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FINAL REPORT

THERMODYNAMIC PROPERTIES BY NON-CALORIMETRIC METHODS

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I. SUMMARY

This report summarizes progress on the research project, "Thermodynamic Properties by Non-Calorimetric Methods," which was supported by DOE contract DE-FG05-87ER13758 during its duration; August 1, 1987, through July 31, 1991. Despite staffing problems (see below for details) leading to the need for a one-year no-cost extension to the original schedule, significant progress was made in all of the research areas outlined in the original proposal. Highlights of the research accomplished include:

- Group-contribution parameters for estimation of thermodynamic properties for polycyclic aromatic hydrocarbons and nitrogen-, oxygen-, and sulfur-containing compounds were derived.
 - Provisional group parameters for polycyclic aromatic hydrocarbons (PAH's) were used to confirm a new experimentally determined value for the enthalpy of formation of phenanthrene.
 - Provisional group parameters for polycyclic nitrogen-containing compounds have been reported. The group-contribution terms were used (J. Chem. Thermodynamics publication) to estimate thermodynamic properties for several previously unstudied benzoquinolines.
 - The provisional group parameters for polycyclic aromatic hydrocarbons (PAH's) were used to derive equilibria in the biphenyl/phenylcyclohexane/

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hydrogen system (Topical Report NIPER-403). The conclusions are in agreement with similar comments made by Girgis and Gates⁽¹⁾ in their just published review of catalytic hydroprocessing.

- A method was developed to calculate the kinetic energy expansions as a function of the coordinate for the ring-puckering, ring-twisting (in-phase), and ring-twisting (out-of-phase) vibrations of 9,10-dihydroanthracene and related molecules. (J. Mol. Spectroscopy publication.)
- The developed method was used to calculate the kinetic energy expansions as a function of the coordinate for the ring-puckering, ring-twisting (in-phase), and ring-twisting (out-of-phase) modes for molecules containing large amplitude anharmonic vibrations. (To be submitted to Spectrochimica Acta.)
 - Results are reported for cyclopentene, 2,5-dihydrofuran, 2,3-dihydrofuran, 2,5-dihydrothiophene, and 2,3-dihydrothiophene with thermodynamic properties derived to 1000 K for the first four listed.
 - IR and Raman spectra were obtained and a complete vibrational assignment was made for 2,3-dihydrofuran. (To be published.)
 - It was found that the direct summation of calculated energy levels to obtain the partition function for the vibration must be extended to approximately $10,000\text{ cm}^{-1}$ before the contribution from subsequent levels becomes negligible.
- Successful operation of a long-pathlength, far-infrared sample cell for the collection of vapor-phase spectra of low vapor-pressure compounds (up to three rings) was accomplished. (Previously only one- and two-ring molecules could be studied.)
- A method was developed to predict the vibrational frequencies of two- and three-ring polycyclic molecules to an accuracy sufficient for identifying the fundamental vibrations in experimental spectra.
 - This allowed assignment of vapor spectra for quinoline and isoquinoline and the reliable calculation of their thermodynamic properties. (Submitted to Spectrochimica Acta.)
- Recent research at NIPER has enabled the determination of heat capacities to within 50 K of the critical point for polycyclic compounds. At temperatures close to the critical point, use of the virial equation of state truncated at the second virial term proved to be inadequate for the calculation of ideal-gas entropies for these compounds.

- Research accomplished within this program delineated the significance of the third virial coefficient even at 1 bar pressure.
- A literature correlation for estimation of third virials was shown to be applicable to monoaromatics.

II. INTRODUCTION

This research program provided a valuable complement to the experimental programs currently in progress here at NIPER for the Advanced Research & Technology Development (AR&TD) and Advanced Exploration & Process Technology (AEPT) divisions of the Department of Energy. These experimental programs are focused on the calorimetric determination of thermodynamic properties of key polynuclear heteroatom-containing aromatic molecules. The project for the Office of Energy Research focused on the non-calorimetric determination of thermodynamic properties through the extension of existing correlation methodologies and through molecular spectroscopy with statistical mechanics.

