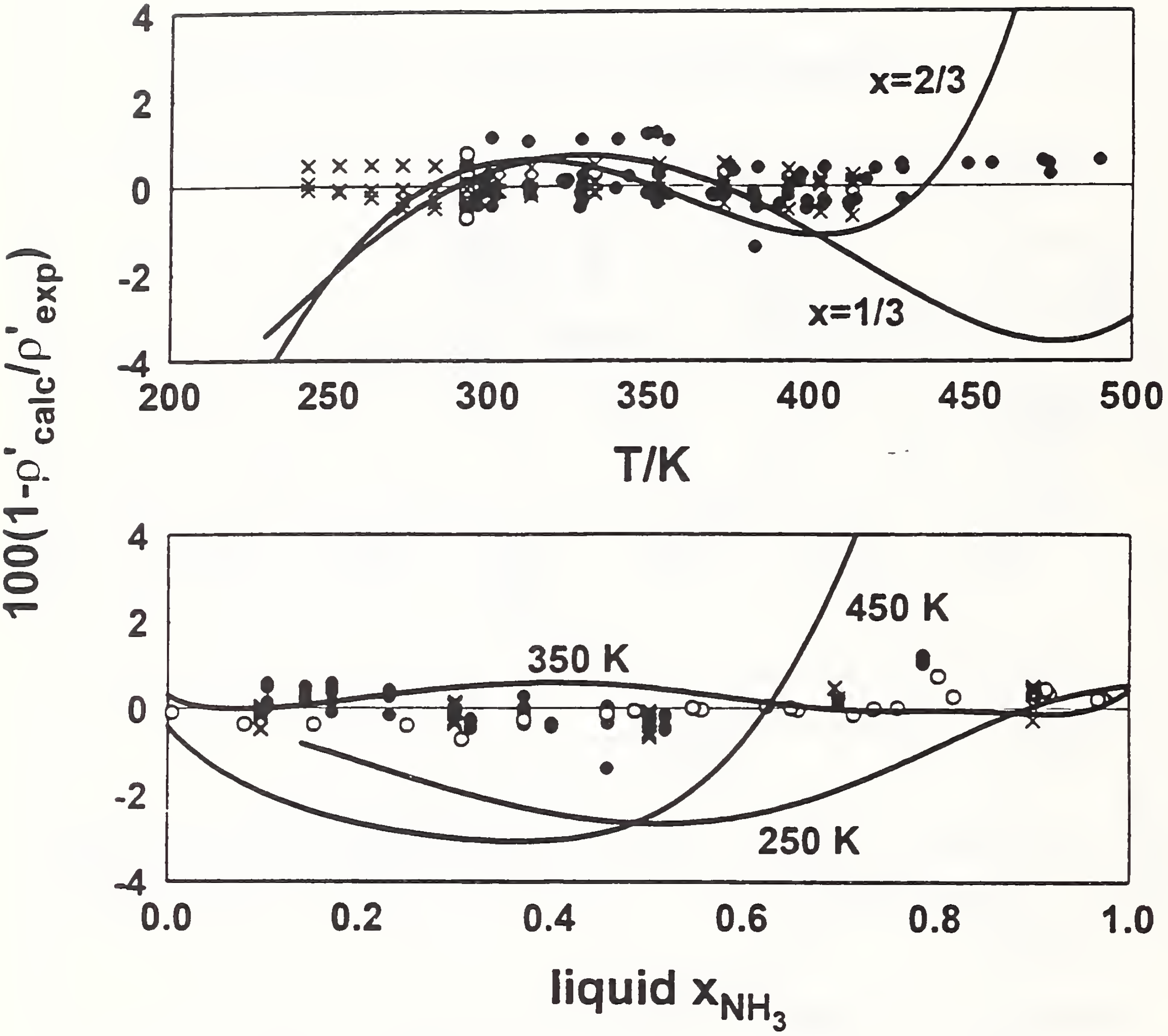
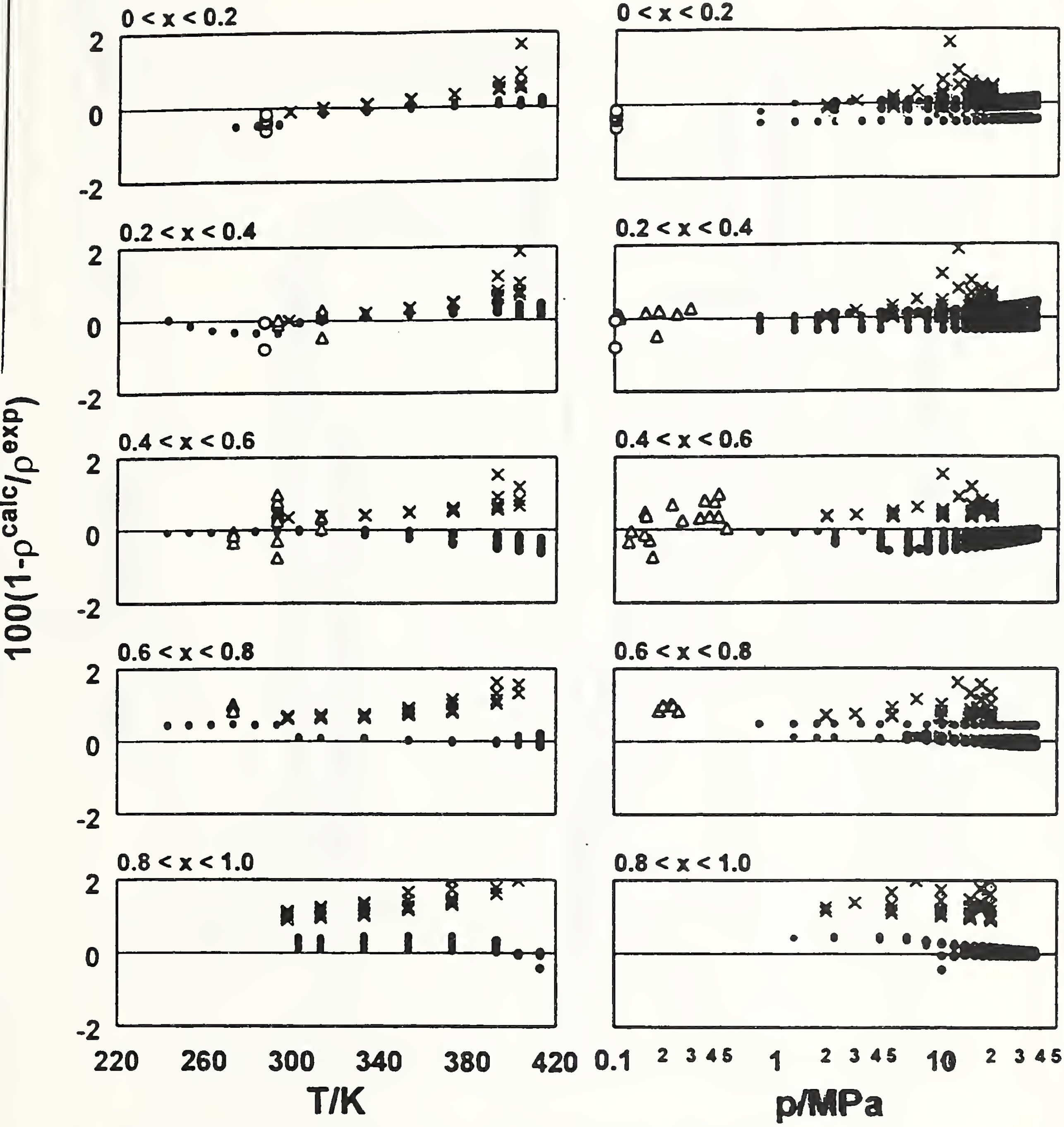
