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Technical Activities 1986 Chemical Thermodynamics Division

S. Abramowitz, Chief

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Labroatory
Center for Chemical Physics
Chemical Thermodynamics Division
Gaithersburg, MD 20899

November 1986

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ABSTRACT

This report summarizes the technical activities of the NBS Chemical
Thermodynamics Division during the Fiscal Year 1986. The activities of the
Division include research on: thermodynamic properties of enzyme - catalyzed
reactions, DSC standards for biological systems, computer modeling of phase
transitions of biomolecules, determination of the structure of proteins and
nucleic acids using x-ray and neutron diffraction, combustion bomb calorimetry
of pure substances, mass balances of chlorine during combustion processes,
high temperature heat capacity measurements, evaluation of the thermochemistry
of calcium and iron compounds, preparation of JANAF Thermochemical Tables, and
automation of Data Center procedures. A listing is provided of publications
and talks given by the Division staff.

Staff of the Chemical Thermodynamics Division

S. Abramowitz, Chief

B. Wiest, Secretary

Biothermodynamics

S. Abramowitz, Group Leader
E. Gajewski
R. Goldberg
W. Kirchhoff
T. O'Leary 1
Y. Tewari
F. Schwarz
A. Shrake 1
D. Steckler 2

Biomolecular Structure

A. Wlodawer, Group Leader
G. Gilliland
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M. Miller 1
J. Nachman 1
H. Savage 7
I. Weber

Thermodynamic Measurements

E.S. Domalski, Group Leader
T. Buckley
M. Bruce 7
M. Burns 2
K. Churney
J. Colbert
E. Diaz 6
D. Ditmars
D. Kirklin
A. Ledford
J. Rukkers 1
S. Sung 2
T. Celano 2

Thermodynamic Data Centers

M. Chase, Group Leader
S. Aronson 2
D. Bickham 5
J. Dill 2
D. Garvin
P. Fagan 7
E. Hearing 4
C. Jackson
T. Jobe
W. King
R. Nuttall 4
V. Parker
R. Schumm 4
D. Smith-Magowan
D. Wagman 1
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R. Wood 6
N. Young 4

1 Guest Worker
2 Summer Student
3 NRC Fellow
4 Contractor
5 Part-time
6 WAE
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CHEMICAL THERMODYNAMICS DIVISION

S. Abramowitz, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1986

1.   INTRODUCTION

A.   Objectives

Chemical Thermodynamics provides measurement techniques, concepts and data on the energetics and equilibria of chemical processes. Chemical thermodynamics is used to predict equilibria in chemical reactions, thermodynamic properties of high temperature refractory materials and gases, activities of aqueous solutions used in technologies varying from power generation and electrorefining to biotechnology. This division develops the models necessary for correlating structure with thermodynamic properties, develops the science of calorimetry in order to obtain precise data from the microwatt to megawatt levels, carries out precise thermodynamic measurements, including those on Standard Reference Materials, develops the measurement capabilities for molecular structure determinations and critically evaluates thermodynamic data in all phases for the use of industry, government and academia. A current emphasis is directed towards the needs of the emerging biotechnology industry. In particular, this division is developing the measurement and computational techniques for obtaining biomolecular structures of proteins, enzymes, enzyme-substrate complexes and DNA species using x-ray and neutron diffraction. The thermochemistry of generic processes of interest to biochemistry and biotechnology are being studied in order to develop standards and provide key data, to develop quantitative models for the energetics of these processes and estimation schemes of demonstrated reliability for the concomitant thermodynamic properties. A new effort is being launched in the coming year aimed at correlating structure and function for proteins. This research will coordinate with the biothermodynamics and biomolecular structure efforts in order to develop structure-function-energetics correlations.

The objectives of the Chemical Thermodynamics Division include:

o Application of the science of calorimetry to the needs of existing and new technologies through the design of novel calorimeters and the development of improved procedures to obtain enhanced measurement precision and accuracy.

o Development and certification of Standard Reference Materials for the use of existing and emerging technologies.

o Measurement of the thermochemical properties of key chemical species and processes including bioprocesses and phase transitions of aqueous biomolecular species.

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o Provision of critically evaluated compilations of the thermodynamic properties of inorganic, organic and bioorganic compounds in the gaseous, liquid, solid and aqueous phases.

o Development of estimation schemes for the prediction of thermodynamic properties of organic, inorganic, and bioorganic species in the gaseous, liquid, solid and aqueous phases.

o Development of measurement and computational methodology for the determination of the structure of biomacromolecular species using the techniques of x-ray and neutron diffraction.

In achieving these objectives Division scientists are encouraged to be aware of and to respond to the needs of industry, government and academic institutions for measurement standards, accurate data and concepts in the field of thermodynamics.

B.   Organization and Staff

The Chemical Thermodynamics Division has four groups. An additional group has been organized, this year, under the leadership of Alex Wlodawer to guide the growth in the biomolecular structure group. Malcolm Chase has assumed the leadership of the Chemical Thermodynamic Data Centers Group, which includes the Chemical Thermodynamics Data Center and Electrolyte Data Center. Dr. Chase has extensive industrial experience in the evaluation of chemical thermodynamic data for both industrial and military technologies. He brings to this position an awareness of the needs of these technologies and will make the products of this group more responsive to those needs. Dr. Chase will also continue his activity as the director of the JANAF Thermochemical Data Project. This change in leadership will allow David Garvin to devote all his energies to the evaluation of chemical thermodynamic data in support of national and international data evaluation programs. The group structure is

o Biothermodynamics, S. Abramowitz, Group Leader

o Biomolecular Structure, A. Wlodawer, Group Leader

o Chemical Thermodynamics Measurements, E.S. Domalski, Group Leader

o Chemical Thermodynamic Data Centers, M.W. Chase, Group Leader

The division has 26 full-time staff, 1 part-time employee, 6 guest workers, 7 students, 5 contractors and 1 consultant. This fiscal year two additional members have joined the Biomolecular Structure Group. Dr. Gilliland will be continuing work he began elsewhere on the maintenance and development of a computer based database for the crystallization of biomolecular species and will conduct research in biomacromolecular structure and on means to systemize the crystallization of proteins and other biomolecular species. Dr. Weber will conduct research on evaluating the effects of selected mutations on the structures of proteins and protein-substrate complexes. In addition the group has a postdoctoral associate, three guest workers and a technician. Funds for one guest worker and the technician are being provided by the Center for Advanced

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Research in Biotechnology (CARB) to support research of mutual interest. This group has acquired state-of-the-art computing and x-ray detector equipment in the last year. It also has access to additional equipment through its collaboration with others including CARB and Genex.

Additional expansion is planned for FY87 in the area of protein structure-function studies. A laboratory will be refurbished for molecular biology work and will be used for protein synthesis and for the investigation of the effect of changes in protein structure on function. It is expected that this new activity will involve close collaboration with the biothermodynamics and biomolecular structure programs.

The division participates in the work of the Office of Standard Reference Data and the Office of Standard Reference Materials. In support of the Standard Reference Data program, the Chemical Thermodynamics Data Centers group evaluates thermochemical data for organic and inorganic species, develops database management systems for chemical thermodynamics, and develops critically evaluated data and reliable estimation schemes for organic and biochemical species. In support of the Standard Reference Materials program, the Thermodynamics Measurements Group maintains standards for oxygen bomb and heat capacity calorimetry and develops new standards as needed. Benzoic acid is a best seller of the Standard Reference Material Program. It is responsible for converting the chemical system of measurements to the electrical system and is used to calibrate combustion bomb calorimeters for the fuel industry, power generation industry and in bomb calorimeter research laboratories.

The research needs of two federal agencies and one industrial trade association are being addressed by the division. We receive funding from the Department of Energy for determining the chlorine content of municipal solid waste and optimizing conditions for the formation and destruction of chlorinated organic species, and for the development of thermodynamic data for flue gas clean-up in fossil fuel technology. Programs being pursued for the Department of Defense include the provision of combustion calorimetric data and estimation methods for the thermodynamic and related properties of organic phosphorus compounds and development of thermodynamic functions for species of importance to high temperature technologies including rocketry, reentry, and energy production. We are developing computer algorithms for aqueous thermodynamics and providing annotated bibliographies for the sources of the data for the Design Institute for Physical Property Data (DIPPR), which is sponsored by AIChE. We have finished the revision of a previous publication on the thermodynamic data for biomass and waste incineration in cooperation with the Solar Energy Research Institute (SERI).

In addition to the interactions which we have with other NBS programs and federal agencies the division cooperates with other NBS units. Within CCP we have a joint program with the Chemical Kinetics Division on database managment systems, with both the Chemical Kinetics and Spectroscopy Divisions in developing and carrying out a research program in support of the high temperature technology needs of AFOSR and with the Surface Science Division in developing computer algorithms for the interpretation of sputtering depth profiles.

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Within NML we are cooperating with the Center for Analytical Chemistry on several programs in the area of biotechnology including the thermodynamics characterization of monoclonal antibody antigen interactions and the use of NMR in speciating carbohydrates. We are also collaborating with the Center for Basic Standards on temperature measurements in combustion studies. We are cooperating in the planning and carrying out of a research program in support of AFOSR needs in cooperation with both IMSE and NEL.

Our staff has many interactions with voluntary standards organizations and international societies such as ASTM, ANSI, ASME, CODATA, IUPAC, and IAEA etc. This past year staff members participated in the planning and formations of a new ASTM committee on Biotechnology. Staff members hold memberships on diverse committees ranging from environmental and health concerns to energy utilization and database management. Members of the Biomolecular Structure Group organized a three-day Mid-Atlantic Protein Cystallography Workshop at NBS in May 1986. The workshop was attended by about 80 scientists.

We are actively planning for the maintenance of a protein crystallization database. Computing expertise for the necessary programming for this task will be provided by the Chemical Thermodynamics Data Centers Group. The differential scanning calorimetry effort has been successfully integrated into the biothermodynamics efforts in this past year. This laboratory is documenting standard procedures for calibrating differential scanning calorimeters that have been designed for use with biochemical samples. Work has continued in the measurement of the thermodynamics of enzyme catalyzed reactions. The work on the five and six membered monosaccharides has been completed and efforts will be made, in the coming year, to construct estimation schemes for the prediction of the thermodynamic formation properties for this class of compounds. Efforts have begun in other areas including the measurement of the thermodynamics of the reactions of monoclonal antibodies with antigens and the use of microcalorimetry to characterize the rates of enzyme catalyzed reactions and to measure enzyme activity.

Work will also continue on the determination of enthalpies of formation of key phosphorus compounds and other biomolecular building blocks including the development of predictive schemes for these compounds. Benzoic acid will be recertified during this fiscal year. Research to characterize the chlorinated organic species present in the effluents resulting from the combustion of municipal solid waste will also be continued.

2. BIOTHERMODYNAMICS

S. Abramowitz, E. Gajewski, R.N. Goldberg, W.H. Kirchhoff,
F.P. Schwarz, D. Steckler, Y.B. Tewari

A. Biochemical Thermodynamics
    (R.N. Goldberg, E. Gajewski, D. Steckler, Y.B. Tewari)

The long term goals of this research are to provide understanding of the thermodynamics of the key processes and interactions relevant to biochemistry and biotechnology. This understanding is needed to predict the feasibility of biochemical processes, optimization of product yields and elimination of side reactions in industrial processes. The data are necessary to construct estimation schemes to reliably predict the thermochemical properties of substances and processes for which measurements are not available. The goals are realized by development of measurement and computational methodology, determination of reliable thermodynamic values, and establishment of the relationship between molecular structure and the formulation of predictive methods.

The thermodynamic investigations include, where feasible, both equilibrium composition and calorimetric measurements on carefully characterized biochemical systems. Independent measurements of enthalpy and equilibrium composition as a function of temperature enable the reliable modelling of reactions outside of the temperature range of the measurements. The effects of pH, metal ion concentration, ionic strength and temperature on the equilibrium and enthalpy measurements are also investigated. An equilibrium model of the system allows one to account for the experimentally determined values and to predict these quantities under a variety of possible conditions. The calculations require identification of the individual molecular processes, activity coefficient models to account for nonideality, and numerical solution of the equilibrium equations which describe the system. The final set of thermodynamic parameters makes possible the prediction of the thermodynamic behavior of a system under a wide range of conditions beyond those used for the measurements. The combined approaches of equilibrium measurements, calorimetry and computer modelling is believed to be unique to NBS.

Written descriptions of the microcalorimeters, procedures and software used in the studies of biochemical systems have been prepared. The documentation includes a detailed description of the construction, calibration, operation, performance and use of these calorimeters. The software allows for the acquisition and treatment of data from three microcalorimeters simultaneously. Software for the acquisition and treatment of data from an isoperibol solution calorimeter, using a quartz thermometer, is also described. Procedures for obtaining kinetic parameters such as enzyme activity and rates of conversion of substrate to product are also described with accompanying examples using glucose isomerase.

Summaries of the accomplishments of the individual projects follow:

1. Thermodynamics of the Hydrolysis of Adenosine 5'-Triphosphate

The enthalpy of the hydrolysis of the enzyme catalyzed conversion of adenosine 5'-triphosphate (ATP) to adenosine 5'-diphosphate (ADP) and inorganic phosphate was investigated using microcalorimetry. There are five measurements of this equilibrium in the literature. Four of these are in agreement. All of them involve the use of coupled reactions to obtain the Gibbs energy change, which is known to ± 1.5 kJ mol^{-1}. These results are sufficiently accurate for our needs. Enthalpies of reaction were measured as a function of ionic strength (0.05 to 0.66 mol kg^{-1}), pH (6.4 to 8.8) and temperature (25 to 37 $^\circ$C) in Tris/HCl buffer. The measured enthalpies were adjusted for the effects of proton ionization and metal ion binding, protonation, interaction with the Tris buffer and ionic strength effects to obtain a value of $\Delta H = -20.5 \pm 0.4$ kJ mol^{-1} at 25 $^\circ$C for the process:

$$ATP^{4-} + H_2O = ADP^{3-} + HPO_4^- + H^+$$

Since earlier investigations did not systematically investigate the effects of pH, ionic strength or temperature the results obtained are currently the best value for the enthalpy change for this biochemical process. The result of $\Delta C_p^0 = -237 \pm 30$ J mol^{-1} K^{-1} is the only direct determination of this thermodynamic quantity.

2. Thermodynamics of Carbohydrate Isomerization Reactions

The thermodynamics of the enzymatic conversion of aqueous D-psicose to D-allose was investigated using high pressure liquid chromatography. The reaction was carried out in phosphate buffer at pH 7.4 over the temperature of 44.1 to 76.1 $^\circ$C. From the temperature dependency of the equilibrium constants, the following results were obtained for the conversion process at 25 C: $\Delta G^0 = -1.41 \pm 0.09$ kJ mol^{-1}, $\Delta H^0 = 7.42 \pm 1.7$ kJ mol^{-1} and ΔC_p^0 was estimated to be 67 ± 50 J mol^{-1}K^{-1}. An approximate equilibrium constant of 0.3 was also obtained at 60 $^\circ$C for the conversion of D-psicose to D-altrose. The kinetics of these reactions are not rapid enough to permit a direct calorimetric determination of the enthalpy changes.