When this project started, the IITRI/NIPER Thermodynamics group contained two staff members competent in the measurement and interpretation of IR and Raman spectra and the calculation of ideal-gas thermodynamic properties via statistical thermodynamics. Within the first year of the project, Dr. William B. Collier accepted a professorship at Oral Roberts University in Tulsa and left the group. Then, as the end of the second year of the project approached, the other spectroscopist, Dr. M. Michael Strube, accepted an appointment within the computing department of Phillips Petroleum Company.

Two attempts to replace one of the two positions were made during the third and fourth years of the project. These attempts included advertising nationally via C&E News. Each attempt produced over 80 responders to the advertisements. However, in the first search no applicant was remotely qualified in the areas of interpretation of IR and Raman spectra or the calculation of ideal-gas thermodynamic properties via statistical thermodynamics. The major research area of most of the applicants was vapor-liquid equilibria (VLE) measurements on binary organic mixtures.

The second search did produce some applicants with backgrounds in thermodynamic property measurements other than VLE. Dr. Timothy D. Klots was selected to

fill the vacant position. Dr. Klots, who joined the staff at NIPER in May 1991, has a strong background in microwave spectroscopy obtained both at the University of Illinois and Argonne National Laboratory.

III. GROUP-CONTRIBUTION APPROACH FOR PAH's

1. Background

The goal of any group-contribution method is the accurate estimation of a given compound property such as heat capacity, density, enthalpy of formation, vapor pressure, etc., based on as small a data base as possible for structurally and chemically related molecules. The properties of primary interest in this research program were the enthalpy of formation, the absolute entropy, and the heat capacity; all for the ideal-gas state. These are the properties which allow calculation of the Gibbs free energies of formation as a function of temperature. Knowledge of the Gibbs free energies of formation for the products and reactants for any reaction allows calculation of the equilibrium constant without further experimentation. Such calculations are invaluable in the development and optimization of chemical processes.⁽¹⁾ Also, equilibrium calculations are used as part of reaction studies to aid in the interpretation of product slates, catalyst comparisons, and reaction modeling.

The existing thermodynamics data base for organic materials is structured toward the processing of light petroleum. Many important chemical differences exist between light petroleum and other fossil materials such as oil shale, heavy petroleum, and the liquids derived from the liquefaction of coal. In their present state, group-contribution methods are ineffective in providing needed thermodynamic property estimates for the highly aromatic, and often heteroatom-containing, compounds which underlie the chemical differences.⁽¹⁾ In this project, two approaches were used to improve the efficacy of the group-contribution approach to thermodynamic property estimation. In the first, the applicability of the group-contribution methodology was broadened via the development of estimation parameters, which were previously non-existent or poorly defined, for polynuclear aromatics and their hydrogenation products. In the second approach, the reliable application of group-contribution methods to high temperatures was facilitated through application of statistical mechanics, based on the molecular spectroscopy of key monocyclic molecules. The monocyclics form the

foundation for the group-contribution method for polycyclic systems. The two approaches were complementary, and highlights of the results of the studies in both areas are presented below.

The present set of group-contribution parameters are defined and quantified in references 2, 3, and 4. The group parameters for polycyclic aromatic hydrocarbons (PAH's) were published in 1977 by Benson and co-workers and are based on thermodynamic data for five compounds: naphthalene, phenanthrene, anthracene, pyrene, and triphenylene.⁽⁴⁾ The approach taken in the derivation of the group parameters was fraught with difficulties due to the limited data base within which the authors were restricted. The principal difficulty involved evaluation of the experimental ideal-gas entropies and enthalpies of formation at 298 K upon which the correlation was based. Determination of these quantities requires vapor pressures and enthalpies of sublimation at 298 K to calculate the effect on the thermal functions of vaporizing the sample to the ideal-gas state and compressing it to the standard state pressure of 101.325 kPa. Vapor pressures for PAH's are extremely low at 298 K and consequently are poorly known. In undertaking a revision of the group-contribution parameters for PAH's, a study was made to determine *exactly* what was known for each of the "key" structures used to define the individual parameters. A summary of the results of the study follows.

