Peer-Review Publication of State-of-the-Art Thermodynamic Property Measurements Completed by Bartlesville Thermodynamics Group

DE-IA26-02NT15338

Goal

DOE's thermodynamics laboratory in Bartlesville, OK, was closed down and moved to Oak Ridge National Laboratory (ORNL) before part of the data—which had been developed with DOE funding—could be published. This project seeks to review and publish the most critical data. There are extensive data available, and priority for analysis and publication will be placed on those data that are most relevant to today's petroleum and petrochemical industries.

Performer

National Institute of Standard & Technology (NIST)
Boulder, CO

Results

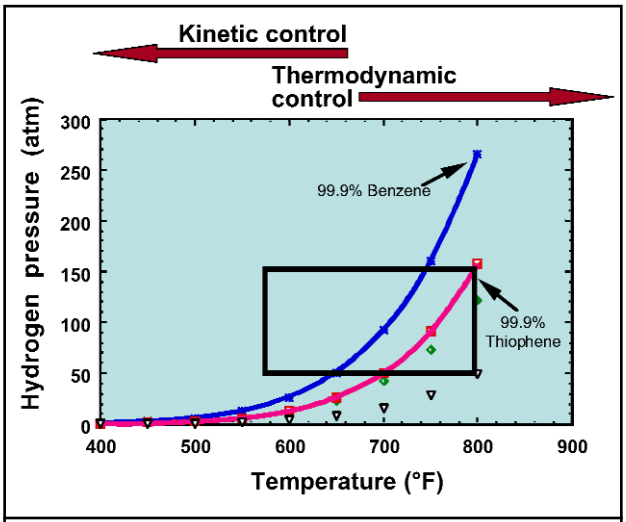
NIST continues to analyze data and reports from previously conducted research and to publish a series of peer-reviewed publications resulting from the thermodynamics research conducted at DOE's thermodynamics laboratory in Bartlesville, OK, before it closed on November 8, 1998. As part of an ongoing program to disseminate the previously acquired thermodynamic data, four publications were completed and published in FY2004, and two were published in FY2005. Two additional papers have been submitted to a refereed journal for consideration for publication.

Benefits

Publication of the thermodynamic property data on series of compounds provides physical-property data upon which chemical processes are designed and processing plants (units) are designed. The heat input, stability, reactivity of chemical compounds defining the boundaries between kinetic and thermodynamic control, and reactions that occur in refineries are examples of the type of benefit that can be obtained from this project. Knowing how chemicals react, their heat of activation, how much heat is required to distill a representative compound, etc., helps process engineers design more-efficient, safer processes and plants. More-efficient plants equate to a lower cost of processing or cleaner products, which benefits the public.

Background

In 1943 a laboratory was established in Bartlesville, OK, by Hugh M. Huffman to measure the thermophysical properties of the components of petroleum, jet fuels, and other strategic chemicals. Over the next 55 years this laboratory established an undisputed world-renowned reputation for the highest-quality measurements on the thermochemical and thermophysical properties of organic and organometallic compounds.



Boundaries between the kinetic and thermodynamic control regions for hydrodesulfurization of thiophenes.

Summary

Results of numerous state-of-the-art thermodynamic-property measurements remained unpublished at the time the laboratory was closed. From the late 1970s until closing of the laboratory, the DOE invested more than $1,000,000 per year in support of this world-class research laboratory. Unpublished results exist for a variety of organic compound types that are key to the production of environmentally acceptable fuels from petroleum. Compound types include saturated and unsaturated aromatic hydrocarbons, as well as their sulfur- and nitrogen-containing analogs. These results will aid the development of new processing technologies through provision of required properties for specific key materials, as well as for numerous related substances, by serving as benchmarks for improved computational chemistry methods, estimations, and correlations.

Part of the work being reported by NIST was done in conjunction with DIPPR (Design Institute for Physical Property Research), the oldest of the America Institute of Chemical Engineers' (AIChE) active Industry Technology Alliances. DIPPR had 36 sponsors from industry and government bodies. Its purpose is to make possible, through joint sponsorship, thermophysical property data measurement, correlation, and dissemination. DIPPR's project steering committees recognized the Bartlesville facility as the only remaining thermodynamics laboratory in the United States with the full-range capability to obtain the type and quality of data required by the sponsors. With the transfer of senior staff and equipment from Bartlesville to the Thermophysical Property Group within the Chemical Technology Separations Group at ORNL, the full-range capability is maintained.

Current Status (February 2007)

Analysis of the research data is anticipated to result in continued publications over the next few years from the previously collected thermodynamic data.

Articles completed and in in-house review at ORNL and NIST to be submitted to peer-reviewed journals in FY2007 include the following topics:

- Thermodynamic properties of aniline and 2,6-dimethylaniline (this work includes new ideal-gas properties computed by the Computational Chemistry Group at NIST in Gaithersburg, MD.
- Thermodynamic properties of 1,2-dihydronaphthalene and hydrogenation equilibria.

Additional articles in preparation in 2007 cover these topics:

- Thermodynamic properties of norbornane.
- Thermodynamic properties of phenanthrene hydrogenation products

Funding

DOE Office of Fossil Energy's Oil & Gas Program funded the National Institute of Standards & Technology to bring the previous work into the public domain. Funding was a one-time grant of $140,000.

Rob Chirico at the adiabatic calorimeter console, circa 1984.

Publications

A historical summary of the Bartlesville Thermodynamics Group is included in Downstream Details, Summer 2003, published by NETL and is available upon request at 918-699-2002.

Steele, W.V., Chirico, R.D., Cowell, A.B., Nguyen, A., Knipmeyer, S.E., "The Thermodynamic Properties of 1,2,3,4-tetrahydrodibenzothiophene, Possible Precursors and Products of Deep Hydrodesulfurization of Gasoline and Distillate Fuels III", J. Chem. Thermodynamics, V. 36, 2004, 497-509.

Steele, W.V., Chirico, R.D., Knipmeyer, S.E., and Nguyen A., "Heat Capacities, Enthalpy Increments, and Derived Thermodynamic Functions for Dicyclohexylsulfide between the Temperatures (5 and 520)K, Possible Precursors and Products of Deep Hydrodesulfurization of Gasoline and Distillate Fuels IV", J. Chem. Thermodynamics, V. 36, 2004, 845-855.

Chirico, R.D., and Steele, W.V., "High-Energy Components of Designer Gasoline and Designer Diesel Fuel I. Heat Capacities, Enthalpy Increments, Vapor Pressures, Critical Properties, and Derived Thermodynamic Functions for Bicyclopentyl between the Temperatures T = (10 to 600)K." J. Chem. Thermodynamics, V. 36, 2004, 633-643.

Chirico, R.D., and Steele, W.V., "The Thermodynamic Properties of 2-methylquinoline and 8-methylquinoline", J. Chem. Eng. Data V. 50, 2005, 697-708.

Chirico, R.D., and Steele, W.V., "The Thermodynamic Properties of Diphenylmethane," J. Chem. Eng. Data, V. 50, 2005, 1052-1059.

Chirico, R.D., and Steele, W.V., "The Thermodynamic Properties of 1,2-dihydronaphthalene, submitted for review and possible publication in the Journal of Chemical & Engineering Data," July 2005

Steele, W.V., and Chirico, R.D., "Studies Related to the Hydrogenation of Phenanthrene. The Thermodynamic Properties of Phenanthrene, 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene." Submitted for review and possible publication in the Journal of Chemical & Engineering Data, July 2005.

Project Start: July 23, 2002
Project End: February 28, 2009

Anticipated DOE Contribution: $140,000
Performer Contribution: $0

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