This study is a continuation of earlier studies of carbohydrate isomerization reactions using the enzyme, glucose isomerase, which included isomerizations of glucose to fructose, xylose to xylulose and ribose to ribulose and arabinose. The possibility of other isomerization reactions involving sorbose, galactose, tagatose and talose were also investigated. Isomerization was not observed for the above carbohydrates.

The available information on the thermodynamics of the aldo/keto isomerization of hexoses and pentose is summarized in Table 1. With the exception of the mannose/fructose system, all the results were determined in this laboratory using both HPLC, for the determination of equilibrium constants, and where feasible, microcalorimetry to determine both the enthalphy and heat capacity changes. This represents the most complete set of information on the thermodynamics of carbohydrate isomerization reactions.

The observed thermodynamic data for the hexoses and pentoses will be coupled with other thermodynamic data such as enthalpies of combustion and solution and heat capacities to estimate the thermodynamic formation properties of the hexoses and pentoses. Available NMR and polarimeteric data will be used, where appropriate, to obtain speciation information for the solutions.

Table 1

Thermodynamics of isomerization reactions involving D-aldohexoses and D-aldopentoses in aqueous solution 298.15K

Process	ΔG^O (kJ mol^{-1})	ΔH^O (kJ mol^{-1})	ΔS^O (J mol^{-1} K^{-1})	$\Delta C_p{}^O$ (J mol^{-1} K^{-1})
Ribose-arabinose	-3.44 ± 0.30	-9.8 ± 3.0[a]	-21.3	
Ribose-ribulose	2.85 ± 0.14	11.0 ± 1.5[a]	27.3	
Xylose-xylulose	$4.38_9\pm0.031$	16.09 ± 0.67[a]	39.2	40 ± 23[a]
Arabinose-ribulose	6.29 ± 0.34	20.75 ± 3.4[a]	48.5	
Allose-psicose	-1.41 ± 0.09	$7.4_2\pm1.7$[b]	29.6	$67+50$[d]
Psicose-altrose	≈3.4			
Allose-altrose	≈2.0			
Glucose-fructose	0.349 ± 0.053	2.78 ± 0.20[a]	8.15	76 ± 30[c]
Mannose-fructose	-2.72	0.0[b]	9.12	
Glucose-mannose	3.07	2.78	$+0.97$	

[a] Based on direct calorimetric measurements.
[b] Calculated from the temperature dependency of equilibrium constants.
[c] Calculated from the temperature dependency of enthalpies of reaction.
[d] Based on both an estimate and the temperature dependency of equilibrium constants.

3.   Equilibrium Studies of the Conversion of Trans-Cinnamic Acid and Ammonia to L-Phenylalanine

The thermodynamics of the enzymatic conversion of aqueous trans-cinnamic acid and ammonia to L-phenylalanine has been investigated using high pressure liquid chromatography. The reaction was carried out in 0.1 M Tris/HCl buffer containing ammonium chloride over the pH range 7.0 to 7.7, at ionic strengths from 1.0 to 2.1 mol kg^{-1} in the temperature range of 12 to 43 °C. Analysis of the HPLC data using an estimated heat capacity change of 50 kJ mol^{-1} K^{-1} and an ion size parameter of 1.6 mol$^{-1/2}$ kg$^{-1/2}$ leads to an equilibrium constant of 0.86 ± 0.22 at 25 °C for the process

Trans-cinnamic$^-$ acid + NH$_4{}^+$ = L-Phenylalanine$^\pm$

We were unable to bring about a sufficiently rapid reaction to permit a direct calorimetric measurement of the enthalpy of this reaction. The use of these thermodynamic parameters in an equilibrium model allows for the

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prediction of values of the apparent equilibrium constant as a function of pH, temperature and composition. These data are useful for optimizing the yield of phenylalanine. The available thermochemical data for this generic type of reaction (ammonia elimination and the formation of a double bond) can be rationalized in terms of a scheme which views the entropy changes for related processes to be comparable and then attributes differences in Gibbs energy changes to the enthalpy changes which can be influenced by resonance stabilization of the double bond which is formed. This study complements an earlier one on the conversion of fumaric acid and ammonia to aspartic acid.

4. Microcalorimetric Measurement of Enzyme Activity

In addition to thermodynamic studies, the microcalorimetric instrumentation can be used for the determination of enzyme activity. If the substrate is present in large excess relative to enzyme, the reaction will be slow and accompanied by a steady rate of heat production per unit time given by

$$dq/dt = (dn/dt)/\Delta H$$

where ΔH is the molar enthalpy of reaction and (dn/dt) is the number of moles of substrate converted per unit time. The quantity (dn/dt) is a measure of the enzyme activity and can be determined from the measured power (dq/dt) if the enthalpy of reaction is known. This technique may prove valuable for the measurement of the activity of creatine kinase. Currently, the activity of this enzyme is measured spectrophotometrically with a precision of about 16%. The procedure requires the coupling of three enzyme catalyzed reactions to produce an increase of absorbance at 340 nm. A single step process can be used to measure this process in a microcalorimeter.

Creatine Phosphate + ADP = Creatine + ATP
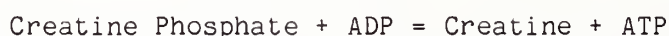
Results obtained have confirmed the literature results for the enthalpy of this reaction. Also the measurement of enzyme activity in aqueous buffer solutions have yielded results having an imprecision less than 10%. Measurements of this activity in human serum will require steps to eliminate and/or correct for possible chemical interferences in the measurements.

5. The Hydrolysis of Glucose 6-Phosphate and Fructose 6-Phosphate and the Isomerization of Glucose 6-Phosphate to Fructose 6-Phosphate.

$$G6P^{-2} = G + HPO_4^{-2}$$
$$F6P^{-2} = F + HPO_4^{-2}$$
$$G6P^{-2} = F6P^{-2}$$
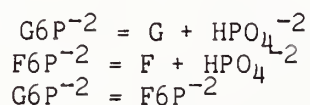
Here glucose and fructose are abbreviated as, G and F, respectively. The aim of this research is to obtain enthalpy, heat capacity and Gibbs energy changes for these processes. The results will be examined in conjunction with the thermodynamic data obtained previously for the hydrolysis of ATP of glucose and fructose, and the phosphorylation of glucose and fructose by ATP.

To date, enthalpy measurements have been made on the first two processes as a function of pH, temperature and concentration of magnesium chloride and of Tris/HCl buffer. A preliminary set of measurements have been made on the third process. After completion of the measurements on the third reaction, the necessary corrections will be made to obtain the enthalpy changes and the formalism applied to the Krebs cycle will be used to obtain the best consistent set of thermodynamic parameters for the above reactions, phosphorylation of glucose and fructose by ATP, and hydrolysis of ATP.

6.   Antigen-Antibody Interactions

A study of antigen-antibody reactions has been started, in cooperation with the Center for Analytical Chemistry, using monoclonal antibodies. This should aid in the molecular interpretation of the thermodynamic properties of the reaction. A sample of a monoclonal antibody, has been obtained. The antibody has a molecular weight of about 150,000 daltons and is specific for E-N-E dinitrophenyl-L-lysine (2,4 DNP). An affinity column is being used to purify the monoclonal antibody. We plan to measure the enthalpy of the antigen-antibody reaction using microcalorimetry and to measure the equilibrium binding using dialysis techniques. Differential scanning calorimetry will also be used to characterize both the bound and unbound antibody.

7.   Plans for Next Year

Thermodynamic formation properties of the five and six membered monosaccharides will be determined using available literature, estimation methods and data from ours and others research. The study of the thermodynamics of the reactions of glucose and fructose with ATP and the isomerization of glucose 6-phosphate to fructose 6-phosphate will be completed. The thermodynamics of the reactions of a monoclonal antibody with its antigen will be completed. An examination will be made of the thermodynamics of the most important processes currently used industrial biotechnology. The available thermodynamic data will be given, best available values will be recommended and, where appropiate, experiments suggested. A thermodynamic investigation of the enzymatic conversion of penicillin G to 6-aminopenicillanic acid and phenylacetic acid will be initiated. Equilibrium measurements will be made using HPLC and, if kinetics allow, microcalorimetric studies will also be pursued.

B. Differential Scanning Calorimetry
    (F. P. Schwarz and W. H. Kirchhoff)

Differential scanning calorimetry, provides thermodynamics information on biological systems which characterizes the interactions and conformational changes of biological molecules in solution. Studies of the effect of ligand concentration on the transition temperature and enthalpy of protein, such as human serum albumin, yield information on the binding energetics of the substrate to the enzyme. Comparison of the transition enthalpies and temperatures of synthetic oligonucleotides in solution yield information on the effect of the nucleotide sequence on the conformational stability of DNA species in solution.

1. Temperature and Enthalpy Standards for Differential Scanning
   Calorimetry
   (F. P. Schwarz)

Differential scanning calorimetry standards for temperature and enthalpy are needed to validate comparisons of data from different laboratories. A differential scanning calorimetric standard should exhibit a well characterized transition in the temperature range from 0 to 100 $^{\circ}$C, the normal operating temperature range for biological studies, with an accuracy in the transition enthalpy of $\pm$ 0.10 mcal and a temperature accuracy of $\pm$ 0.10 $^{\circ}$C. It is also desirable to use a biological solution as a standard since many of the differential scanning calorimeters contain fixed cells which are filled through small capillary tubes. Ribonuclease A is a candidate. Ribonuclease A is an enzyme consisting of 124 amino acid residues (G.M.W. = 13,700). In buffer solutions, ribonuclease a exhibits an unfolding transition with a transition temperature and enthalpy depending on the pH of the solution. It is readily available in relatively high purity and is highly stable. Furthermore, its concentration can be readily determined by several simple spectroscopic methods.

Solutions of ribonuclease A in a HCL-glycine buffer were prepared, dialyzed, analyzed, and thermally scanned on a differential scanning calorimeter to evaluate the suitability of ribonuclease A as an enthalpy and temperature standard. The calorimetric results from solutions prepared from four different samples of ribonuclease A were determined with a computer-controlled, heat flow differential scanning calorimeter. The solutions ranged in concentration from 0.7 to 1.7 mM and a glycine buffer concentration of 0.1 and 0.2 M. A straight baseline was interpolated under the transition peak to obtain the enthalpy of transition. The transition enthalpies exhibited a linear dependence on the transition temperature, ranging from 66.0 $\pm$ 0.4 kcal/mole at 37.4 $\pm$ 0:1 $^{\circ}$C (pH = 1.9), to 110.0 $\pm$ 0.5 kcal/mole at 64.0 $\pm$ 0.1 $^{\circ}$C (pH = 4.2), with a standard deviation of 2.47 kcal/mole. The enthalpy determinations are in good agreement with values reported in the literature. The results are independent of the source of the ribonuclease A and the concentration of the buffer. The solutions are stable when stored in a refrigerator and can be analyzed by measuring the UV absorption at 278 nm at a pH of 7.0. An error analysis revealed that the major source of error was in determining the temperature limits in the integration of the enthalpy transition peak. It is anticipated that a computer algorithm based on the two state model, being developed by W.H. Kirchhoff, to fit the entire thermal scan, will further reduce the standard deviation in the linear fit of the enthalpy to the temperature.

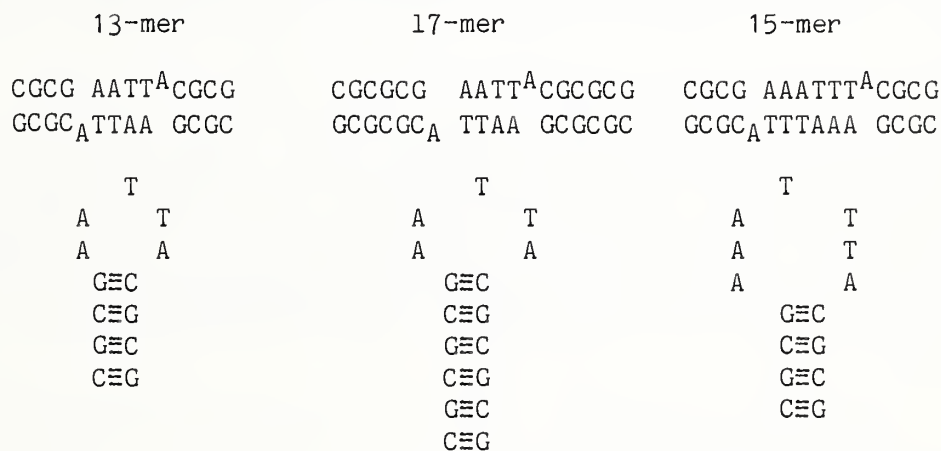In summary, from the standpoint of ease of preparation, ease of characterization of the transition properties of ribonuclease A, and stability, ribonuclease A is an acceptable standard for the calibration of differential scanning calorimeters. The value of a ribonuclease A standard for measurement accuracy of the transition enthalpy and transition temperature is expected to be improved by the algorithms being developed.

2. Studies of the Thermal Stability of Synthetic, Quasipalindromic DNA Sequences in Solution.
   (M. Miller, F.P. Schwarz, E. Appella (NIH), and W. H. Kirchoff)

Oligonucleotides consisting of prepared palindromic sequences have served as model systems for studying the effects of environmental variable (e.g. pH, temperature, electrolytic strength, etc.) on the stability of various forms of DNA - duplex (Z or B double-helix structures), cruciforms and hairpin loops. The palindromic sequences, which have the property of being self-complementary enabling the oligonucleotides to form exactly matching double-helices or exactly matching ends for stabilizing loop structures, have been extensively studied by crystallography, differential scanning calorimetry, UV spectroscopy and NMR. From these studies, the stabilities of all possible nearest-neighbor configurations have been computed and from this limited data base, the stability of any double-helix form of DNA may be estimated from its base-pair sequence.

We have begun to study a series of quasipalindromic sequences in order to determine the effects of mismatches on the stability and structure of DNA. In addition, spectroscopic and calorimetric measurements on systems with small enthalpies of reaction provide very broad transition envelopes which can further test mathematical models for the description of phase transitions in small systems. This work complements structural work being conducted in the Biomolecular Structure Group of the division. The species studied, along with their duplex and hairpin forms are shown below.

13-mer	17-mer	15-mer
CGCG AATT^{A}CGCG	CGCGCG AATT^{A}CGCGCG	CGCG AAATTT^{A}CGCG
GCGC$_A$TTAA GCGC	GCGCGC$_A$ TTAA GCGCGC	GCGC$_A$TTTAAA GCGC

```
        T                    T                    T
   A        T           A         T          A         T
   A        A           A         A          A         T
      G≡C                   G≡C               A         A
      C≡G                   C≡G                  G≡C
      G≡C                   G≡C                  C≡G
      C≡G                   C≡G                  G≡C
                            G≡C                  C≡G
                            C≡G
```

One of the variables in the study of these species is the total concentration of DNA strands. At high concentrations, the duplex form is favored. At low concentrations, the hairpin form is favored. The high concentration forms are most easily measured with a differential scanning calorimeter, the low concentration forms with a uv spectrometer. Both techniques were used and transitions between the species were analyzed. The van't Hoff enthalpies of transition were most accurately determined from the UV data. The 15-mer was found to form the most stable duplex form at low temperature and was selected for crystallographic studies. The thermodynamic data have been interpreted in terms of the relative

strengths of G≡C vs A=T base pairs. Circular dichroism measurements indicate the presence of the Z form of the duplex and observed transitions have been tentatively ascribed to Z-B transitions.