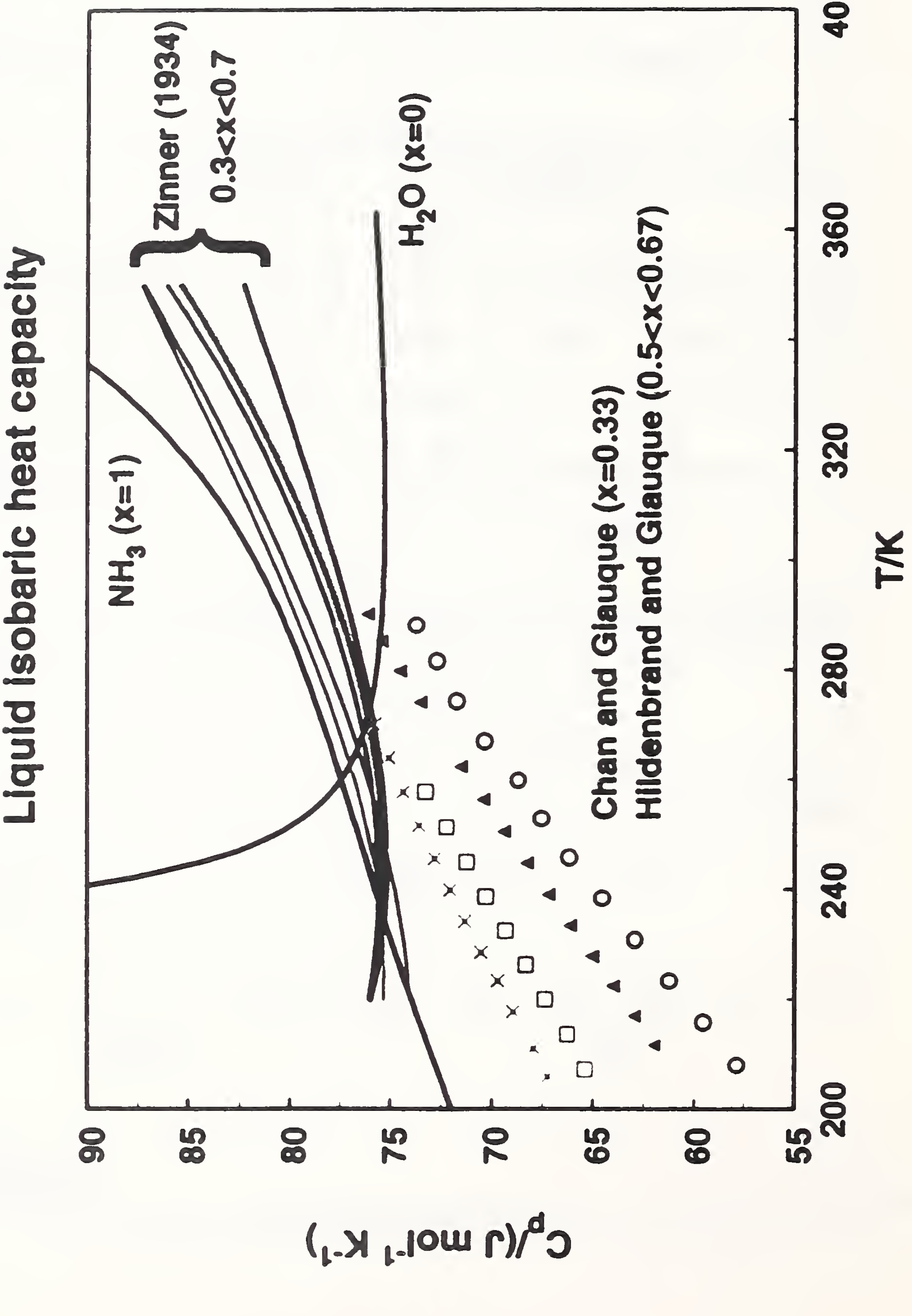