2. Knowledge Gaps for PAH's Prior to This Project

a) Naphthalene

There is a 50 percent range in the sublimation pressures of naphthalene at 298.15 K reported in the literature (see reference 5). The thermodynamic functions for naphthalene given in reference 6 appear to have been force-fitted to an enthalpy of sublimation value obtained by Morawetz.⁽⁷⁾ The entropy quoted at 400 K is 0.4 percent different from that obtained in reference 5. Liquid-phase heat capacities for naphthalene reported in the literature⁽⁸⁾ only span a 20 K range prohibiting any accurate extrapolation to higher temperatures. Vapor pressures of naphthalene above its melting point (see reference 5) were as discordant as those for the solid phase.

b) Phenanthrene

A comparison of thermodynamic equilibria calculated using calorimetric data for the phenanthrene/9,10-dihydrophenanthrene/1,2,3,4-tetrahydrophenanthrene with experimentally (in a batch reactor) determined values⁽⁹⁾ was made in NIPER-247.⁽¹⁰⁾ The results indicated the possibility of an error of $-4.5 \text{ kJ}\cdot\text{mol}^{-1}$ in the enthalpy of formation of phenanthrene.

c) Anthracene

The ideal-gas phase thermodynamic properties of anthracene are not well defined at any temperature due to the absence of reliable vapor-pressure data for the liquid phase and the availability of liquid-phase heat capacities over only a 10 K range.^(5,11)

d) Pyrene

The ideal-gas phase thermodynamic properties of pyrene are not well defined at any temperature due to the absence of reliable vapor-pressure data for the liquid phase and the availability of liquid-phase heat capacities over only a 60 K range.^(5,12,13)

3. Research to Fill the Gaps

a) Naphthalene

Since the initial study, a new set of accurate vapor-pressure measurements in the temperature range 418 to 613 K (14 kPa to 865 kPa) has been reported by Ambrose et al.⁽¹⁴⁾ In addition NIPER's recent work (funded by DOE ARL research program) in the development of a differential-scanning-calorimetric (DSC) method to measure two-phase heat capacities to temperatures approaching the critical point⁽¹⁵⁾ has led to the determination of the critical properties $\{T_c$, and p_c directly with P_c obtained by the fitting procedure} for a range of compounds. That methodology was applied to naphthalene resulting in the determination of C_{sat} heat capacities for the liquid phase from the melting point to within 50 K of the critical point.

b) Phenanthrene

Within a project jointly funded by DOE/Fossil Energy and DIPPR (Design Institute for Physical Property Data funded by chemical industry and administrated by AIChE), the standard enthalpy of formation of phenanthrene was redetermined at NIPER.⁽¹⁶⁾ The new enthalpy of formation bears out the assertion made above that the literature value was in error. The new value obtained for the enthalpy of formation of phenanthrene at 298.15 K was 201.2 ± 4.7 kJ·mol⁻¹.

The DSC method was used to determine two-phase heat capacities to 800 K. Rapid decomposition at temperatures greater than 820 K precluded direct determination of either the critical temperature, T_c , or the critical density, ρ_c , but by using the method of rectilinear diameters, both have been estimated from the experimental measurements. Saturation heat capacities in the liquid phase from the melting point to within 50 K of the critical point (920 K) was derived from the results.

c) Pyrene

Liquid-phase vapor-pressure measurements in the temperature range 504 to 668 K (2 kPa to 101.325 kPa) were obtained at NIPER as part of a project funded by Exxon Research & Engineering to measure vapor pressures of a range of aromatic compounds. The DSC method was used to determine two-phase heat capacities to temperatures approaching the critical point. Rapid decomposition at temperatures greater than 820 K precluded direct determination of either the critical temperature, T_c , or the critical density, ρ_c , but using the method of rectilinear diameters, both were estimated from the experimental measurements. Saturation heat capacities for the liquid phase from the melting point to within 50 K of the critical point were derived from the results.