3. The Effect of Ligand Concentration on the Thermal Stability of Human Serum Albumin
(F.P. Schwarz and A. Shrake)

Serum albumin is the most abundant protein in blood plasma, and information on its thermal stability can be used to improve commercial preparations of blood plasma. A detailed differential scanning calorimetry study has been completed on the dependence of the thermal stabilization of human serum albumin on the concentration of alkanoate anion ligands in solution. The increase in the thermal stabilization of serum albumin is monitored by the increase in its denaturation temperature and in its denaturation enthalpy in the presence of increasing ligand concentration. Two trends in the thermal stabilization were observed:
(1) The optimum denaturation temperature increased from 66.1 ^{o}C in the absense of ligand to 76.1 ^{o}C in the presence of formate and then to 79.0 ^{o}C in the presence of acetate, propionate, and butanoate.
(2) The optimum denaturation temperature increased to 81.2 ^{o}C in the presence of pentanoate and monotonically thereafter with increasing carbon chain length to 88.8 ^{o}C for the decanoate anion. An increase in thermal stability with chain length is anticipated since the binding constants of the alkanoate ligand to the serum albumin increase with chain length. The departure of propionate and butanoate from this behavior have been explained by assuming two different types of binding sites for the ligand to the serum albumin: (1) A large number of sterically hindered binding sites which bind only small ligands (formate to butanoate) and (2) a small number of large binding sites which bind all the ligands from formate to decanoate.

For FY 87, a number of studies are being planned which should serve as prototypes for assessing the applicability of DSC to the measurement of protein-substrate binding energies. The studies currently under consideration include: the thermal stability of monoclonal antibodies and their complexes with antigens; the thermal stability of the avidine and its unusually strong complex with biotin (vitamin H), and the effects of structural alterations on the thermal stabililty of chymotrypsin and trypsin and their respective proenzymes, chymotrypsinogen and trypsinogen.

4. Calculational Methods for the Characterization of Phase Transitions in Biomolecules
(W. H. Kirchhoff)

Computer programs have been written for analyzing phase transitions in biomolecules as measured by calorimetry or spectroscopy. The purpose of the programs is to characterize the measurement process and to determine the limits within which simple thermodynamic theories can duplilcate temperature profile measurements. Since the same theories are applied to both spectroscopic and calorimetric profiles, we may be able to separate instrumental effects from effects due to the non-ideality of true phase transition behavior.

The basis for the description of the spectroscopic and calorimetric profiles is the explicit dependence of the concentration of species on temperature. Phase transitions can be considered to be chemical reactions between initial and final states and can be written most generally as:

$$A \iff nB$$
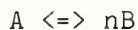
and the concentration of species in states A and B is expressed in terms of the equilibrium coefficient

$$K = \frac{[B]^n}{[A]} \qquad \text{and its temperature dependence } d[\ln K]/dT = -\Delta H/RT^2.$$

The enthalpy change, ΔH, is expressed as a power series about the standard state temperature, T_O:

$$\Delta H = \Delta H^O + \Delta C_p{}^O(T-T_O) + \ldots$$

The expression for the differential scanning calorimetry heat capacity, dQ/dT, is

$$dQ/dT = -\Delta H(dN_A/dt) + N_A C_{PA} + N_B C_{PB} + \text{baseline parameters}$$

while the expression for the temperature dependence of the spectrum of a biomolecule undergoing a phase transition is given by:

$$I = I_A[A] + I_B[B] + \text{baseline paramenters}$$

were I_A and I_B are the absorption coefficients or scattering intensities for the two species (which themselves may be expressed as power series in temperature). Simple algebra provides explicit expressions for dQ/dT and for I as functions of temperature.

Computer programs have been written for fitting these expressions by the methods of non-linear least squares to the experimental data. From the spectroscopic data, T_O and ΔH^O can be obtained, though the data are generally not sensitive enough to determine $\Delta C_p{}^O$. In the cases tested thus far, which have included the main phase transition in lipid bilayers, DNA fragments, and ribonuclease, the data have been fit to within experimental error. As a corollary, additional information may be obtainable from spectal measurements only through improved sensitivity, precision and temperature control.

From the calorimetric data, T_O, ΔH^O, $\Delta C_p{}^O$, and N, the number of moles of material present in the cell, can be determined. This approach differs from traditional approaches to the analysis of calorimetric data in that the baseline is a varying function of composition, and hence temperature. A so-called calorimetric enthalpy is not calculated. Instead, the van't Hoff enthalpy, ΔH^O, and the number of moles, N, are deemed the fundamental quantities to be determined. Although the fit of the model to experimental data seems excellent on casual inspection (the observed and calculated profiles are indistinguishable in graphical depictions) the difference between the calculated and observed profiles shows distinct trends and the standard deviation of the fit is an order of magnitude greater than the scatter in the data. This systematic error may be due to diffusion and other dynamic effects which have not been

included in the analysis, the inadequacy of a simple power series in describing the instrumental background or a breakdown in the purely two state nature of the transition in ribonuclease A. Work in the coming year will focus on distinguishing between instrumental effects and effects due to the limitations of the purely thermodynamics model. The programs will also be expanded to include values of n greater than 1, the only case for which the programs have thus far been tested.

The computer programs have been written in standard Fortran 77 for personal computers compatible with the IBM AT and XT computers. In developing the programs, some degree of portability had to be sacrificed for ease of use. The lack of portability is related directly to the graphical displays that accompany the analysis. At this time, no standard protocols for graphical displays for Fortran-based programs exist. The programs are currently being distributed on a limited basis to those individuals who are willing to share their experience with the programs and who can offer critical reviews of the thermodynamic models, the statistics of the data analysis, the robustness of the algorithms, and ease of use.

The function for the spectral profiles is known as the logistic function and is commonly encountered in chemistry and other fields. Consequently, the spectral fitting program has been written in a more general manner for wider dissemination. It has been successfully used to analyze sputter depth profiles through interfaces where a simple diffusion model gives rise to the logistic function. The program has been distributed to laboratories performing depth profile analyses and is gaining in popularity.

3. BIOMOLECULAR STRUCTURE

A. Wlodawer, G. Gilliland, R. Harrison, M. Miller,
H. Savage, I. Weber

The Biomolecular Structure Group has developed an active program in measurement and analysis of the structure of biological macromolecules. We are developing new methods of X-ray and neutron structure determination and are applying these and other, more conventional, methods to selected structures of proteins and nucleic acids. Our general aim is to advance the understanding of the structure-function relationship in macromolecules, in particular by modifying the structure using genetic technology, by binding of ligands and by studying families of closely related proteins with different properties. We are also interested in the interactions of macromolecules with solvent, and such studies can particularly benefit from the availability of neutron diffraction data.

The physical facility available to us includes a well-equipped general purpose laboratory for protein purification, crystal growth and mounting, including a walk-in cold room, as well as computer and graphics areas. Instrumentation include a flat-cone neutron diffractometer located on the NBS Reactor, a conventional X-ray generator with two Buerger precession cameras (useful for preliminary data collection, but not for intensity measurements), and a gas-flow crystal temperature controller with a range of -80 °C to +60 °C. In the reporting period, we had no facilities for quantitative x-ray measurements, owing to the slow delivery cycle of a Nicolet area detector. For these reasons our capability to collect data was limited to the time donated to us by Genex Corporation, in collaborative efforts with Dr. Gary Gilliland, who subsequently joined our group in August 1986. Our computing facility includes an IBM4381 shared with the Quantum Chemistry Group of the Molecular Spectroscopy Division, a dedicated Evans and Sutherland Graphics facility which was upgraded this year from PS330 (vector graphics) to PS340 (vector and raster screens). This modification enables us to create both dynamic line drawings as well as static space-filling pictures. We have implemented programs for hard copy output of the images generated using various graphics programs. A recent upgrade to our computational facility includes a MicroVAX II equipped with a large disk and a tape drive, which will be dedicated to processing area detector data.

A number of problems initiated previously were continued in the last year and several new ones were initiated. Those individual projects on which significant progress was achieved are summarized below.

A. Structural Studies of Mutations in Catabolite Gene Activator Protein
(I.T. Weber)

Catabolite gene activator protein (CAP) regulates transcription in E. coli in response to the level of cyclic adenine monophosphate (cAMP) which is an allosteric activator of CAP. CAP recognizes and binds to specific sequences of DNA at several operons, causing the stimulation or repression of transcription of cAMP-dependent genes. The crystal structure of a dimmer of CAP with bound cAMP has been determined at 2.5Å resolution and refined to an R factor of 0.207.

Several laboratories are investigating mutations in the crp gene that produces CAP. Three CAP mutants, 91, 220 and 222, that function in the absence of cAMP have been subjected to crystallization trials in order to study the structural changes associated with these mutations in amino acid sequence. Both CAP 91 and 222 form crystals with cAMP. CAP 91 also crystallizes in the presence of adenosine, an alternate activator for this mutant.

X-ray intensity data have been obtained for the crystals of CAP91 with cAMP which are isomorphous with the crystals of wild type CAP. These data have been refined to 2.4A resolution and an R factor of 0.186. The CAP91 structures are very similar although the Ala to Thr mutation is clearly visible. There also is a movement of Cys178. There are no significant differences around cAMP-binding sites. Smaller differences have been located by a vector average of the differences in atomic coordinates. These differences are located far from the site of mutation, in the hinge region between the two domains in the CAP subunit and in an adjacent loop between two β strands. These differences suggest that the Ala 144 to Thr mutation in CAP91 produces structural changes that propagate through the hinge region towards the DNA-binding site.

The CAP91 structure is being investigated in the absence of cAMP and in the presence of the analog, adenosine. Other CAP mutants will be studied.

B.   Predicted Structure for Two Domains of the Regulatory Subunit of
     cAMP-dependent Protein Kinase
     (I.T. Weber)

The mammalian cAMP-dependent protein kinase is an important regulator of many biochemical reactions. In the inactive state the holoenzyme consists of a complex of two regulatory subunits and two catalytic subunits. This is activated by the binding of cAMP to the regulatory subunits which then dissociate from the catalytic subunit. The active catalytic subunit phosphorylates other proteins. The regulatory subunit (R) contains two domains that bind to cAMP and have amino acid sequences that are homologous with the sequence of catabolite gene activator protein (CAP) from the bacterium, E. coli.

The crystal structure of the cAMP-binding domain of CAP has been used to model the cAMP-binding domains of the regulatory subunits. The amino acid sequence for the R-subunits was fitted into the CAP structure using a computer graphics system. The predicted R structure was overall very similar to CAP. The model structure was evaluated by comparison with other experimental evidence including photolabeling with 8-azido cAMP, the binding of cAMP analogs, and fluorescence quenching. This gave good agreement and the predicted structure of the regulatory subunits can be used as a model for site directed mutagenesis.

C.   Structural Studies of Anti-tumor Amidohydrolases
     (I.T. Weber, A. Wlodawer and R.W. Harrison)

Three homologous bacterial amidohydrolases with anti-tumor properties have been crystallized: a glutaminase-asparaginase from Acinetobacter glutaminasificans (AGA), a glutaminase-asparaginase from Pseudomonas 7A

(PGA) and an asparaginase from <u>Vibrio succinogenes</u> (VA). These enzymes in solution are tetramers with subunit molecular weights of ca. 34,000 daltons. AGA crystallizes in space group I222 with one subunit per asymmetric unit. PGA crystallizes as a tetramer in space group $P2_12_12_1$ and VA crystallizes in the same space group with a dimer in the asymmetric unit.

Native data are available to 2.9A resolution for AGA and MIR data on three derivatives (5.3 to 4.0A) permitted the direct phasing of 2617 reflections. Phase improvement and extension to 2.9A resolution for an additional 4784 reflections was achieved by two complementary techniques of density modification. These are the method of B.C. Wang which flattens the solvent region and improves protein connectivity, and the method devised by R.W. Harrison that maps the distribution of density values onto a Gaussian distribution with the same mean and standard deviation. By examining electron density maps produced by the two methods it proved possible to trace a polypeptide chain, although the connectivity is ambiguous in several places. Since the amino acid sequence has not yet been determined, the type of amino acid was estimated from the shape of the electron density, and these coordinates were refined to an R factor of 0.30. The AGA polypeptide chain folds into two domains. The first amino terminal domain, contains a five-stranded β sheet and four of helices. The second domain has four of helices and several β strands. This model for the AGA structure has been used to phase the PGA data.

Intensity data have been obtained to 2.5A resolution for the PGA crystals using a Nicolet-Xentronix area detector at Genex Corporation. The starting point for phase determination has been rotation and translation function techniques using the AGA map. This solultion was confirmed by using the AGA polyalanine coordinates. The rotation function has also been solved for VA. A starting PGA model was produced by rotation and translation of an AGA tetramer and this was refined to improve the phases. The tetramer model phases are being used as a prior in the maximum entropy technique that is under development by R.W. Harrison and the new electron density map is being intepreted. An active site inhibitor has been soaked into the PGA crystals in order to locate the active site of the enzyme.

D. Comparison of Two High Resolution Structures of Bovine Pancreatic Trypsin Inhibitor
    (A. Wlodawer, with J. Deisenhofer and R. Huber (Max Planck Institute, Munich))

While it has been known for a long time that the structure of a protein in a crystal is similar to that present in solution, the limits of discrepancy have not been rigorously established. The availability of two distinct crystal forms for bovine pancreatic trypsin inhibitor (BPTI) made it a system of choice for such studies.

The structure of deuterated crystals of form II of BPTI has been refined using X-ray and neutron diffraction data. These crystals belong to space group $P2_12_12$, a=74.1A, b=23.4A, c=28.9A and the packing of the molecules is related to form I structure previously solved in Munich by rotation of about 45° around y. X-ray intensities were collected on form

II crystals by the Munich group using standard diffractometry, while
neutron data extending to 1.8Å resolution were collected at NBS. Joint
restrained refinement using both types of data was performed by J. Walter
and A. Wlodawer, resulting in a final model characterized by R values of
0.200 (X-ray) and 0.197 (neutron).

The two available high resolution structures of bovine pancreatic
trypsin inhibitor, refined in two distinct crystal forms, have now been
compared. After superposition, the molecules show an overall
root-mean-squares deviation of 0.40 Å for the atoms in the main chain,
while the deviations for the side chain atoms are 1.53 Å. The latter
number decreases to 0.61 Å when those side chains which adopted drastic-
ally different conformations are excluded from comparison. The discrep-
ancy between atomic temperature factors in the two models was 6.7 $Å^2$,
while their general trends are highly correlated. About half of the
solvent molecules occupy similar positions in the two models, while the
others are different. As expected, solvents with the lowest temperature
factors are most likely to be common in the two crystal forms. While the
two models are clearly similar, the differences are significantly larger
than the errors inherent in the structure determination. This study
established the limits of discrepancy of atomic coordinates of proteins
which can be expected to result from differences in crystal packing.