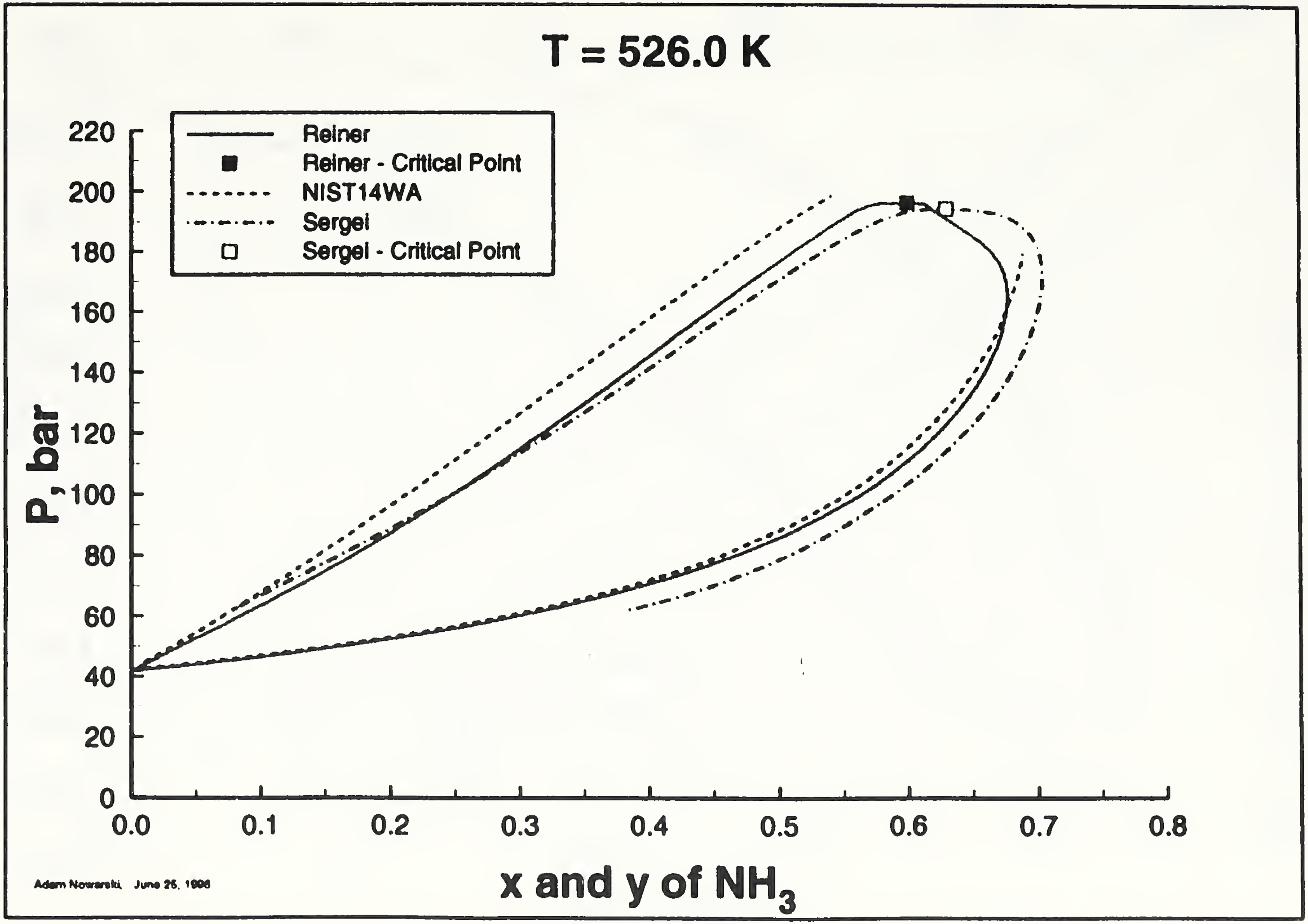
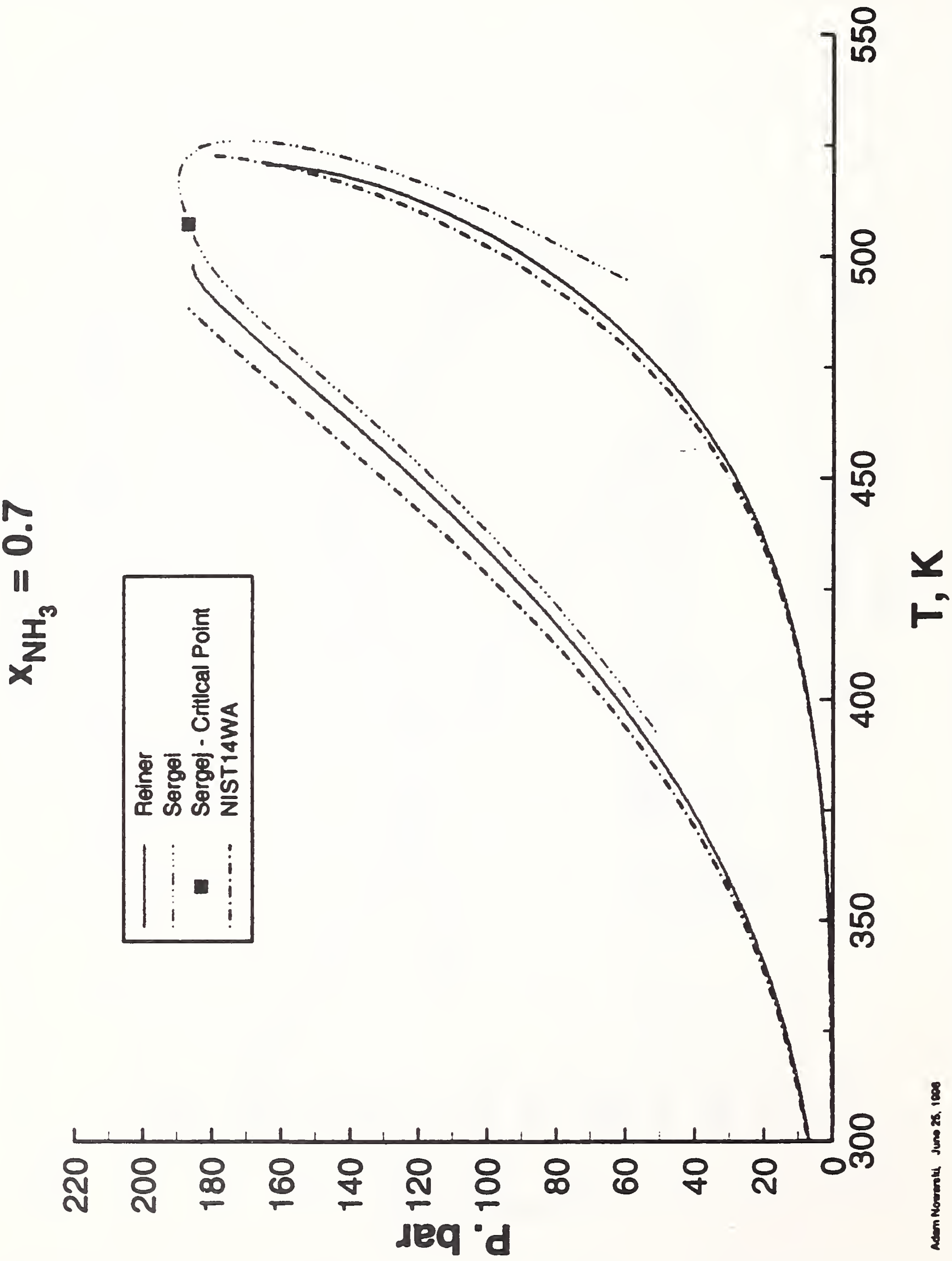