d) Anthracene

A different approach is being followed to solve the problems with the accurate determination of the thermodynamic properties of anthracene. A decision was made to deduce the properties of the parent aromatic hydrocarbon from the thermodynamic properties of a dimethylantracene. The dimethylantracenes have much lower melting points than the parent compound, which eliminates most of the experimental difficulties associated with anthracene. The contributions of the methyl groups to the results can be calculated accurately and removed. This research is funded within the DOE AEPT research program, and the synthesis of 1,3-dimethylantracene is in progress.

4. Application of the Results

a) General

A provisional set of group-contribution parameters applicable to polycyclic aromatic compounds have been derived from the available results. The provisional set are not yet defined sufficiently to be applicable across the entire range of polycyclic aromatics (see Table 2 below for a listing of the group-contribution parameters). However, as described below, within some areas the new group-contribution parameters were used to estimate thermodynamic functions for reaction schemes of interest within projects funded by DOE/Fossil Energy.

b) 3-Methylphenanthrene

Although the redetermination of the energy of combustion of phenanthrene seemed to reconcile the discrepancy between the calorimetric and experimental equilibria (batch reaction/analysis) for the phenanthrene/hydrogen system, a further test of the calorimetric values was needed. Within the ARL DOE/Fossil Energy research program at NIPER, measurements of the thermodynamic properties of 3-methylphenanthrene were

completed. The results helped confirm the derived group-contribution parameters for the non-calorimetric determination of thermodynamic properties for molecules containing phenanthrene-type structural entities. Table 1 compares the ideal-gas entropies at 400 K and 500 K and the ideal-gas enthalpy of formation at 298.15 K for 3-methylphenanthrene derived using the provisional group-contribution parameters with the calorimetric values. The excellent agreement confirms validity of the thermodynamic properties for phenanthrene used in this research.

Table 1. Comparison of predicted and calorimetrically determined ideal-gas entropies at 400 K and 500 K and the ideal-gas enthalpy of formation at 298.15 K for 3-methylphenanthrene. ($R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $p^\circ = 101.325 \text{ kPa}$)

T / K	S_m° / R		Δ / R
	Predicted	Experimental	
400	61.15	61.10 ± 0.10	0.05
500	69.44	69.30 ± 0.12	0.14

$\Delta_f H_m^\circ (\text{C}_{15}\text{H}_{12}, \text{g}, 298.15 \text{ K})$	
predicted	observed
170.0 $\text{kJ}\cdot\text{mol}^{-1}$	$171.22 \pm 1.04 \text{ kJ}\cdot\text{mol}^{-1}$

c) Benzoquinolines

Provisional group parameters for polycyclic nitrogen-containing compounds were reported by NIPER in reference 17 (Exhibit 1 enclosed). The group-contribution terms were used to estimate thermodynamic properties for 5,6- and 6,7-benzoquinoline, a reaction scheme for the formation of the benzoquinolines was outlined, and the mole fractions of the isomers were estimated for the reactions proceeding under thermodynamic control.

d) Biphenyl/Hydrogen System (NIPER-403 Exhibit 2 enclosed)

Biphenyl is representative of the least reactive aromatic hydrocarbons present in heavy crude oils. Biphenyl is also one of the major products in the hydrogenolysis of fluorene, dibenzothiophene, dibenzofuran, and carbazole-type ring structures. These

ring structures are representative of the heteroatom-containing compounds present at increased levels in the heavier feedstocks. In the absence of experimentally measured thermodynamic properties for both phenylcyclohexane and bicyclohexane, values were estimated using the group-contribution approach. Experimental (i.e., batch reaction/chemical analysis) equilibria measurements for the biphenyl/hydrogen system are available in the literature. Hence, comparison of these experimental equilibria measurements with values calculated using group-contribution parameters provided an excellent opportunity to demonstrate the applicability and present limitations of the estimation techniques for a hydroaromatic system.