E. High Resolution Refinement of Ribonuclease A
    (A. Wlodawer, with G. Gilliland and B. Finzel (Genex Corporation),
    A. Svensson and L. Sjolin (Chalmers Polytechnic)).

The structure of ribonuclease A was reinvestigated using a new set of
X-ray diffraction data extending to 1.26 Å, the limits of detectable
diffraction. The X-ray diffraction data were obtained from two
phosphate-free crystals which were isomorphous with previously reported
monoclinic crystals containing phosphate, or perhaps sulfate. The data
were collected using an area detector, the Xentronics-Nicolet image
proportional counter at Genex, and included 129,694 observations of 25,732
unique reflections out of the total of 31,730 possible at 1.26 Å. The data
scaled with a weighted least squares R-factor on intensity for
symmetry-related observations of 0.05, with 23,398 of the measured unique
reflections having significant intensity ($F>2\sigma(F)$).

One of the first significant observations with the new data was the
detection of a large number of side chains with multiple conformations.
The structure was highly refined (R = 0.15) and was modeled with 13 resi-
dues having discrete multiple conformations of side chains. These resi-
dues are widely distributed over the protein surface, but only one of
them, Lys 61, is involved in crystal interactions. The discrete
conformers have no unusual torsion angles and their interactions with the
solvent and with the atoms of the protein are similar to those residues
modeled with a single conformation. For three of the residues, Val 43,
Asp 83, and Arg 85, two correlated conformations are found. The observed
plasticity in the protein surface will be of significance in analyzing
structure-function relationships and in performing protein engineering.

Other new observations resulting from this refinement, in particular
the details of the structure of ordered solvent, are still being analyzed.

F.   Structure of the Solvent in Crystalline BPTI
      (R. Harrison and A. Wlodawer)

     Neutron data for bovine pancreatic trypsin inhibitor (BPTI) have been
collected for crystals soaked in both deuterated and hydrogenous solvents.
Deuterated data extending to 1.8A resolution have been available for some
time, while hydrogenous data were collected recently. This data set was
virtually complete to 1.8A resolution, with 3416 reflections showing
observed intensity.

     Since deuterium and hydrogen have greatly different scattering lengths
it should be possible to use the difference between the scattering from
deuterated and hydrogenous crystals to determine the positions and
occupancies of exchangeable and solvent hydrogens. With X-ray diffraction
data, differences in the scattering due to a change in the crystal such as
the addition of a substrate can be used directly via a difference Fourier
synthesis to show the location and orientation of the changes in the
molecule or the complex. Because the differences are much larger with
deuterium-hydrogen exchange, such a simple treatment is not correct when
applied to neutron diffraction data. The problem with a simple treatment
is the choice of the phase of each term used in the difference Fourier
synthesis. With small differences in the scattering there are only small
differences in the phase of the reflection. However, the phases of the
deuterated data and the hydrogenous data determined by independently
refined models are quite different, and there is no a priori reason to
choose one or the other.

     We have attempted to resolve this problem by constructing an enhanced
model of the scattering from the protein. The scattering is treated as
coming from two non-overlapping regions. Scattering from the part of the
molecule that should not be altered by solvent exchange is required to be
the same in both the hydrogenous and deuterated models, and scattering
from everywhere else is independently refined for each model. Requiring
that the structure in the non-exchanged regions of the map be the same for
two different sets of data results in an improved model for the protein.
The solvent regions are required to be featureless when far (>4 A) away
from the protein. In addition a correction to the F(000) term of the
Fourier series is refined. These procedures should result in a
significantly enhanced model for the solvent near the protein surface.
The structure of this local solvent is critical to the stability and
function of proteins. The structure of solvent in BPTI is now analyzed in
these terms.

G. Crystallization of Synthetic Fragments of DNA
   (M. Miller, A. Wlodawer, and E. Appella (NIH))

We have been crystallizing a series of DNA oligonucleotides predicted
to form structures deviating from the classical double-helix. A 13-mer
d(CGCGAATTACGCG) derived from the self-complementary dodecamer
d(CGCGAATTCGCG) by inserting an extra adenosine in the 9th position from
the 5'-end was synthesized as a model of a frame-shift mutation. This
sequence was expected to form an improper duplex with the unpaired adenine
residue either looped out or intercalated into the double helix. The
crystals that were grown were disorderd (or unstable). Our solution
studies (done in collaboration with F. Schwarz and W. Kirchhoff of the
Biothermodynamic's Group, see separate report) showed that the duplex
undergoes a transition to a single stranded hairpin loop in the temperature
range 0 - 6 $^\circ$C. Subsequently we found that a 15-mer d(CGCGAAATTTACGCG) forms
a much more stable duplex. The inserted nucleotides are now separated by
an AT sequence two base pairs longer. Crystals of this material have
been grown by the vapor diffusion technique at 4 $^\circ$C. The space group is
I222 with a=36.9 A, b=53.8 A, and c=102.7 A. We are modifying the
conditions of crystal growth with the aim of preparing a sufficient
number of them for data collection. We have been also continuing our
efforts to find a DNA oligomer which would crystallize in the form of a
single stranded hairpin loop, but so far with little success.

H. Application of Repulsive Regularities Found in Water Structures.
   (H. Savage)

Water structures in crystal hydrate systems have been studied in
order to categorize the repulsive interactions between different classes
of atoms (Nature 322, 717,(1986)). These interactions are divided into
four groups (RR1 - RR4).

RR1: O...O repulsion of the H-bonds (H-bonds may bend, if necessary, to
within a certain limit).

RR2: O...O repulsion between non-bonded water oxygens (minimum contacts
of 3.1-3.6A depending on orientations).

RR3: H2...O1 repulsion between H2 and O1 of the configuration
        O1-H1...O2-H2 (minimum contacts of 3.0A).

RR4: H...H repulsions (minimum contacts of 2.1A).

(where H1, H2, etc, refer to atoms belonging to two distinct water
molecules)

These repulsive restraints explain several of the basic features found in water structures. For example, they can be used to describe the different structures found in the ice phase diagram. The pressure-temperature phase space can be divided into 4 separate regions (Fig 3.1) with respect to which of the repulsive restraints RR2 and RR3 are fully strained:

Region 1: H2...O1 remote contacts,

Region 2: O....O non-bonded contact   for a single lattice of H-bonds

            H2...O1 remote contacts
Region 3: H2...O1 remote contacts,

Region 4: O....O non-bonded contacts   for two interdigitating lattices of
                                              H-bonds

            H2...O1 remote contacts

In region 1 the RR3 contacts are fully strained, but the non-bonded RR2 O...O contacts are not (all >3.5A). Thus, a reduction in volume can only take place with respect to reducing the RR2 contacts. In region 2 both the RR2 and RR3 contacts are at their limit and further contraction at higher pressures has to take place by the formation of interpenetrating lattices of H-bonds (self-clathrates). Compression of the 'double' lattice follows along similar lines to that of the single H-bond lattice case; firstly the RR3 contacts are fully strained (region 3), and then both the RR2 and RR3 contacts are at their minimum limits (region 4).

In regions 1 and 3 the non-bonded RR2 interactions are not fully strained and it is possible that some disorder of the water oxygens may be present. This has been found in some recent ultra-high resolution neutron diffraction experiments carried out at the Institute Laue-Langevin on ices Ih (Kuhs and Lehmann, 1986) and VI (Kuhs and Finney, 1986). In ice Ih the position of the oxygen was found to be disordered by up to 0.04A, while in Ice VI variations of up ~0.15A are present.

I.   Plans for Next Year

We are planning to commission the X-ray diffraction instrumentation within the next few months. The system will consist of a Nicolet area detector mounted on a Huber diffractometer, with controlling electronics locally adapted by T. Buckley. When fully operational, this facility will obviate the need for the use of X-ray data collection facilities.
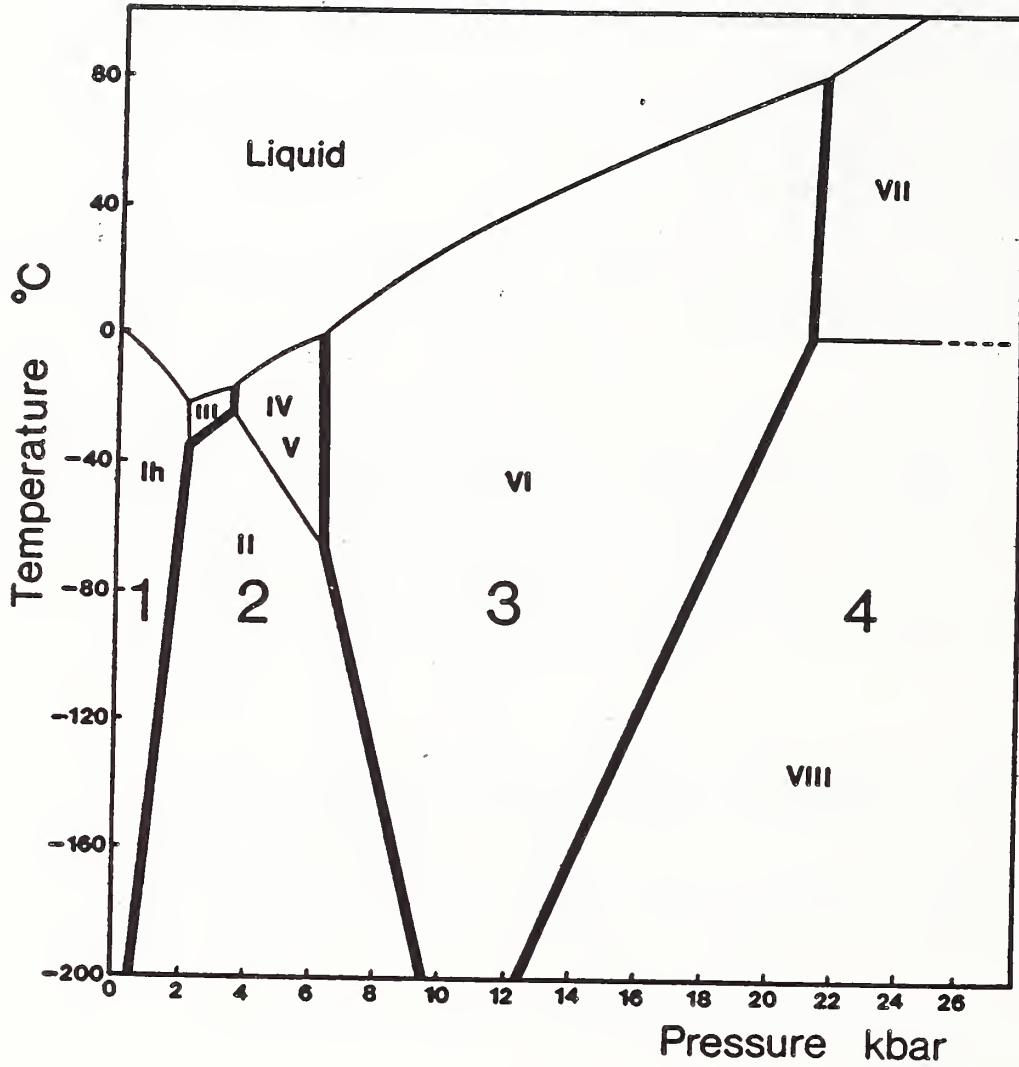
Fig. 3.1. Division of the pressure-temperature ice phase diagram into four regions with respect to the RR2 and RR3 repulsive limitations

Scientifically, we are planning a concerted effort directed to improving the ability to grow protein crystals in a predictable and reproducible manner. To that effect, we will implement a crystallization data base, originally developed by G. Gilliland at NIH, which lists all published conditions for growth of macromolecular crystals. We will develop software, in cooperation with the Chemical Thermodynamics Data Center's Group for manipulation and updating of this data base.

4. CHEMICAL THERMODYNAMIC MEASUREMENTS

E.S. Domalski, S.S. Bruce, K.L. Churney, T.J. Buckley, J. Colbert,
E. Diaz, D.A. Ditmars, D.R. Kirklin, A.E. Ledford

A.   Large Sample Combustion Calorimetry
     (E.S. Domalski, J.C. Colbert, K.L. Churney, J.E. Diaz, A.E. Ledford,
     S.S. Bruce, and T.J. Buckley)

This research is being performed in support of the Resource Conserva-
tion and Recovery Act and is funded by the U.S. Department of Energy.
The purpose of this work is to provide measurement methods, standards, and
baseline data for establishing calorific (heating) values and optimal
combustion conditions for the control of pollutants for municipal
solid waste (MSW) from various sources. Current emphasis is directed
toward monitoring the fate of chlorine from input through MSW combustion.
The presence of trace amounts of chlorinated organic compounds (i.e.,
dioxins) in the effluent and fly ash has hindered the construction and
operation of MSW incinerators used for the generation of steam and
electric power.

During FY 1984, samples of MSW were obtained from Brooklyn, NY, and
Baltimore County, MD to generate data on the chlorine content of MSW.
Quantitative information of this type is meager and is needed to evaluate
the methods that have been proposed for reducing the emission of
chlorinated dioxins and furans from incinerators. The main methods
proposed are: (1) removal of the responsible components of the waste, (2)
proper incinerator design, and (3) efficient operation of the incinerator.
The results of the sampling study, which were evaluated in 1985, showed
that all combustible components of MSW contained chlorine. Our study has
shown that removal of plastics from MSW is not sufficient to reduce the
chlorinated organic species formed during the combustion of MSW to
negligible levels.

During FY 1985, studies were conducted dealing with laboratory and
field data for the calorific value of MSW. The calorific value of the MSW
that is needed in a performance or acceptance test is the heat liberated in
the actual incineration process, however, the combustion of the organic
fraction of MSW is incomplete in this process. The calorific value
determined in laboratory tests is for conditions of complete combustion.
Currently, no data are available for validating methods either for the
measurement of incomplete combustion or the making appropriate
calculations to correct for incomplete combustion. To obtain such data,
the heat liberated for varying degrees of complete combustion was
determined by burning microcrystalline cellulose and synthetic MSW in
O_2/N_2 mixtures containing 100, 50, 35, and 21 mole % O_2 in the O_2 in the
2.5 kg capacity flow calorimeter. The synthetic MSW is microcrystalline
cellulose which contains 20 mass % silica as the noncombustible component.
The particle size of the silica and combustion conditions were such that the
amount of char formed in the combustion of the synthetic MSW in air was
about 5% of the mass of the ash, the approximate value for the amount of
char formed in MSW incinerators. Gaseous hydrocarbons and CO were
monitored as a measure of gaseous products of incomplete combustion. The
combustion results are being examined to establish the methods for the
determination of calorific corrrections for incomplete combustion.