100(1-ρ'calc/ρ'exp)
4
2
0
-2
-4
200
250
300
350
400
450
500
T/K
x=2/3
x=1/3
4
2
0
-2
-4
0.0
0.2
0.4
0.6
0.8
1.0
liquid x_{NH_3}
450 K
350 K
250 K

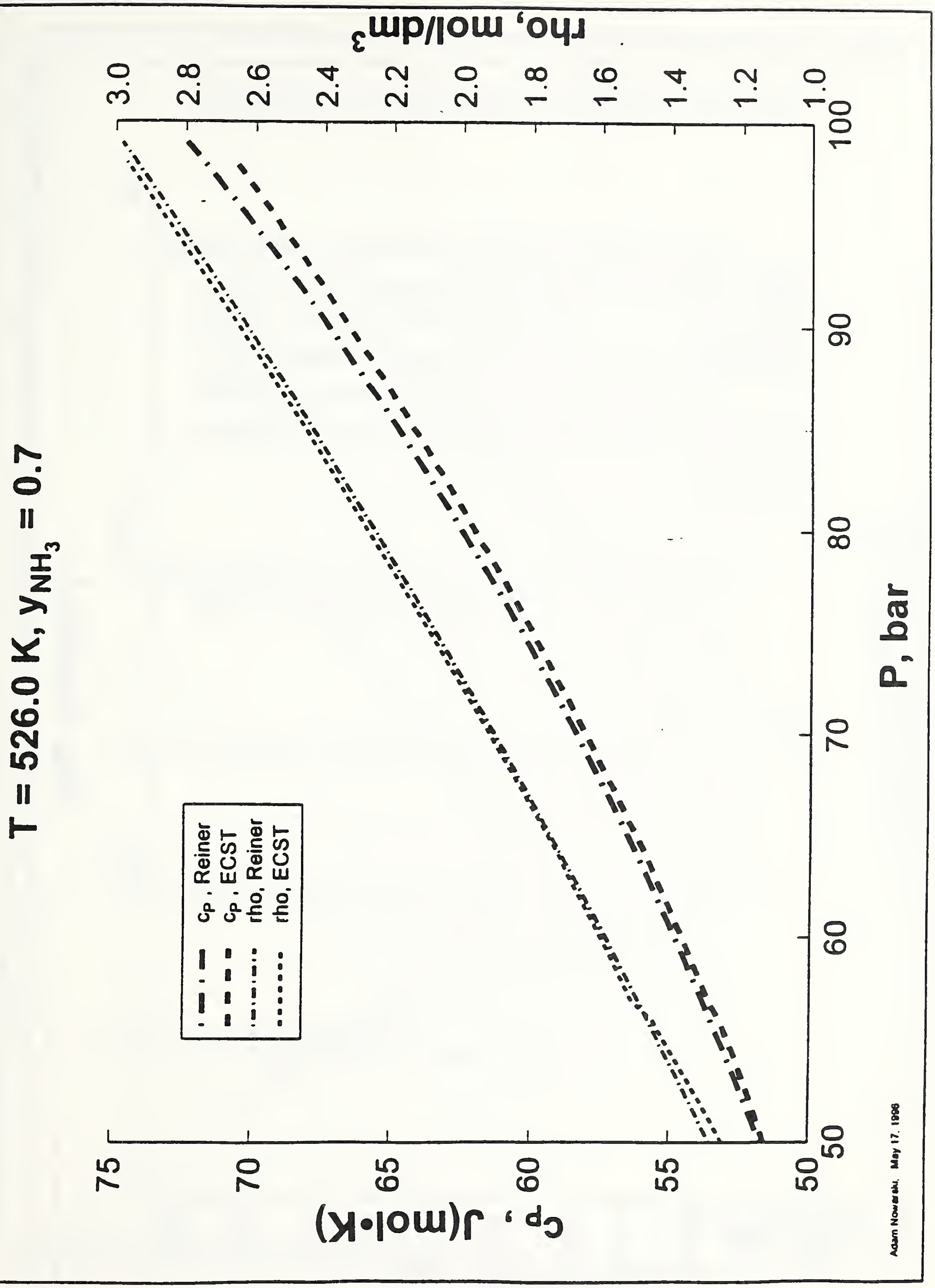
Fig. 8

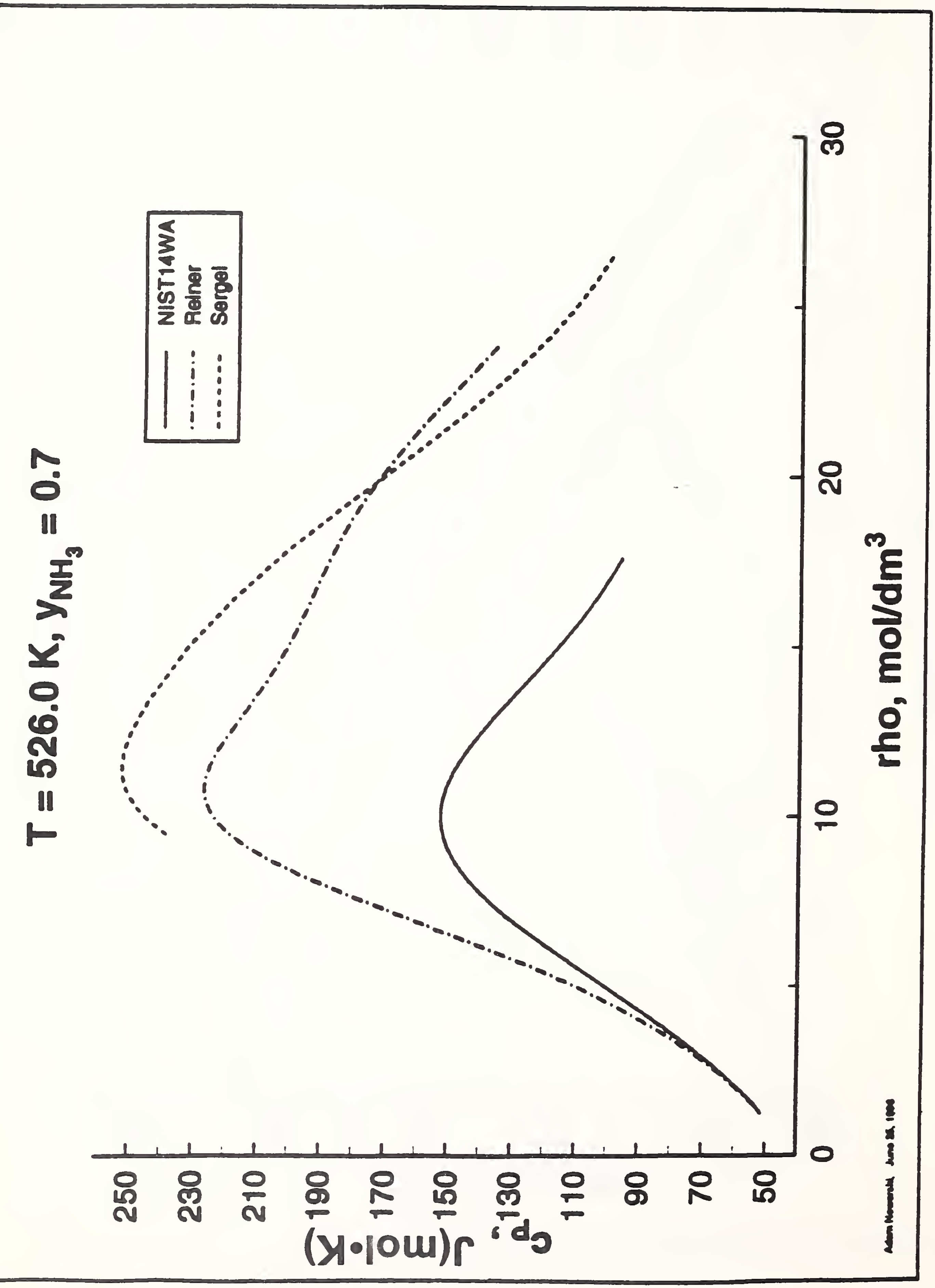

0 < x < 0.2
0.2 < x < 0.4
0.4 < x < 0.6
0.6 < x < 0.8
0.8 < x < 1.0
2
0
-2
$100(1-\rho^{calc}/\rho^{exp})$
220
260
300
340
380
420
T/K
0.1
2
3
4
5
1
2
3
4
5
10
2
3
4
5
p/MPa


Liquid isobaric heat capacity
NH_3 (x=1)
Zinner (1934)
0.3<x<0.7
H_2O (x=0)
Chan and Glauque (x=0.33)
Hildenbrand and Glauque (0.5<x<0.67)
$C_p/(J\ mol^{-1}\ K^{-1})$
90
85
80
75
70
65
60
55
200
240
280
320
360
400
T/K


T = 526.0 K
Reiner
Reiner - Critical Point
NIST14WA
Sergei
Sergei - Critical Point
P, bar
220
200
180
160
140
120
100
80
60
40
20
0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
x and y of NH3
Adam Nowarski, June 25, 1996


$X_{NH_3} = 0.7$
Reiner
Sergei
Sergei - Critical Point
NIST14WA
P, bar
220
200
180
160
140
120
100
80
60
40
20
0
T, K
300
350
400
450
500
550
Adam Novaresti, June 26, 1996