For the biphenyl/phenylcyclohexane/bicyclohexane/hydrogen system the experimental equilibrium conditions and those calculated using values derived, in part, from group-contribution parameters agreed within their combined uncertainty intervals; however, the uncertainty intervals for both determinations were broad. By having to estimate only ideal-gas entropies for phenylcyclohexane and bicyclohexane, sufficient precision was retained to justify comparison with the experimental equilibria. If ideal-gas enthalpies of formation were unavailable as well, the uncertainties in the estimates would be too large for meaningful interpretation. Therefore, the report concludes that an order of magnitude improvement in the group-contribution methodology (i.e., a significant but realizable improvement in the accuracy and precision of the group-contribution parameters) is required to enable useful calculation of the conditions under which thermodynamic equilibria exist in the hydrogenation of multi-ring aromatic systems.

Girgis and Gates⁽¹⁾ in their very recent (i.e., 1991) review of high-pressure catalytic hydroprocessing agree with the conclusions given in NIPER-403. To quote:

"It would be of great value to obtain correlations indicating equilibrium concentrations of species at different temperatures and hydrogen partial pressures for representative one-, two-, three-, and four-ring aromatic hydrocarbons and selected sulfur, nitrogen, and oxygen compounds. Such correlations could be used to determine accurately hydrogen partial pressure effects on the equilibrium position at conditions representative of industrial practice. **The estimates that can now be obtained with group contribution methods are too crude for design or modelling purposes.**" (Our highlighting.)

5. Future of the Research

The research accomplished under this OER program lays a sound foundation for the attainment of group-contribution parameters which will allow the accurate

estimation of the ideal-gas thermodynamic properties necessary for calculation of equilibria in systems containing PAH's. Table 2 lists the relevant group-contribution parameters. The $C_b-(C_{bf})(C_b)_2$, and $C_b-(C_{bf})_2(C_b)$ groups will require measurements on 1-phenylnaphthalene and 9-phenylanthracene, respectively. Measurements on both these compounds are included in the DOE/AEPT Fossil Energy Heavy Oil research program plans for FY92. Upon completion of the calorimetric measurements on both compounds, a topical report/journal article will be published listing the group-contribution parameters for entropy, heat capacity, and enthalpy of formation. The parameters for entropy and heat capacity will be listed at temperature intervals between 300 K and 800 K to give maximum benefit to researchers modeling such systems over the range of temperature encountered in processing within the petroleum and chemical industries.

Table 2. Listing of the group-contribution parameters necessary for the estimation of the thermodynamic properties of PAH's

$C-(C_b)(H)_3$	$C_b-(C_b)_2(C)$
$C-(C_b)(C)(H)_2$	$C_b-(C_b)_3$
$C-(C_b)(C)_2(H)$	$C_b-(C_b)(C_{bf})(H)$
$C-(C_b)(C)_3$	$C_b-(C_{bf})_2(C)$
$C-(C_b)_2(C)_2$	$C_b-(C_{bf})_2(C_b)$
$C-(C_b)_2(C)(H)$	$C_b-(C_{bf})(C_b)_2$
$C-(C_b)_2(H)_2$	$C_b-(C_{bf})_2(H)$
$C-(C_b)_3(C)$	$C_b-(C_b)(C_{bf})(C)$
$C-(C_b)_3(H)$	$C_{bf}-(C_{bf})(C_b)_2$
$C-(C_b)_4$	$C_{bf}-(C_{bf})_2(C_b)$
$C_b-(C_b)_2(H)$	$C_{bf}-(C_{bf})_3$

IV. GROUP-CONTRIBUTION APPROACH FOR KEY MONOCYCLIC ORGANIC COMPOUNDS

Figure 1 depicts the structural relationships between polycyclic aromatic heteroatom-containing compounds which contain a five-membered ring. These ring structures are prevalent in alternate fossil fuel sources (heavy petroleum, oil shale, tar sands, and the products of the liquefaction of coal). The NIPER thermodynamic property data base contains values for the ideal-gas enthalpies of formation and entropies for a large majority of the compounds shown. However, particularly for the monocyclic compounds, the calorimetric measurements do not extend above approximately 400 K. Application of the group-contribution scheme to two- and three-ring systems requires accurate knowledge of the groups derived from the monocyclics over a range of temperature (to at least 700 K) much greater than the extant calorimetric measurements. Molecular spectroscopy and statistical mechanical calculations would make extension to high temperature possible, if such calculations also reliably reproduced the available low-temperature calorimetric measurements.