Also during FY 1985, studies were carried out to develop procedures needed for the determination of the threshold conditions for the formation and for destruction of organic chlorine compounds during MSW combustion. The purpose of this study is to determine if we can reproducibly form and/or destroy these compounds and, if so, whether the combustion conditions in a large, laboratory-size combustor can be sufficiently well-characterized to allow application of the results to design or operation of real-world MSW incinerators.

An EPA modified method 5 (MM5) gas and particulate sample train for sampling the product gas and trapping both particulates and volatile organic chlorine compounds was constructed and installed as part of the combustion flow calorimeter. Procedures were developed by S. Chesler and R. Parris of the NBS Organic Analytical Research Division for separating the organic chlorine compounds trapped in the MM5 train into chemical classes of increasing clarity. The organic chlorine compounds were formed in the combustion of synthetic MSW doped with 1.5 mass % polyvinyl chloride (PVC) in 35 mass % O_2/65 mass % N_2. A qualitative analysis using gas chromatography with an electron capture detector was carried out on the separated organic chlorine product formed in the combustion of PVC doped synthetic MSW. Dioxin or furans were not found but could have been present below the detection of the instrumentation (several ppb), but substantial quantities chlorinated benzenes, chlorophenols, and chlorinated biphenyls (PCB's) were detected.

In FY 1986, significant accomplishments were made in the following areas:

1. Gram-size Test Samples to Characterize 2.5 kg Increments

An experimental test was conducted to verify the method used to calculate the heat exchange between the 2.5 kg capacity flow calorimeter and its environment. The test showed that the overall heat exchange corrections to the experimental data were negligible, less than 0.1%, despite significant departures from conventional gram-size combustion calorimeter operating conditions. The results were used to complete an evaluation of the bounds of systematic errors in the calorific values determined in the FY 1984 study involving gram-size test samples prepared from kilogram-size parent increments. The results of the error analysis are reported in a manuscript describing the 2.5 kg flow calorimeter and appears in the September 1986 issue of the NBS Journal of Research.

A summary of the results of the study concerning gram-size test samples from kilogram-size increments was prepared and published in the proceedings of the Twelfth National Waste Processing Conference sponsored by the American Society of Mechanical Engineers (ASME) held in Denver, CO, June 1986.

2. Chlorine Content of MSW

The results of the chlorine content of MSW study completed in FY 1985 are in press for a 1986 issue of Chemosphere devoted to papers presented at the 5th International Symposium on Chlorinated Dioxins and

Related Compounds held at the University of Bayreuth, West Germany, September, 1985 and also appear in the Proceedings of the Twelth National Waste Processing Conference sponsored by the American Society of Mechanical Engineers (ASME).

Four samples of MSW from Baltimore County, MD and Brooklyn, NY which were analyzed in the 1985 chlorine content study were sent to R. Wingender of Argonne National Laboratory for determination of the presence and amounts of chlorinated dioxins, furans, and related compounds (e. g. PCB's and chlorophenols). Input composition data of this type are not clearly established for MSW and are essential to establish how much dioxins or furans are formed during the incineration process.

3.   Development of Corrections for Incomplete Combustion

The determinations of the calorific value and moisture content of the cellulose burned in the study to develop methods for correction for incomplete combustion were carried out. The determinations provide necessary auxiliary data to convert laboratory results so that they have a closer correspondence to real-world incinerator conditions. The combustion results obtained in the study for development of corrections for incomplete combustion were summarized and appear in a second manuscript published in Chemosphere (see following section).

4.   Threshold Condition for Formation/Destruction of Organic Chlorine Compounds

The results of the FY 1985 combustion of synthetic MSW doped with PVC appear in a second manuscript in press for Chemnosphere, devoted to papers presented in the 5th International Symposium on chlorinated Dioxins and Related Compounds.

5.   Modifications to Apparatus and Procedures

A number of hardware and software changes were made as a result of the shift in emphasis of the experiments from calorimetry to controlled combustion studies and chlorine monitoring. The changes were as follows:

o To better simulate combustion conditions in real-world incinerators, the combustor of the 2.5 kg capacity flow calorimeter was modified so that the CO produced in the combustion of synthetic MSW in air could be reduced to less than 1000 ppm. (In the FY 1985 study to develop corrections for incomplete combustion, the CO was in the 10,000-15,000 ppm range.) This was accomplished in a sequence of experiments in which various sources of heat loss from the combustion zone (i.e. region near the burning sample) were successively reduced, the most critical of which amounted to providing insulation between the combustor and combustor enclosure in the region below the reaction zone baffle. The option of burning synthetic MSW in dispersed rather than in pellet form

was not explored in order to have a capability of studying the formation or destruction of dioxins under various conditions in the absence of fly ash.

o To minimize the time necessary to break down, reassemble, and leak check the gas supply and sampling lines in a calorimetric experiments, the combustor was permanently mounted on a frame outside the 2.5 kg capacity flow calorimeter. Auxiliary cooling sources were built for the outside of the combustor enclosure, for the heat exchange coil for the product gas, and for the collector for the water liberated in the combustion reaction to replace the cooling originally provided by the calorimeter water.

o Two oxygen detectors have been installed to improve the characterization of inlet and exit gas streams to the combustor. Backup CO and CO_2 detectors (NDIR) were installed in the product gas analysis train to provide redundancy and loss of data due to detector malfunction.

o To improve the collection of trace chlorinated organic species, the MM5 train was redesigned and is being rebuilt in cooperation with R. Wingender of Argonne National Laboratory, who will carry out the dioxin analysis in subsequent experiments. Changes are oriented towards improving the efficiency of recovery of organic chlorine compounds and reduction of possible contamination of the XAD-2 resin (used to trap gaseous organic chlorine compounds) prior to analysis by gas chromatography and mass spectrometry.

o To upgrade monitoring of the detectors for O_2, CO and Co_2, a new thirty channel scanner was installed. Since each combustion experiment now tends to be quite different in terms of the need for and time sequence for monitoring the various detectors, the original software for data acquisition for the fixed routine of a calorimetric experiment has become obsolete and has had to be replaced. We were fortunate to have a guest computer scientist from the Twente University of Technology, Netherlands, to help us in redesigning the data acquisition software. As a result of Mr. Rukkers three and a half month stay with us, we have a well designed data acquisition system which can be modified rapidly to fit the varying demands of any particular laboratory experiment. Other software for data analysis and plotting was developed by two summer students (S. Sung, R. Metz).

In the initial phase of the combustion experiments of this study, we are currently carrying out a set of chlorine mass balance experiments. The aim of these experiments is to determine the degree to which suitable clean up procedures will ensure that organic chlorine compounds detected in the combustion products of a given run are formed from chlorine containing compounds burned in the same rather than in previous runs.

During FY 1987 we plan to complete the remaining auxiliary measurements and analysis of the study for development of corrections for incomplete combustion. The initial phase of the study of threshold conditions for the formation/destruction of chlorinated organics will be completed with an attempt to determine the combined recovery efficiency of the combustor plus the MM5 sampling train for chlorinated organic compounds. In the second phase of the study, we plan to evaluate the use of calcium oxide binder in densified pellets of processed MSW as a possible method for reducing dioxin emissions from combustion of refuse. In the third phase of the study, we plan to resume our study of the combustion of synthetic MSW doped with inorganic as well as organic chlorine compounds.

Because the combustor of the 2.5 kg flow calorimeter cannot be economically altered to provide all the combustion conditions that must be studied in the threshold study, a new laboratory-size, two stage incinerator was purchased in FY 1986. It is our plan to instrument this unit and conduct trial experiments toward the latter part of FY 1987.

B. Calorimetric Update on SRM Coals 2682, 2683, 2684 and 2685
   (J.C. Colbert)

The annual calorimetric update was performed on SRM Coals 2682, 2683, 2684 and 2685 to determine if there has been any change in the calorific value of these coals due to sample degradation as a result of aging or normal oxidation. Sixteen unopened bottles of coals were received from OSRM, four of each of the latter SRM's. One measurement was made for residual moisture and one for calorific value. The original certified value for sulfur was used in making the calculations since this constituent remains constant with time. All of the measurements were made in random order with one duplicate measurement for SRM 2684. The sampling procedure and run protocol was designed by R.C. Paule, NML Statistician.

Good agreement (<50 Btu/lb) was obtained between calorific values obtained for SRM 2683, 2684, and 2685 and their 1985 certified values, however, the average calorific value for SRM 2682 was 300 BTU/lb higher than the average result for 1985.

As a further check on the results, an additional set of four unopened coals were measured with only one sample giving a high calorific value. These eight coal samples were sent to an outside testing laboratory by the OSRM. The results of our lab and the outside lab agree to within 7 Btu/lb. The final statistical evaluation of the data led the OSRM to remove the calorific value certification from SRM 2682. This is due to a larger variability in the sample than anticipated, resulting in a larger variability in the calorific value than was predicted. It appears that the bottled material maybe degrading at an uneven rate, the cause of which is unknown at this time. Another parameter which should be examined is particle size variability in SRM 2682, within and between bottles, since particle size variability can influence the dispersion of results.

C.   Bomb Calorimetric Measurements for Biotechnology
     (J.C. Colbert and E.S. Domalski)

     The enthalpy of combustion of the crystalline monsaccharides D-ribose
and 2-deoxy-D-ribose (2-deoxy-D-erythro-pentose) have been determined by
combustion bomb calorimetry. The standard molar enthalpies of combustion
(Δ_cH) and formation (Δ_fH) at 298.15 K for crystalline D-ribose are:
-2349.47 ± 0.95 kJ/mol and -1047.23 ± 1.66 kJ/mol, respectively.
Similarly, for 2-deoxy-D-ribose, Δ_cH = -2527.39 ± 0.98 kJ/mol and Δ_fH =
-869.31 ± 1.68 kJ/ mol. Proton NMR and C-13 NMR studies were conducted by
B. Coxon of the Center for Analytical Chemistry, to determine the anomeric
composition of the crystalline sugars. The crystalline D-ribose sample
consisted of 64.4 mass % beta-pyranose, 35.4 mass % alpha-pyranose, and
0.2 mass % beta-furanose anomers. The sample of 2-deoxy-D-ribose was made
up of 98.8 mass % beta-pyranose, 0.5 mass % alpha-pyranose, and 0.7 mass %
beta-furanose anomers.

     Combustion bomb calorimetric studies are in progress on crystalline
hexaglycine. Elemental analyses on this compound for carbon, hydrogen,
and nitrogen from two independent testing laboratories indicates that it
is the hemihydrate. An examination of the literature combined with some
preliminary calculations on diglycine, triglycine, and tetraglycine shows
that the energy of the peptide bond in these compounds is constant. If
one extends this energy constancy to hexaglycine, then the energy or
enthalpy of hydration can be estimated as a result of conducting the
combustion calorimetric measurements. This value for the enthalpy of
hydration should provide some useful insight into the magnitude of
hydration forces between an oligopeptide and water under conditions of
initial bonding interaction.

     Previous bomb calorimetric measurements in this laboratory on
crystalline adenine, guanine, purine adenosine, guanosine dihydrate,
D-ribose, and 2-deoxy-D-ribose provide the basis for establishing several
energetic cycles for the formation of nucleosides as well as indicating
research paths in which to pursue combustion bomb calorimetric
measurements on key compounds. Three key compounds which are immediate
candidates are: deoxyadenosine, deoxyguanosine, and nebularine.
Energetic differences between ribose/deoxyribose, adenine/adenosine,
guanine/guanosine, and purine/nebularine moieties in nucleoside formation
could be established more precisely than are presently available and could
be regarded as standard reference value points for thermodynamic
assessments involving reaction processes of nucleosides.

D.   Estimation Methods and Combustion Calorimetry of Organic Phosphorus
     Compounds
     (D.R. Kirklin and E.S. Domalski)

     Precise enthalpies of formation are not available for important
industrial and biochemical compounds that contain phosphorus.
Experimental determination of these properties for some of the compounds
is not feasible because of their toxicity or limited availability. The
objective of this research is to develop correlation and estimation
schemes which are needed to predict enthalpies of formation at 298 K for

compounds that have no reported experimental values. Also, combustion calorimetric determination of enthalpies of combustion will be conducted on key organic phosphorus compounds.

Precise and accurate enthalpies of formation are necessary to develop an adequate correlation and estimation scheme. However, there is a lack of precise and accurate thermodynamics literature data on organic phosphorus compounds. The existing thermodynamic data for organic phosphorus compounds, which are based upon bomb calorimetric data, are often inaccurate due to several problems associated with the combustion calorimetry of organic phosphorus compounds. Until the present time, there is only one set of data in the literature which has adequately addressed all of these problems. These data were obtained by Harrop and Head (J. Chem. Thermodynam. 9, 1067 (1977).) on crystalline triphenylphosphine oxide.

There are four major problems associated with the combustion calorimetry of organic phosphorus compounds. The first problem is the selection of an unreactive crucible material. Platinum crucibles, which work well with most organic compounds, are unsuitable because platinum reacts with organic phosphorus compounds at high temperatures. The second problem is that organic phosphorus combustion samples usually do not burn completely in a bomb combustion experiment. Phosphorus compounds are used commercially as flame retardants for various fabrics because of their resistance to burning. When phosphorus compounds burn in oxygen they produce oxides of phosphorus which dissolve in the water in the bomb to form various kinds of phosphoric acids. These phosphoric acids have appreciable energies of dilution and are produced as various concentrations in different parts of the bomb. Therefore, the attainment of a homogeneous solution of uniform concentration of these phosphoric acids constitutes the third problem area. The fourth problem is that the bomb solution must be analyzed to determine, qualitatively and quantitatively, the speciation of phosphorus acids formed as rapidly after the calorimetric measurement as possible because of slow oxidation of all phosphoric acids present to H_3PO_4.

The solution to the above mentioned problems are straightforward, but most laboratories are not equipped to handle them. Gold crucibles are found to be unreactive with organic phosphorus compounds but have a relatively low melting point. A sufficiently massive gold crucible performs well in most experiments. The problem of incomplete combustion can be overcome by determining the amount of carbon dioxide produced or by measuring the amount of carbon residue formed. The problem of obtaining a homogeneous solution of the phosphoric acids can only be solved by using a rotating bomb calorimeter. Most laboratories use static bomb calorimeters and therefore cannot obtain a homogeneous bomb at the end of the reaction period. The qualitative and quantitative analysis of bomb solutions can be only done by various forms of chromatography. Harrop and Head used paper chromatography, however, this method is very slow and not very quantitative. Ion chromatography seems to be ideally suited to solve this problem because it is quantitative and offers reasonable precision.

The NBS bomb calorimetry laboratory has a rotating bomb calorimeter that utilizes sample sizes on the order of 100-200 milligrams. The laboratory has equipment for measuring the amount of carbon dioxide

produced during each combustion experiment. A DIONEX 2000i Ion Chromatograph was borrowed from the DIONEX Corporation to check the feasibility of analyzing the bomb solution composition for the various forms of phosphoric acids.