T = 526.0 K, y_{NH_3} = 0.7
c_P , J(mol•K)
75
70
65
60
55
50
rho, mol/dm^3
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
P, bar
50
60
70
80
90
100
c_P , Reiner
c_P , ECST
rho, Reiner
rho, ECST
Adam Nowarski, May 17, 1996



T = 526.0 K, y_{NH_3} = 0.7

Status of Models--Future Work

- Reasonable agreement with existing data:
  - solid-liquid-vapor boundary to critical locus
  - vapor and liquid to 40 MPa
  - VLE uncertainties about ±0.01 in x and y
  - density uncertainties about ±0.5%
  - enthalpy uncertainties about ±250 J/mol
- Must compare and re-optimize to new data
  - NIST; Delaware; Russian
- Must develop usable computer codes
- Must investigate extrapolation region
- Complete ECS model approach

NIST

Status of Models--Future Work (2)

- Priority data needs to improve model
  - Supercritical region--all data
  - Low temperature liquid densities down SLE line
  - Compressed liquid densities to 40 MPa
  - Heat capacities in entire liquid range
  - $PT\rho x$ for ammonia-rich mixtures 400 to 650 K
  - $PT\rho y$ for ammonia-rich mixtures 400 to 650 K
  - Sound speed data throughout range
  - Resolve questions about critical line
  - Improved data for dilute ammonia mixtures

- Next generation of Helmholtz energy models

  - Theoretical basis
    - examine local composition approximation
    - account explicitly for polarity and association
    - simulation studies
    - advanced mixing rules
    - chemistry & impurities

  - Focus on calculational speed for design work

NIST

APPENDIX K.

M. McLINDEN: OVERVIEW OF EXPERIMENTAL CAPABILITIES AT NIST

Experimental Properties of Fluids Group
Physical and Chemical Division
National Institute of Standards and Technology
Boulder, Colorado

Experimental Properties of Fluids Group (838.07)
Staff (+ students/guest workers) and Apparatus

○ C. Holcomb/S. Outcalt (M. Thompson)
- cryogenic VLE
- air-bath VLE
- liquid-bath VLE/surface tension

○ A. Laesecke (N. Kagawa, R. Hafer, D. Morris)
- low-T vibrating quartz crystal viscometer
- high-T vibrating quartz crystal viscometer
- capillary viscometer

○ J. Magee (J. Blanco)
- isochoric p-V-T
- low-T C_v
- high-T twin-cell C_v
- total enthalpy (flow) calorimeter

○ M. McLinden (N. Frederick)
- dual sinker densimeter (p-V-T)

○ R. Perkins (G. Straty, T. Lüddecke)
- low-T hot-wire thermal conductivity
- high-T hot-wire thermal conductivity (platinum and tantalum wire cells)
- light-scattering thermal diffusivity
- vibrating wire viscometer
- high-T (ammonia/water) vibrating wire viscometer

○ J. Scott (B. Younglove)
- cylindrical resonator (liquid speed of sound)
- spherical resonator (vapor speed of sound)

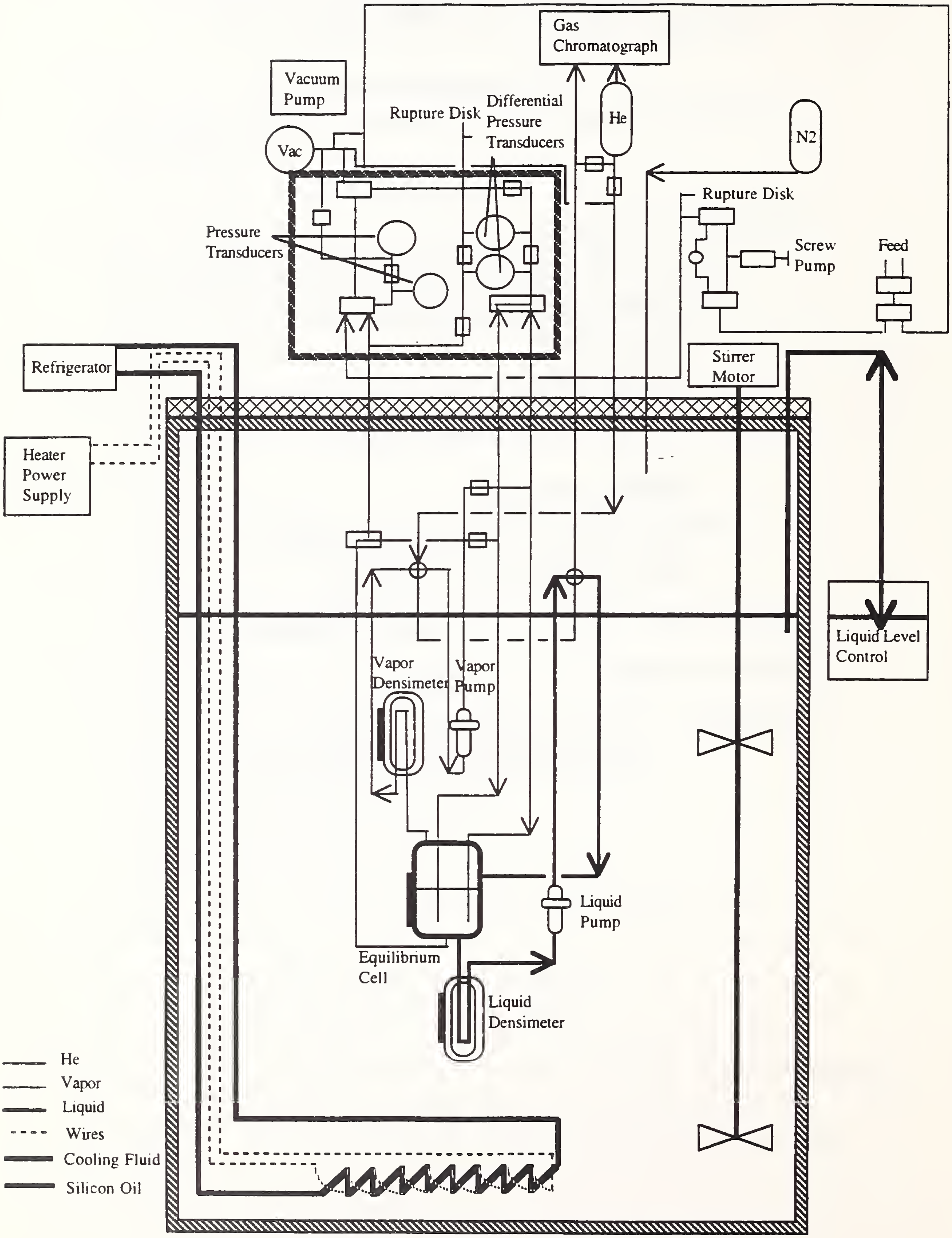
○ G. Straty/B. Butler (838.08)/H. Hanley (838.00) (C. Muzny, E. Schwarzberg)
- couette shearing cells for rheometry (neutron scattering (at Gaithersburg reactor) and light scattering)