In order to calculate ideal-gas thermodynamic properties of a compound via statistical mechanics, a complete vibrational assignment of the molecule is needed. Low-frequency, large-amplitude vibrations such as ring-puckering, bending, or twisting require additional detailed analysis to determine the form of the potential functions that describe these vibrations. Since some of these vibrations are highly anharmonic and make a significant contribution to the thermodynamic properties of the molecules, a direct summation of the energy levels for these vibrations is necessary.

In collaboration with Professor Jaan Laane of Texas A&M University, vector-based computer programs were written to calculate the kinetic energy (reciprocal reduced mass) expansions as a function of the coordinate for the ring-puckering, ring-twisting (in-phase) and ring-twisting (out-of-phase) vibrations of 9,10-dihydroanthracene. The same programs also permit the kinetic energy expansions for all three vibrations to be calculated for smaller molecules including 1,4-cyclohexadiene and 1,4-dioxo-cyclohexa-2,5-diene. The kinetic energy expansion for the ring-puckering vibrations of 1,4-cyclohexadiene, used along with a harmonic ring-puckering potential with a small quartic term, quantitatively accounts for the observed far-infrared spectra. The potential energy function for 1,4-cyclohexadiene calculated from Allinger's MM2 molecular mechanics program⁽¹⁸⁾ does a remarkable job in predicting the ring-puckering frequencies when the calculated reduced mass expansion is used. Although the anharmonicity predicted by the molecular mechanics potential is in the

Figure 1 5-Membered ring systems under study

wrong direction, the results are much better than could have been anticipated since the MM2 program was not optimized for generation of vibrational frequencies. The kinetic energy expansions for the puckering and twisting vibrations of 1,4-dioxacyclohexa-2,5-diene and 9,10-dihydroanthracene have also been used in conjunction with potential functions to help analyze the observed spectra for these molecules. Exhibit 3 is a reprint of the journal article describing this work.

Exhibit 4 is a draft of a paper to be submitted to *Spectrochimica Acta* on the effect of large-amplitude ring-puckering vibrations on the thermodynamic properties of monocyclic compounds. The paper collects together various literature discussions of large-amplitude ring-puckering vibrations in cyclopentene, 2,5-dihydrofuran, 2,3-dihydrofuran, 2,5-dihydrothiophene, and 2,3-dihydrothiophene. The existence of complete vibrational assignments for the first four of these compounds enabled derivation of the thermodynamic properties to 1000 K. (For 2,3-dihydrofuran, the complete vibrational analysis was obtained at NIPER and summary details are included.) Results of the study showed that in the calculation of the thermodynamic functions, ring-puckering contributions should not be determined using a harmonic potential function. It was also shown that, although use of kinetic energy expansions in calculating the ring-puckering energy levels does improve the quality of the spectral fit, they make only minor effects on the calculated thermodynamic functions when compared to a model with constant reduced mass. Significantly, it was found that the direct summation of calculated energy levels to obtain the partition function for the vibration must be extended to approximately $10,000\text{ cm}^{-1}$ before the contribution from subsequent levels becomes negligible. The paper also shows that there is excellent agreement between the calorimetric thermodynamic functions and those calculated therein within the narrow range of the former. A more complete test would require a wider set of vapor pressures and measurement of saturation heat capacities above 350 K for cyclopentene.