A set of measurements on triphenylphosphine oxide was made in the NBS rotating bomb calorimeter. Negligible amounts of carbon residue were produced. The carbon dioxide analyses verified these results. A DIONEX 2000i Ion Chromatograph was utilized to analyze the homogeneous bomb solution for the various oxyacids of phosphorus. Orthophosphoric acid, H_3PO_4, pyrophosphoric acid, $H_4P_2O_7$, and tripolyphosphoric acid, $H_5P_3O_{10}$, were observed to be produced in the following percentages, respectively: 76.3, 20.0, and 3.7. The analysis means that 59.9 % of the total phosphorus was quantitatively converted to orthophosphoric acid while 31.4 % and 8.7 % of the total phosphorus was converted to pyrophosphoric acid and tripolyphosphoric acid, respectively. These values were used to determine the amount of energy that would be needed to hydrolyze the condensed phosphoric acids to orthophosphoric acid.

A correction of -11.08 J/g for the hydrolysis of condensed phosphates to orthophosphate was added to our experimental energy of combustion, -35,778.15 ± 5.06 J/g, for triphenylphosphine oxide to calculate the correct energy of combustion, -35,789.2 ± 5.06 J/g. This value agrees very well with the previous reported value of -35,789.6 ± 6.0 J/g by Harrop and Head. (J. Chem. Thermodynam. 9, 1067 (1977)). These authors have reported the only precise combustion data for an organic phosphorus compound which was based on a comprehensive analysis of the products of combustion, which included the quantitative determination of condensed phosphoric acids present in the bomb solution from a rotating bomb calorimeter. Bedford and Mortimer (J. Chem. Soc. 1622 (1960)) reported an energy of combustion of -35,943 ± 45 J/g based upon measurement using a static bomb calorimeter.

Experimental measurements were also made on triphenylphosphine. The methods and procedures established during the triphenyl phospohine oxide were utilized. The sample was vacuum dried for 12 h and found to contain 0.0077 % moisture. The sample was investigated with no further purification. The mean of seven measurements yielded a value of -39,200.73 ± 3.85 J/g for the internal energy of combustion without a correction for the hydrolysis of condensed phosphates to orthophosphate. Assuming that the condensed phosphates were produced in the same proportions as for the triphenylphosphine oxide would require an additional correction of -11.08 J/g. This would make the actual value determined to be -39,211.81 J/g. However, the actual correction for the hydrolsis of condensed phosphates must be determined on a set of combustions of triphenyl phosphine and will be performed during fiscal year 1987 when the combustion calorimetry laboratory receives a DIONEX Ion Chromatograph. The internal energy of combustion reported by Bedford and Mortimer is -39,245.8 ± 36.7 J/g based upon measurements using a static bomb calorimeter.

Future plans include bomb calorimetric measurements on other key organic phosphorus compounds. These measurements will provide the data necessary to determine estimation parameters for other organic phosphorus compounds. Proposed compounds are triphenyl phosphate, tri-n-octyl phosphine oxide and tricyanophosphine.

E. Drop Calorimetry of Non-Reacting Systems Below 2800 K
    (D.A. Ditmars)

This activity is a continuation of a calorimetric research program whose goals are:

o to obtain accurate thermodynamics data on non reacting refractory materials in either the solid or liquid state up to 2800 K.

o to measure the specific heat at temperatures above 273 K of well-characterized materials of the highest attainable purity for which existing C_p data are insufficient or in conflict and which are: (a) critical to energy and space related technology, or (b) especially suited as a model on which to test refined lattice-dynamic calculations of thermodynamic properties.

o to produce and support high-temperature calorimetric standard reference materials (SMR's) for heat capacity and for differential thermal analysis (DTA) calorimetric measurements.

The number of facilities, nationally, which can sustain programs of high-temperature calorimetric research is seriously diminishing at a time of increasing needs for just the data produced through this type of investigation. There is a constant demand for thermodynamic data on new materials capable of functioning acceptably in the harsh environments associated with space propulsion systems or upon re-entry, new energy technologies and defense-generated needs for materials to enable space systems to withstand overt aggression. Also, the existing thermodynamic data on some elements is often not accurate enough to allow a meaningful test of theories which have recently been formulated to calculate thermodynamic functions directly.

The Chemical Thermodynamics Division has available two operative precision drop calorimeters for the ranges 273-1200 K (isothermal, phase-change calorimeter) and 1200-2800 K (adiabatic receiving calorimeter). These are being used in research intended to provide calorimetric measurements at the highest accuracy on materials related to the high temperature applications mentioned above. Every effort is made to coordinate this research with that of another NBS facility (very-high-temperature pulse calorimeter) in order to provide the capacity for continuous coverage of high-temperature thermodynamics studies up to 5000 K or above on especially important systems. We have in addition an operative high-temperature discrete-heating adiabatic calorimeter (300-800 K) and we maintain in reserve a low-temperature (4-300 K) adiabatic calorimeter for possible future research needs.

In order that NBS thermal data and that of other high-temperature investigations can be fairly intercompared and assessed for accuracy, we maintain a continuing effort to update or extend the range of coverage of high-temperature standard reference materials. In recognition of the growing need for accurate DTA temperature and enthalpy standards, we attempt to identify systems whose thermal properties can be measured by both conventional calorimetric and DTA techniques.

We have concentrated our experimental and data-analysis activity in FY 1986 among the alkaline earths Ca, Sr, and Ba and have continued our work on pure Cu. Of the alkaline earths, calcium is of particular economic and biological importance, yet the literature thermodynamic functions for calcium are certain to be seriously in error due to sample impurity effects. The situation of the thermodynamic functions for strontium is similarly unclear for no original published heat-capacity data exists for this element above room temperature. This is unfortunate, as knowledge of the thermodynamic properties of strontium compounds figures prominently in assessing the course and effects of potential nuclear power accidents.

In the conduct of thermodynamic research on these alkaline earth metals, one must confront the effects of low, but virtually irreducible, oxide and hydride impurity levels which nevertheless exert a substantial influence on the phase relationships among the allotropes of Ca and Sr and on Ba. Thus, a large fraction on ones total effort must be devoted obtaining pure samples, maintaining their integrity, and obtaining credible analysis for the oxygen and hydrogen present.

Our prior (FY 84) heat-capacity data on calcium, measured partly at NBS (T>300 K) and partly at the U.S. Geological Survey in Reston, VA (in the cryogenic range) employed two calcium samples of differing oxygen and hydrogen impurities. Of these data, only those in the high-temperature fcc region (715>T>300 K) were obtained using the sample of lower purity. Comparison at NBS with enthalpy data obtained in the fcc region for the high-purity sample led to the conclusion that the earlier NBS high-temperature data were subject to serious and uncorrectable systematic error arising from the method of encapsulation. Therefore, in FY 86 we repeated the entire fcc series of measurements on the higher-purity sample. In addition, a number of enthalpy measurements were made at closely and carefully-spaced temperatures throughout the fcc-bcc transition region. This new fcc data for calcium was analyzed in FY 86 and shown to merge, uncorrected, with the cryogenic data mentioned above. The enthalpy data for calcium in the fcc-bcc transition region indicated not a sharply temperature-resolved transition, but one occurring gradually over a 5 or 6-degree interval. This, we have interpreted using a model in which a trace contaminant (in this case CaH_2) enters into ideal solution with each of two allotropes of calcium. The results (Fig 4.1) indicate a lower temperature for the fcc-bcc transition temperature (710 K) than current values proposed in the literature (716 to 720 K).

Analysis of the strontium sample we had obtained from Prof. Westrum of the University of Michigan measured in FY 86 showed an unacceptably high level of hydrogen contamination. Therefore, we obtained in FY 86 a new,

specially-prepared, diffusion-distilled strontium sample from the Metallurgy Department of Iowa State University. At the same time, we obtained a similar sample of barium.

Considerable effort was expended in FY 86 on the encapsulation of these materials and preparation of them for purification of hydrogen as well as for oxygen and hydrogen analyses. To bring this about, we developed a cooperative arrangement with the Metallurgy Division of the Naval Research Laboratory (Wash. D.C.) for the use of their electron-beam materials-processing facility.

In FY 87 we plan to extend the heat capacity measurements on calcium through the melting point into the liquid range. Also, purification and analysis of the strontium and barium samples will be carried out and measurement of their heat capacity in the solid range begun. Heat capacity measurements on the purified barium sample in the cryogenic range will concurrently be performed. In FY 86 we collaborated with a guest worker from Brock University (C. Plint, Ontario) to complete measurements on the heat capacity of highly-pure, polycrystalline copper (NBS Special Research Material 5 : a low-temperature heat capacity standard) up to 1173 K. We plan to extend these measurements in FY 87 to the melting point and to begin the analysis of our data and comparison to the extensive literature data available on copper. These copper data will have potential value in extension of the temperature range of the copper heat-capacity standard and in establishing more accurate heat capacity data against which to test new theoretical model in the calculation from first principles of the thermodynamic properties of fcc metals.
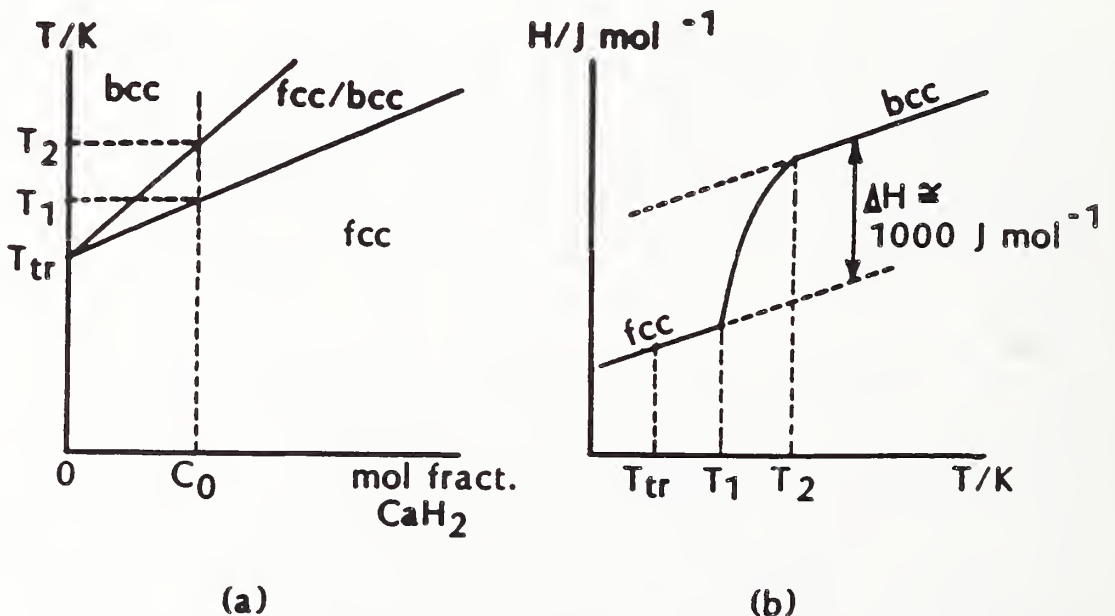

(a)   (b)

Fig.4.1(a): Idealized Ca-CaH$_2$ phase diagram including 2-phase region near peritectoid. Overall CaH$_2$ concentration (C_0)= 0.24 mol % ; (b): Schematic measured enthalpy function for Ca containing 0.24 mol % CaH$_2$ in solution. T_1= 714 K, T_2= 720 K, $T_{tr} \cong$ 710 K.

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5. CHEMICAL THERMODYNAMIC DATA ACTIVITIES

M.W. Chase, D.M. Bickham, D. Garvin, C.R. Jackson, T.L. Jobe, Jr.
W.L. King, D.B. Neumann, V.B. Parker, D. Smith-Magowan, R.H. Wood,
(Consultant), D.D Wagman (Guest Worker), E.D. Hearing, R.H. Nuttall,
R.H. Schumm, N. Young, and S.D. Wasik (Contractors)

The goal of this work is to provide reliable values of thermochemical
and thermophysical properties of chemicals, both inorganic and organic. The
values are intended to be useful throughout science and industry. Because of
the widely differing needs of users, emphasis is placed in this work on
generic information and methods of wide applicability. Two data centers carry
on this function: the Chemical Thermodynamics Data Center (CTDC) and the
Electrolyte Data Center (ELDC). Both are partly supported by the NBS Office
of Standard Reference Data (OSRD).

The data group now consists of five thermochemists, a computer systems
manager, two computer programmers, a chemical information specialist, a
clerk, a consultant and a guest worker. In addition, four thermochemists do
special tasks under contract.

The work of the two data centers is inter-linked. Together they cover the
evaluation of thermochemical properties of chemical reactions, thermal func-
tions of chemical species and thermophysical properties of solutions. These
activities are being extended by extramural collaborations: participation in
the CODATA Thermodynamic Tables project to build an international set of
recommended values, and, cooperative work with the University of Delaware on
methods for correlating thermophysical properties of solutions.

A major expansion of the data centers occured during the year. The JANAF
Thermochemical Tables project was moved to NBS from the Dow Chemical
Co., Midland, MI. Dr. M.W. Chase, leader of the JANAF project, became a
member of the data center staff, and, at the end of the year, head of the
Chemical Thermodynamics Data Centers Group.

The data centers are supported by a vigorous computer group which
manages the mini- and microcomputer facility used by five CCP data
activities.

The outputs from the centers are published in the Journal of Physical and
Chemical Reference Data, the Journal of Research of NBS, CODATA Special
Publications, Handbooks of DIPPR, and proceedings of various meetings. The
annual index to the thermochemical literature on inorganic compounds that is
prepared at NBS is published in the Bulletin of Chemical Thermodynamics.

Most of our prime activities are described in the following paragraphs.
Topics in progress which will not be discussed further are:

o Installation of the computer program GAMPHI (calulates activity
   coefficients) on a microcomputer

o Final selection and documentation of the CODATA key values for chemical thermodynamics

o Preparation of recommendations for the solubility of eleven types of organic compounds in water

o Converted network calculation programs (CATCH) to be operational on the NOS CYBER (from the NBS UNIVAC); these programs are necessary for the evaluation of the calcium and key values results for CODATA and the rubidium network
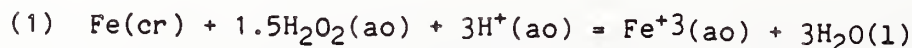
A. Chemical Thermodynamics Data

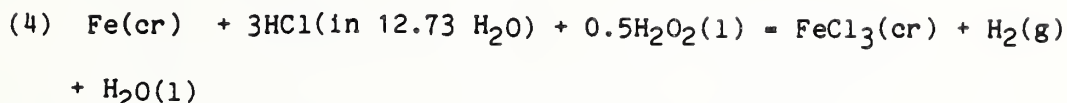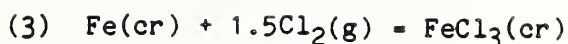### 1. Thermochemistry of Compounds of Iron
   (V.B. Parker)

The evaluation of the thermochemical properties of iron compounds is being undertaken as part of a larger project, sponsored by CODATA, that will include thermal functions and the analysis of several binary systems. The thermochemical analysis is well underway. A reaction catalog (listing of pertinent measurements, each expressed as a chemical reaction, together with the values of the properties measured) has been assembled. It contains the evaluated thermochemical data on the reactions of the "key" iron compounds.