Phase-Equilibria Apparatus

bubble point pressure
coexisting liquid and vapor densities and compositions

- ○ Principles of operation
  - = vapor-liquid equilibria cell (volume = 150 cm^3)
  - = circulation of liquid and vapor
    - for mixing
    - through vibrating tube densimeters
    - through GC sampling valve
    - —or—
    - capillary sampling
  - = surface tension (under development)
    - differential pressure method
- ○ Temperature range: 218 – 425 K (liquid bath)
- ○ Pressure range: < 14 MPa
- ○ Materials: 316SS, sapphire, 440SS, graphite-reinforced PTFE seal

VLE Apparatus



Twin-Cell Adiabatic Calorimeter

isochoric (constant volume) heat capacity C_V

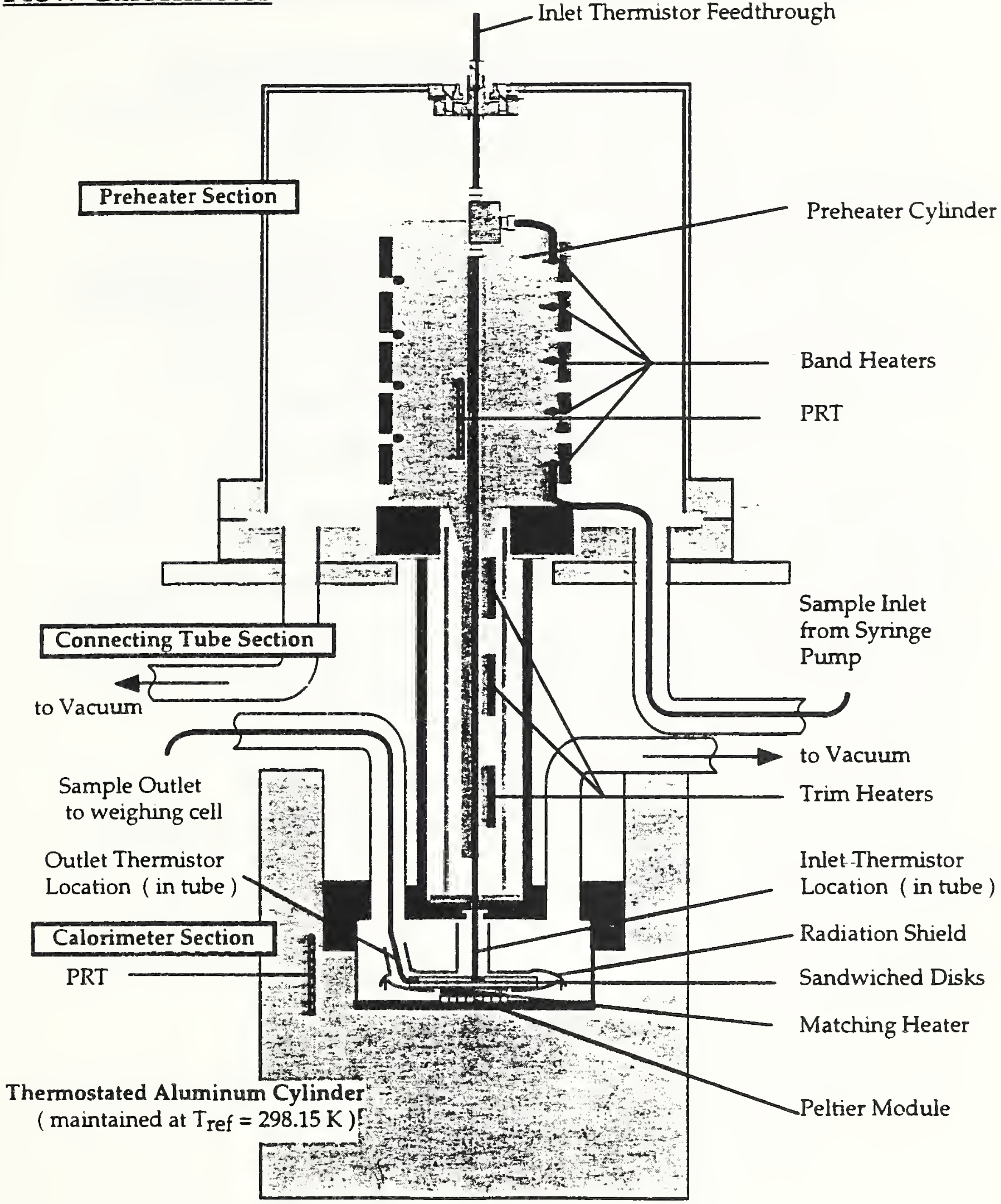
- Principle of operation
  - twin bombs of identical construction and surroundings
  - ramp temperature of sample + spherical bomb (~2K/hr)
  - adiabatic method
  - measure heat input to sample and reference bombs
- Temperature range: 250 – 523 K (furnace) (liquids and dense gases)
- Pressure range: < 20 MPa
- Materials: Inconel 718, 316SS
- $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$