V. MOLECULAR SPECTROSCOPY AND STATISTICAL MECHANICS

1. Equipment Development

One of the limiting factors in the derivation of thermodynamic properties from spectroscopic information is the collection of vapor-phase, far-infrared spectra. NIPER's previous efforts have focused on heating commercially available, multipass, long-pathlength vapor cells. Maintaining alignment of these multipass cells at the

elevated temperatures necessary for polynuclear compounds has been a major problem. Maintaining an even temperature distribution in these vapor cells, not originally designed to be heated, has also been troublesome. To circumvent these problems, a new design was employed in the construction of a far-infrared vapor cell.

It has been found that far-infrared radiation propagates down long lengths of copper tubing with minimal energy losses. An 8-foot length of 1-inch diameter copper tubing with suitable windows at either end was coupled to the laboratory's Digilab FTS-20E FTIR infrared spectrometer as an external gas-sampling cell. Two mirrors were used to shape and direct the far-infrared radiation down the length of the tube, with a liquid helium-cooled bolometer detector mounted at the far end of the cell. This cell was used in the successful collection of vapor-phase, far-infrared spectra of 3,4-dihydro-2H-pyran.

The high-temperature capabilities of this new cell were demonstrated in the collection of vapor-phase, far-infrared spectra of 3-methylphenanthrene at 475 K. The single-crystal silicon windows used in the high-temperature cells begin to absorb the far-infrared radiation at higher temperatures, limiting usefulness to below 500 K. The primary advantages of this new cell over the commercial cells used previously are greater energy throughput and vastly simpler alignment. Temperature gradients are also less in a copper tube than in a combination glass/aluminum cell. This new cell represents a significant advancement in the high-temperature, vapor-phase, far-infrared capabilities of this laboratory.

The work on 3,4-dihydro-2H-pyran and 3-methylphenanthrene was terminated when the staffing problems delineated above happened. In both cases, full vibrational assignments await further measurements, particularly that of the Raman spectra.

2. Developments in Interpretation and Assignment of Spectra

A method (Exhibit 5) was developed to predict the vibrational frequencies of two- and three-ring polycyclic molecules to an accuracy generally sufficient for identifying the fundamental vibrations. The predicted frequencies are *not of sufficient accuracy to allow the direct statistical calculation of ideal-gas thermodynamic properties*, but serve as a valuable aid in assigning experimental spectra. The scaled internal coordinate method of Pulay and co-workers⁽¹⁹⁾ was applied to force constants calculated with the Austin Method 1 semi-empirical Hamiltonian.⁽²⁰⁾ The technique was applied to benzene, furan, and pyrrole to generate a set of scale factors that allowed the prediction of the vibrational spectra for benzofuran and indole. The predicted

frequencies had root mean squared deviations of roughly 20 cm^{-1} from the observed frequencies. Exhibit 6 is a journal article describing the application of this technique to the vibrational assignment of quinoline and isoquinoline.

VI. THERMOPHYSICAL PROPERTY CORRELATIONS

Recent research at NIPER has provided the means to determine by calorimetric methods ideal-gas thermodynamic properties from near the triple-point temperature to within 50 K of T_c for polycyclic molecules such as biphenyl^(15d), dibenzofuran⁽²⁰⁾, benzo[b]thiophene⁽²¹⁾, dibenzothiophene⁽²²⁾, and 2-aminobiphenyl.⁽²³⁾ In that research the critical temperature and critical density were determined experimentally and the critical pressure was derived.^(15a,15d) Excellent accord with reliable literature values for biphenyl were reported.^(15d)

At high temperatures/high pressures, the virial equation truncated at the second virial term proved to be inadequate in the calculation of ideal-gas thermodynamic properties (see NIPER-360^(15a)). However, little is known about virial coefficients (even second virials) for molecules of the size studied at NIPER. A literature search revealed a corresponding states correlation for the estimation of third virial coefficients. Research tested the applicability of this correlation to monoaromatics.