A "key" compound is a species whose thermochemical properties are of strategic importance because many other compounds are dependent upon its thermochemical properties. The properties of this compound may, in turn, be dependent upon those of other compounds (from various reaction paths). This group of compounds and its interconnections comprises the "key network".

The thermochemistry of iron compounds is complex. An example of this complexity is shown in Figure 5.1, which indicates the enthalpy relationships among the key compounds. A similar diagram, not shown, indicates the Gibbs energy relationships and measured entropies. Considering the importance of iron and its compounds, the disarray of the data for the basic thermochemical relationships is disturbing. Calculations of the same property via different paths in the network yield discordant values. This is demonstrated in the following brief analysis of the thermochemical properties of Fe^{+2}(aq) and Fe^{+3}(aq) in their standard states at 298.15 K. The cited reactions are from the network shown in Figure 5.1, the values are from individual studies or combinations of them. The enthalpy data are given first for the two ions and then the Gibbs energy data. The tentative selected values made to date conclude the presentation. The state designation "ao" means standard state. All thermochemical values are in kJ/mol.

Enthalpy of Formation: For the determination of the enthalpy of formation of Fe^{+3}(ao) the measurements on the following reactions are used.

(1) $Fe(cr) + 1.5H_2O_2(ao) + 3H^+(ao) = Fe^{+3}(ao) + 3H_2O(l)$

(2) $FeCl_3(cr) = Fe^{+3}(ao) + 3Cl^-(ao)$

(3) $Fe(cr) + 1.5Cl_2(g) = FeCl_3(cr)$

(4) $Fe(cr) + 3HCl(in\ 12.73\ H_2O) + 0.5H_2O_2(l) = FeCl_3(cr) + H_2(g)$

   $+ H_2O(l)$

Values obtained are:

From Reaction	$\Delta_f H^o(Fe^{+3}, aq)$	$\Delta_f H^o(FeCl_3, cr)$
(1)	-46.6±0.8	
(2) and (3)	-53.8±0.9	
(2) and (4)	-57.0±1.0	
(3)		-396.02±0.14
(4)		-399.24±0.35

The agreement of the results in each column is not as good as anticipated, based on the claimed reliability of the individual studies.
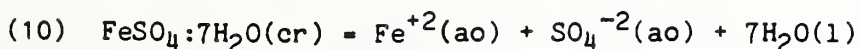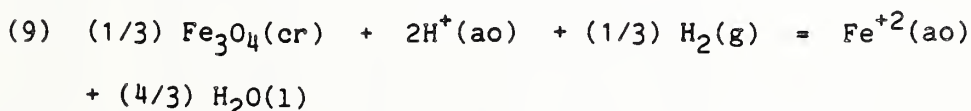
Similarly a more extensive set of measurements may be used for the determination of the enthalpy of formation of $Fe^{+2}(ao)$. A similar conclusion is obtained. The resulting values show too much scatter; much larger than would have been expected based on interpretation of the individual studies.

In a third independent path, the difference between the enthalpies of formation of ferric and ferrous ion can be determined from:

(5) $Fe^{+2}(ao) + 0.5H_2O_2(ao) + H^+(ao) = Fe^{+3}(ao) + H_2O(l)$

(6) $Fe^{+2}(ao) + H^+(ao) = Fe^{+3}(ao) + 0.5H_2(g)$.

Again, from a collection of six results, the scatter in this enthalpy of formation difference is too great, casting suspicion on the results.

Gibbs energies of formations: The Gibbs energies of each of these species can be determined (independently) from cell measurements (7), equilibria and solubilities (8-10).

(7) $Fe(cr) + 2H^+(ao) = Fe^{+2}(ao) + H_2(g)$

(8) $Fe^{+2}(ao) + 2Tl(cr) = Fe(cr) + 2Tl^+(ao)$

(9) $(1/3)\ Fe_3O_4(cr) + 2H^+(ao) + (1/3)\ H_2(g) = Fe^{+2}(ao)$

   $+ (4/3)\ H_2O(l)$

(10) $FeSO_4:7H_2O(cr) = Fe^{+2}(ao) + SO_4^{-2}(ao) + 7H_2O(l)$
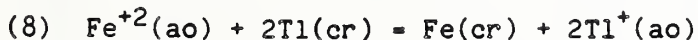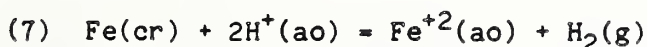
The Gibb's energy of the ferrous ion $\Delta_f G^o(Fe^{+2}, ao)$ is determined to be:

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from (7)	from reaction shown
-80.14±0.20	-78.7±1.5 (8)
-90.11±0.80	-90.0±5.0 (9)
-78.8±0.5	-90.6±1.2 (10)
-84.91±0.20	

These numbers should exhibit much greater agreement. On the basis of the EMF data alone, a value $\Delta_f G^o(Fe^{+2}, ao)$ of -80.14± 0.20 would be selected, using a study in which great care was taken to avoid electrode contamination by $H_2(g)$ (from its preparation) and $O_2(g)$. The more negative values from (9) and (10), however, cast suspicion on this choice.

The Gibbs energy of formation of ferric ion, -11.4±1.5 kJ/mol can be obtained from:

(11) $FeOOH(cr, alpha) + H_2O(l) = Fe^{+3}(ao) + 3 \ OH^-(ao)$
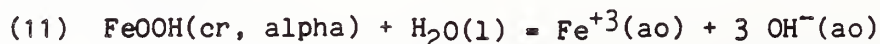
where $\Delta_f G^o(FeOOH, cr)$ is dependent upon $\Delta_f H^o(Fe_3O_4, cr)$ and

$S^o(FeOOH, cr, alpha)$.

Independently, the half cell

(12) $Fe^{+2}(ao) + H^+(ao) = Fe^{+3}(ao) + 0.5H_2(g)$
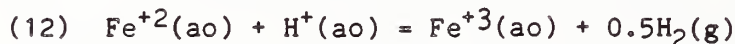
for which agreement among the various investigations is excellent,

yields $\Delta(\Delta_f G^o(Fe^{+3}(ao) - \Delta_f G^o(Fe^{+2}, ao)) = 74.27±0.20$.

Selected values. Tentative selections have been made, based on the data given above:

	$\Delta_f H^o$	$\Delta(\Delta_f H^o)$	$\Delta(\Delta_f G^o)$
$Fe^{+2}(ao)$	-91.5±1.0		
$Fe^{+3}(ao) - Fe^{+2}(ao)$		42.5±1.5	74.27±0.20

so that:

$Fe^{+3}(ao)$	-49.0±2.0
$FeCl_2(cr)$	-342.8±1.1
$FeCl_3(cr)$	-396.0±2.0
$FeSO_4:7H_2O(cr)$	-3013.7±0.3

It is hoped that further analysis of the data, and the inclusion of more data, based on current measurements, will help establish the selections above and clarify the situation, particularly that for $\Delta_f G^o(Fe^{+2}, ao)$. The following experimental data would be useful.

Activity coefficients for aqueous $FeSO_4$ solutions. Those used now for $\Delta^{sol}G^o(FeSO_4:7H_2O, cr)$ are estimated from $NiSO_4$, but it is not known how good this analogy is.

IRON KEY NETWORK – ENTHALPY

GUIDE:

substance —process— substance

Fe₂O₃(cr) — $Fe_2O_3(cr)$

5a, 5b, 5c

7

FeOOH(cr) — $FeOOH(cr)$

32

Fe(OH)₃(cr) — $Fe(OH)_3(cr)$

13

FeCl₃·6H₂O(cr) — $FeCl_3 \cdot 6H_2O(cr)$

16a, 16b

FeOCl(cr) — $FeOCl(cr)$

Fe⁺³(aq) — $Fe^{+3}(aq)$

25

FeCl₃(cr) — $FeCl_3(cr)$

24

15

33

18

34

1,2

5a, 5b, 5c

5c, 5d

16a, 16b

10

19a, 19b

Fe₂Cl₆(g) — $Fe_2Cl_6(g)$

FeCl₃(g) — $FeCl_3(g)$

Fe(cr) — $Fe(cr)$

11b

17g

29

27a, 27b

6

Fe₃O₄(cr) — $Fe_3O_4(cr)$

4

FeO(cr) — $FeO(cr)$

Fe(OH)₂(cr) — $Fe(OH)_2(cr)$

10

9,12a

Fe⁺²(aq) — $Fe^{+2}(aq)$

30

(NH₄)₂Fe(SO₄)₂·6H₂O(cr) — $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O(cr)$

26a, 26b

FeSO₄·7H₂O(cr) — $FeSO_4 \cdot 7H_2O(cr)$

28

FeSO₄(cr) — $FeSO_4(cr)$

3a, 3b

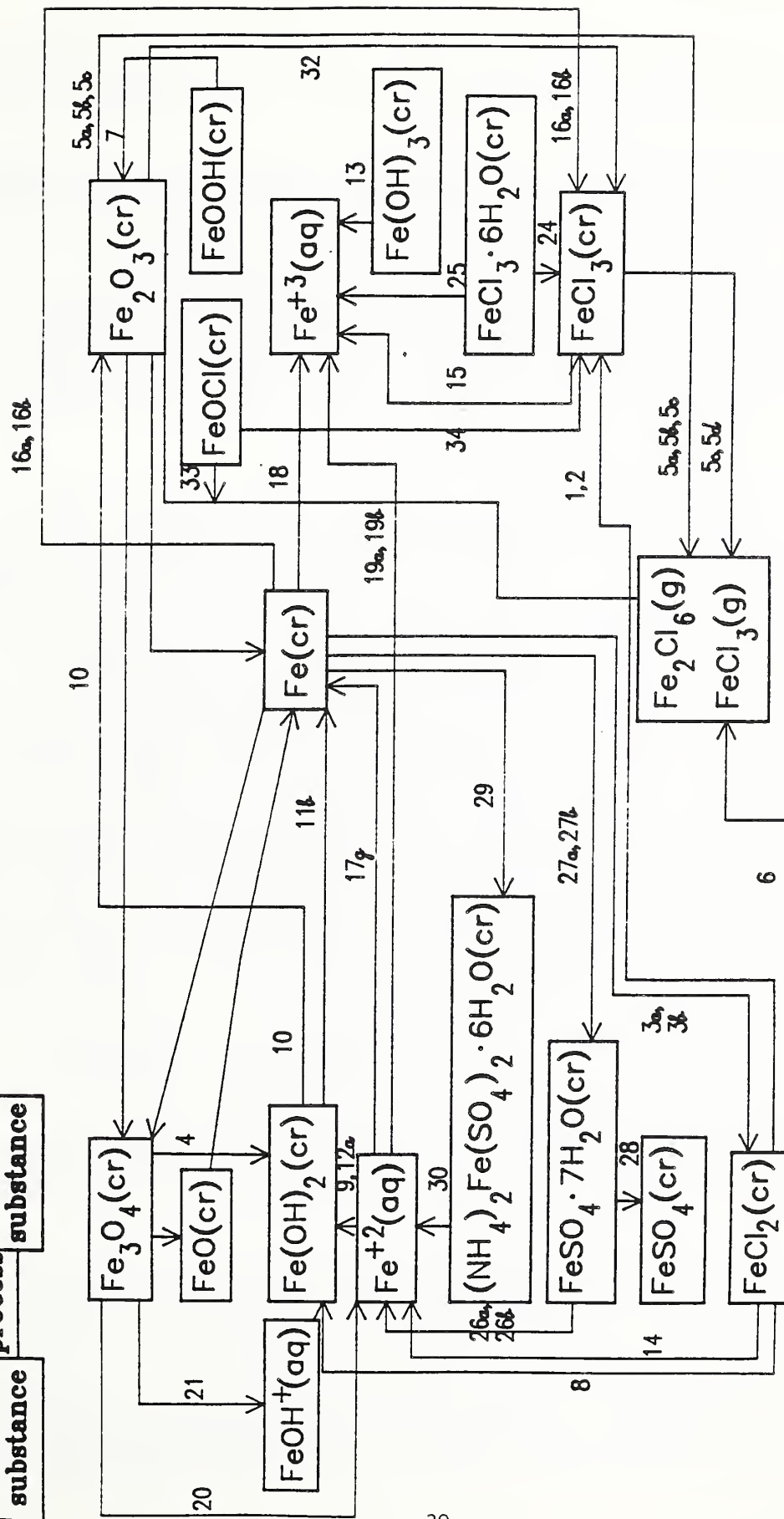FeCl₂(cr) — $FeCl_2(cr)$

14

8

21

FeOH⁺(aq) — $FeOH^+(aq)$

20

Fig. 5.1. Iron Key Network—Enthalpy. Measured processes are shown by arrows connecting the substances. (The numbers on the arrows refer to a larger reaction catalog than that discussed here, and are not the same as those used in the text).

39

o The $\Delta_f G^O(Fe^{+2},ao)$ value, now -80.14 ± 0.20 from EMF data should be verified.

o $\Delta_{sol}H_{sol}H(FeCl_3,cr)$ is needed as a function of concentration in water and aqueous HCl. The present data are not of high enough quality to permit confident extrapolation to the standard state.

o $\Delta_f H^O(FeCl_2,cr)$, $\Delta_f H^O(FeCl_3,cr)$, and $\Delta_r H^O$ for $FeCl_2(cr) + 0.5\ Cl_2(g) = FeCl^2(cr)$ should be redetermined. The $FeCl_2/FeCl$ couple is important outside the iron system as auxiliary data in redox reactions. The "NBS Tables" and others use $\Delta_r H_O = -57.5$, but there are conflicts in data in the uranium halide thermochemical network which might be a result of using this value.

2.   JANAF Thermochemical Tables
     (M.W. Chase)

This project was transferred in February 1986 from The Dow Chemical Company, Midland, MI to the Center for Chemical Physics at the National Bureau of Standards. Since that time, most of the effort has been directed at the establishment of JANAF resources within the Chemical Thermodynamics Data Centers. This includes the calculational programs, the literature and data files, and the backup information for the existing tabulations. In parallel with this, the third Edition of the JANAF Thermochemical Tables has been completed, at Dow Chemical, and sent to the American Institute of Physics for publication later this year in Journal of Physical Chemical Reference Data.

In our data evaluation activities reviews and thermochemical tables are being prepared for three classes of species: the alkaline earth metals, their monohydroxides and their dihydroxides. For the 3rd Edition of the JANAF Thermochemical Tables, the calcium thermal functions were estimated to be intermediate between those for magnesium and strontium; the strontium thermal functions being based on unpublished enthalpy data of Stephens and Roth. However, there now is additional information available from the recent heat capacity study of calcium by Robie (USGS) and the enthalpy studies of calcium and strontium by Ditmars. The low temperature study by Robie is in qualitative agreement with the recent JANAF analysis. However, the experimental results yield a considerably different Cp curve in the region below ~20 K, raising the entropy of calcium at 298.15 K by ~ 1.5 J/(mol K) above our recommendations. When the analysis of new information is completed, the thermodynamic functions of the metals will be much more firmly based. We will then be in a better position to judge the reliability of the existing enthalpy data for barium.