Total Enthalpy (Flow) Calorimeter

enthalpy difference

- Principle of operation
  - precondition fluid to desired temperature
  - measure heat (or cooling) required to bring outlet flow to $T_{reference} = 298.15$ K
  - flow controlled by precision syringe pumps
  - flow rate measured by direct weighing
- Temperature range: 250 – 523 K (furnace)
  (liquids and dense gases)
- Pressure range: < 20 MPa
- Material: 316SS

Flow Calorimeter



High-Temperature Transient Hot-Wire Cell

thermal conductivity, thermal diffusivity

○ Principle of operation
  - electrically heated wire approximates line heat source and also serves as resistance thermometer
  - measure temperature rise as *f*(t)
    slope related to thermal conductivity
    intercept related to thermal diffusivity

○ Temperature range: 223 – 523 K (furnace)

○ Pressure range: ~0.1 – 70 MPa (liquids and gases)

○ Wire materials (and diameters):

bare:	platinum (12 μm)
	tungsten (4 μm)
insulated:	anodized tantalum (25 μm)
	polyimide-coated platinum (12 μm)

○ Cell materials: Hastelloy C, 316SS

Vibrating-Wire Viscometer

viscosity
(under development; expected completion late 1996)
(future provision for density)

- ○ Principle of operation
  - vibration damping of tensioned wire gives viscosity
  - resonant frequency of tensioned wire gives density
- ○ Temperature range: 80 – 500 K (cryostat)
- ○ Pressure range: < 70 MPa
- ○ Materials: 316SS, 440SS, sapphire, Al_2O_3 ceramic, tungsten (wire), Sm-Co (magnets)

  (must plate magnets to measure NH_3/H_2O)

High-Temperature Vibrating-Wire Viscometer

viscosity
(under development; expected completion late 1996)

- ○ Designed for ammonia/water
- ○ Principle of operation
  - vibration damping of tensioned wire
- ○ Temperature range: 300 – 700 K (furnace)
- ○ Pressure range: < 70 MPa
- ○ Materials: 316SS, sapphire, Al_2O_3 ceramic

High-Temperature Burnett Apparatus

pressure-volume-temperature (PVT) relations
(presently inactive)

○ Principle of operation
  - determine sample quantity by expansions (no need to calibrate sample volume)
  - measure P, T along isochores density from expansion information

○ Temperature range: 300 – 873 K (furnace)
(dilute and dense gases)

○ Pressure range: < 35 MPa

○ Material: 316SS

Mixture Preparation Facility

- Principle of operation
  - gravimetric preparation from pure (research grade) components
  - prepare, store, and transfer in single phase
- Major components—vapor mixture facility
  - aluminum cylinders up to 16 L
  - high-vacuum system for evacuating bottles
  - charging manifold
  - double-pan balance (25 kg x 0.005 g)
  - typical composition accuracy ±0.00005 mass frac
- Major components—liquid (NH_3/H_2O) mixture facility
  - diaphragm cells (100 cm^3 capacity)
  - charging pumps and manifold
  - double-pan balance (25 kg x 0.005 g)
  - typical composition accuracy ±0.0002 mass frac

Possibilities for Extended Capabilities

○ Apparatus modifications to lower/higher temperatures
  - Total enthalpy calorimeter to 700 K
  - Twin-cell calorimeter to 700 K
  - Transient hot-wire cell 80 K to 700 K

○ Restart high-temperature Burnette apparatus

○ New apparatus

APPENDIX L.

W. M. HAYNES AND D. FRIEND: SUMMARY OF RESEARCH FACILITIES AND CAPABILITIES FOR AMMONIA/WATER PROPERTIES

Summary of Experimental Research Facilities with Possible Capabilities for Ammonia/Water Mixtures

- **UNITED STATES**
  - NIST
  - University of Delaware (Woods)
  - Texas A&M (Holste)
  - Cornell University (Zollweg and Streett)
  - Colorado School of Mines (Yesavage, Sloan)
  - Wiltec Research (Wilson)
  - Oak Ridge National Laboratory (Palmer, Zaltash)
  - Fluor Daniel, Inc. (Won)

NIST

- **CANADA**
  Memorial University of Newfoundland (Tremaine)
  University of Calgary (Heidemann)

- **GERMANY**
  University of Hannover (Baehr, Tillner-Roth, Harms-Watzenberg)
  University of Karlsruhe (Franck, Bier)
  University of Kaiserslautern (Maurer)

- **GREAT BRITAIN**
  National Engineering Laboratory (Watson)
  Imperial College (Wakeham)
  University of Bristol (Wormald)

- **JAPAN**
  Keio University (Uematsu)

- **RUSSIA** (former Soviet Union)
  Russian Academy of Sciences
  (Zharov, Yaroslavtsev, etc.)
  Dagestan Scientific Center
  (Abdulagatov)
  Moscow Power Institute
  (Alexandrov)

- **NETHERLANDS**
  University of Delft (deLoos, Peters,
  de Swaan Arons)

NIST

- **FRANCE**
  Ecole Nat. Sup. des Mines, Paris
  (Renon)

- **SWEDEN**
  Royal Inst. Technology (Svedberg)

- **Other Laboratories ???**