Figures 4 and 5 of Exhibit 7 show the differences between the calorimetric and spectroscopically derived ideal-gas entropies for benzene and methylbenzene. Differences are shown for three different calculations of the calorimetric values: 1) without consideration of gas imperfection (i.e., virial coefficients are ignored), 2) with the second virial coefficient alone, and 3) with the second and third virial coefficients included in the calculations.

Several generalizations can be drawn from the figures. Failure to include the effects of gas imperfections leads to significant errors starting at approximately $T/T_c = 0.5$. Inclusion of the second virial coefficient is sufficient for calculations to $T/T_c = 0.8$, while excellent accord between the spectroscopic and calorimetric ideal-gas is achieved to above $T/T_c = 0.9$, if the third virial coefficient estimates are included.

Gas-imperfection effects impact two terms in the summation used to calculate the calorimetric ideal-gas entropy; the entropy of vaporization and the entropy of compression. Figure 6 of Exhibit 7 shows how these terms are affected by the inclusion of the second and third virial coefficients in the calculations for methylbenzene. The analogous plot for benzene is nearly identical to figure 6. The effects are opposite in

sign, but, because the corrections to the entropy of vaporization larger, there is a net reduction in the calculated ideal-gas entropy when the virial coefficients are included.

Figure 7 of Exhibit 7 shows the percentage change in the entropy of vaporization calculated with the Clapeyron equation, if, 1) the vapor is assumed to be ideal, and, 2) if the second virial coefficient alone is used in the calculation of the molar volume of the vapor. Changes are plotted relative to values calculated with the second and third virial coefficients. **The figure shows that inclusion of the third virial coefficients has a significant impact on the calculated entropies of vaporization for pressures as low as 1 bar.**

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2. Steele, W. V.; Chirico, R. D. *Thermodynamic Equilibria in the Biphenyl/Hydrogen System.* NIPER-403, July **1989**. NTIS DE89000754.
3. Strube, M. M.; Laane, J. *Reduced mass calculations, low-frequency vibrations, and conformations of 1,4-cyclohexadiene, 1,4-dioxacyclohexadiene-2,5, and 9,10-dihydroanthracene.* *J. Mol. Spectrosc.*, **1988**, 129, 126.
4. Collier, W. B.; Gammon, B. E.; Strube, M. M. *Far-Infrared Spectra, Raman Spectra, and Vibrational Analysis for Quinoline and Isoquinoline.* Submitted to *Spectrochimica Acta*, August **1991**.
5. Collier, W. B.; Strube, M. M.; Klots, T. D. *The Effect of Large Amplitude Ring-Puckering Vibrations on the Thermodynamic Properties of Single Ring Compounds.* Submitted to *Spectrochimica Acta*, September **1991**.
6. Steele, W. V.; Chirico, R. D. *Reconciliation of Calorimetrically and Spectroscopically Derived Thermodynamic Properties at Pressures Greater Than 1 Bar for Benzene and Methylbenzene; The Importance of the Third Virial Coefficient.* In draft form; to be submitted to *Ind. Eng. Chem. Res.*, October **1991**.
7. Collier, W. B.; Strube, M. M.; Klots, T. D. *A Complete Assignment of the Fundamental Vibrations of 2,3-Dihydrofuran.* In preparation for submission to *Spectrochimica Acta*, October **1991**.

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1. Chirico, R. D.; Steele, W. V. *The Group Additivity Method of Thermodynamic Property Estimation*. Presented at the 43rd Calorimetry Conference, Bartlesville, Oklahoma, August 9-12, 1988.
2. Collier, W. B.; Strube, M. M. *The Effect of Large-Amplitude Molecular Vibrations on the Thermodynamic Properties of Monocyclic Molecules*. Presented at the 43rd Calorimetry Conference, Bartlesville, Oklahoma, August 9-12, 1988.
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Exhibits

1. Steele, W. V.; Chirico, R. D.; Hossenlopp, I. A.; Nguyen, A.; Smith, N. K.; Gammon, B. E. *The Thermodynamic Properties of the Five Benzoquinolines*. *J. Chem. Thermodynamics*, **1989**, 21, 81.
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