The alkaline earth monohydroxides have been studied experimentally during the last few years. A thorough spectroscopic study has been carried out for the magnesium, calcium, strontium, and barium species by Harris et al. and Bernath et al. These studies have yielded structures and two of the three vibrational frequencies v_1, and v_2. In all cases, v_3, the O-H stretch is assumed to be ~3650 cm-1 in comparison with the alkali metal hydroxides. Now the thermal functions, in particular the entropy, are well-established, in comparison with the previously available entirely-estimated values. This

results in the entropy at 298.15 K being shifted by 2.5 J/(mol K). However, for the case of beryllium, we still must rely on theoretical calculations for the structure and the vibrational frequencies.

Our review of the alkaline earth dihydroxide species is nearing completion. The full analysis of these species is limited by the lack of low temperature heat capacity data for $Sr(OH)_2$ and $Ba(OH)_2$ and high temperature enthalpy data for $Be(OH)_2$. The low temperature data for $Be(OH)_2$ has been measured in USSR, is available through VINITI (Russian Depository of Technical Data), and will enhance the quality of the beryllium dihydroxide thermal functions. The gas phase dihydroxide species are estimated based on comparisons with the gaseous difluorides, dichlorides and the monohydroxides. With more reliable data avalilable on these latter species, the resulting gaseous dihydroxide thermal functions (still estimated) should be much improved.

In addition, information has been collected for the analysis of the alkaline earth oxides, sulfides, sulfates, carbonates, and the halides. For each of these classes of species, annotated bibliographies exist and are being updated continuously. Data summaries are in preparation for these classes of species.

3. Thermochemical Properties of Compounds of Rubidium
    (V.B. Parker, W.H. Evans, R.L. Nuttall)

The thermochemistry of rubidium compounds has been summarized in a paper accepted for J. Phys. Chem. Reference Data. This paper presents a catalog of the 420 measurements on 250 substances used in the preparation of the rubidium table in the "NBS Tables of Chemical Thermochemical Properties". It represents a comprehensive survey of thermochemical measurements on rubidium compounds. Included are enthalpies of reaction, Gibbs energies of reaction, based on equilibria and cell potentials, and entropies. For each process a comparison is made between the observed value and that calculated from the "NBS Tables". A feature novel to thermodynamic tables is that estimated reliabilities are given for the recommended values for each measured process.

4. Thermodynamic Properties of Compounds of Calcium
    (D. Garvin, V.B. Parker)

The first volume of a new series of tables of evaluated thermodynamic properties of chemicals is being published this year. It is the "CODATA Thermodynamic Tables. Selections for Some Compounds of Calcium and Related Mixtures. (A Prototype Set of Tables.)", D. Garvin, V.B. Parker and H.J. White, Jr., editors. This is the report of the CODATA Task Group on Chemical Thermodynamic Tables and covers six years of work by an international team of data evaluators. NBS has taken the lead, providing evaluated thermochemical data, a definitive analysis of the $CaCl_2-H_2O$ system, some thermal functions, extensive "catalogs of data", technical editing and preparation of the final book. Its contents are summarized below.

Recommended values are presented for chemical thermodynamic properties of selected compounds of calcium and their mixtures. These have been prepared in accord with and as a test of a plan developed by the CODATA Task Group on

Substance	Molar mass g.mol⁻¹	$\Delta_f H°(0\ K)$	$\Delta_f H°$	$\Delta_f G°$	$H°-H°(0)$	S	$C_p°$
			·········· kJ.mol⁻¹ ··········			·· J.(mol.K)⁻¹ ··	
Mg(cr)	24.3050	0	0	0	4.998	32.671	24.869
CODATA Key Value [84COD].					±0.030	±0.100	±0.100
Mg(l)	24.3050		4.790	14.044	9.788 a	1.633	34.309
Extrapolated from high			±1.000	±1.200	±1.000	±2.000	±3.000
temperature.							
Mg(g)	24.3050	145.901	147.10	112.521	6.197	148.649	20.786
CODATA Key Value [84COD].		±0.800	±0.80	±0.800	±0.002	±0.005	±0.001
MgO(cr)	40.3044	-597.422	-601.60	-569.311	5.160	26.950	37.237
CODATA Key Value [84COD].		±0.300	±0.30	±0.30	±0.020	±0.150	±0.200
MgF₂(cr)	62.3018	-1120.297	-1124.2	-1071.051	9.920	57.200	61.587
CODATA Key Value [84COD].		±1.200	±1.2	±1.300	±0.060	±0.500	±0.2
Ca(cr)	40.0800	0	0	0	5.736	41.588	25.929
CODATA Key Value [84COD].					±0.040	±0.400	±0.300
Alpha							
Ca(cr2)	40.0800		1.056	0.614	0.792 a	43.070	25.951
Beta, extrapolated from			±0.300	±0.800	±0.300	±0.700	±1.200
high temperature.							
Ca(l)	40.0800		7.788	6.619	13.524 a	45.510	35.000
Extrapolated from high			±1.000	±1.200	±1.000	±2.000	±3.000
temperature.							
Ca(g)	40.0800	177.339	177.80	144.020	6.197	154.887	20.786
CODATA Key Value [84COD].		±0.800	±0.80	±0.810	±0.002	±0.004	±0.001
Ca⁺(g)	40.0795	767.152	773.81	732.057	6.197	160.650	20.786
		±0.830	±0.83	±0.84	±0.002	±0.002	±0.001
Ca⁺²(g)	40.0789	1913.645	1926.50	1880.210	6.197	154.887	20.786
		±0.920	±0.92	±0.930	±0.002	±0.005	±0.001
Ca⁺²(ao)	40.0789		-543.0	-552.807		-56.2	-281.38
CODATA Key Value [84COD].			±1.0	±1.100		±1.0	±5.0
Ca₂(g)	80.1600	341.982	341.7	289.819	11.190	257.185	36.577
		±1.800	±1.7	±1.800	±0.100	±1.500	±0.500
CaO(cr)	56.0794	-631.594	-634.92	-603.297	6.750	38.100	42.049
CODATA Key Value [84COD].		±0.900	±0.90	±0.920	±0.060	±0.40	±0.400
CaO(g)	56.0794	24.623	23.5	0.974	8.953	219.718	32.455
		±8.000	±8.0	±8.000	±0.001	±0.020	±0.010

Fig. 5.2. Selected values for $\Delta_f H°$, $\Delta_f G°$, $H°-H°(0\ K)$, $S°$, $C_p°$ at 298.15 K and $\Delta_f H°(0\ K)$ at 0.1 MPa. First page of a 5 page table of thermochemical data in the CODATA Thermodynamic Tables.

Chemical Thermodynamic Tables. All values in the present table are mutually consistent and are consistent with the CODATA Key Values for Thermodynamics. The values are recommended for general use.

The evaluated data are for common compounds of calcium (element, oxide, hydroxide, peroxide, fluoride, chloride, sulfate, nitrate and carbonate, their hydrates and their ions in aqueous solution) and for three systems: Ca-Mg, $CaCl_2$-KCl and $CaCl_2$-H_2O.

Forty one tables of thermal functions (heat capacity, entropy, enthalpy and Gibbs energy functions) are given for those compounds of magnesium, calcium and potassium for which the properties have been evaluated in this work. Twenty four tables of thermal functions are given for auxiliary substances. Each table spans the temperature range 0 to 4000 K, to the extent that data are available. Formation properties at 298.15 K (enthalpy and Gibbs energy of formation) are given for 68 compounds of calcium, magnesium and potassium plus the relevant values of 54 auxiliary substances. A sample page from the formation property table is given in Figure 5.2.

For each of three binary systems recommendations are given for mixing properties (enthalpies and Gibbs energies), partial molar or excess properties of the components (activities, enthalpies, heat capacities) and phase transformation data. All selections of data are accompanied by uncertainties, and are documented. Detailed lists of the measurements used in the evaluations are given for the thermochemical, alloy and aqueous solution sections.

The preparation of this compendium involved work at five geographically separated institutions, assembly of machine readable data bases, transfer of data by magnetic tape and interactively, and extensive development of computer programs for both thermodynamic calculations and document preparation and printing.

5.   Needs for Thermochemical Data
      (D. Garvin, V.B. Parker)

In the course of work on the CODATA Key Values for Thermodynamics and the CODATA tables on calcium compounds, deficiencies in the presently available thermodynamic data have become apparent. Very brief summaries of these are given here. Publication of this material is planned, in order to alert the thermodynamic and spectroscopic communities to these needs.

(a) $K_2(g)$: Dissociation Energy. The 1930's spectroscopic data (used in a Birge-Sponer extrapolation), the vapor pressure data and recent theoretical calculations do not agree (range 4 kJ). Current spectroscopic techniques are adequate for the solution of this problem.

(b) Ca(cr): Thermal Properties. Ditmars (NBS) and Robie (U.S.G.S) have measured the heat capacity of Ca up through the alpha-beta transition. On the basis of preliminary results, their work leads to a value for S(298.15 K) that is 1.5 J/(mol.K) greater than the CODATA Key Value, to different heat capacities for the alpha and beta forms, a lower T_{fus}, 710 K versus 716 K, and a revised $\Delta_{tr}H\Delta_{tr}H$. (Only the liquid remains to be done). These data, if accepted, will change selections for all species whose properties depend on high temperature data, such as Ca(g), a CODATA Key Substance, $CaH_2(cr)$, and

possibly $Ca(OH)_2(cr)$ and $CaCO_3(cr)$. Gibbs energies of calcium compounds will also change. However, these changes, <0.5 kJ/mol of Ca, usually are less than the uncertainties in the values themselves.

(c) $CaCl_2 \cdot nH_2O(cr)$, n= 1,2,4,6: Heat Capacity. These hydrates are the stable forms of the salt in equilibrium with aqueous solutions, ~50 to +175 $^{\circ}$C. For none of them are there low temperature C_p data from which entropies can be calculated. Instead, the entropies are calculated from enthalpy and Gibbs energy of solution data, and the resulting values of S do not show the smooth variation that might be expected. Recent measurements by Meisingset and Gronvold treat the hexa-, tetra- and di-hydrates above 288 K and can be combined with low temperature data to provide the thermal functions needed for a modern optimization of the $CaCl_2$-H_2O system. Such data will also be useful in the development of estimation methods.

(d) $CaF_2(cr)$: Solubility and Thermal Properties. Existing measurements give pK_{sp} values varying from 11.6 to 8 at 298.15 K. The likely value is 10.6, although the most recent extensive study gives 11.6. Solubility should be studied between 298 and 500 K (to allow for geochemical applications), from both under- and over-saturation as a function of ionic strength, acid concentration, particle size, time to reach equilibrium, source and preparation of the samples. Choice of method will be important.

In addition this substance has a lambda-type transition in the heat capacity at 1424 K. There are enthalpy measurements, but these are insufficient to define the transition. Heat capacity measurements are needed.

(e) $Ca(OH)_2(cr)$: Enthalpy of Formation. The "best" data lead to $\Delta_f H$ values that do not mesh well with those for $CaCO_3$ and CaO. Nor do the Gibbs energy data (solubility and high temperature decomposition). Enthalpy of solution and solubility studies should be repeated.

(f) $Ca^{+2}(aq,std. state)$: Entropy and Enthalpy of Formation. This Key Substance has surprisingly poorly defined properties: S to ±1.0 J/mol K, $\Delta_f H$ to ±1.0 kJ/mol. Its properties are based on those of $Ca(OH)_2$, $CaSO_4$, $CaCO_3$ and $Ca(NO_3)_2$ and their aqueous solutions. The spread in values from system to system is larger than within each system. Any type of experimentation that would improve the properties of $Ca^{+2}(aq)$ would be useful.

(g) $CaO(cr)$ and $MgO(cr)$: Enthalpy of Fusion. Both of these substances melt above 3000 K. Measurements of T_{fus} have proved to be very difficult, the melting point of CaO may still be in dispute. The enthalpies of fusion are derived from phase boundary information: $d(\ln a_i)/dT = \Delta_{fus}H_i/R$. Older values are 77 kJ/mol for MgO (from the MgO-ZrO_2 system) and 52 kJ/mol for CaO (CaO-ZrO_2 system), in both cases assuming ideal solutions. A recent optimization of the MgO-CaO system [Chand and Howald, 1982] selected values of about 58 kJ/mol for both, allowing for non-ideality in the liquid and solid phases. Unfortunately, phase boundaries in the CaO-MgO system are very poorly delineated and are based in part on studies that lead to incorrect melting points. A comparative study of other binary systems should be made.

(h) $CaMg_2$: Thermochemical and Thermophysical Data. The analysis of this system in the CODATA Thermodynamic tables showed that the data are in very poor shape. Enthalpy data above 298 K show large scatter, a new study is needed. This may indicate that the limited low temperature heat capacities need to be remeasured. Enthalpies of fusion measurements disagree, and are not consistent with mixing data and enthalpies of formation. Almost any attack would help.

B. Electrolyte Data

1. Electrolyte Data: The Calcium Chloride-Water System
    (D. Smith-Magowan)

Evaluation of data on the physical and chemical properties of aqueous electrolytes is done by the Electrolyte Data Center with two fundamental objectives: (1) to provide reference data for use in scientific and technical applications and (2) to present data and analyses which will highlight challenges for future experimetal or theoretical investigations. The results of a study of the $CaCl_2-H_2O$ system provide an example of the realization of these two goals.

A correlation of experimental data on the heat capacity of $CaCl_2$ solutions as a function of temperature and composition has been combined with separate NBS correlations of excess Gibbs energy and excess enthalpy as functions of composition at room temperature to create a "skeleton table" of values for all three properties throughout the temperature range 273.15-373.15 K and composition range 0-11 molal. The heat capacity correlation was made using a model-independent spline fit on the T-x surface. The other two correlations used the Pitzer formulation (although this was not essential). The apparent molar heat capacities are shown in Figure 5.3. The maximum with respect to temperature in the apparent molar heat capacity is found in other salts and is analogous to the trends observed for excess volume. This behavior has not yet been interpreted in terms of the structure of the solutions.

The resulting values for the excess properties C_p^{ex}, H^{ex} and G^{ex} are considered to be the most accurate representation of the experimental data available and cover the broadest range of composition of any study presented to date. The procedure includes the systematic treatment of data on aqueous systems at elevated temperatures, where the pressure is greater than one atmosphere. The effect of pressure has routinely been neglected in most previous treatments of the data for this system. Comparison with previous correlations where the effect of pressure has been neglected reveals a tangible systematic error in those studies.

Heat capacity data are lacking or of low quality in several temperature-composition regions. Below 298.15 K, the evaluation is based on scattered, imprecise data at intermediate compositions. More accurate measurements at all concentrations are desirable, but measurements below 1 molal and above 8 molal are imperative if the correlations are to be improved. This is an important temperature region as the structure of water and of solutions is changing rapidly with temperature. Data at high concentrations (7 molal to saturation) are needed at all temperatures. Experimental values are not available, even at 298.15 K and estimates had to be made in our work, based
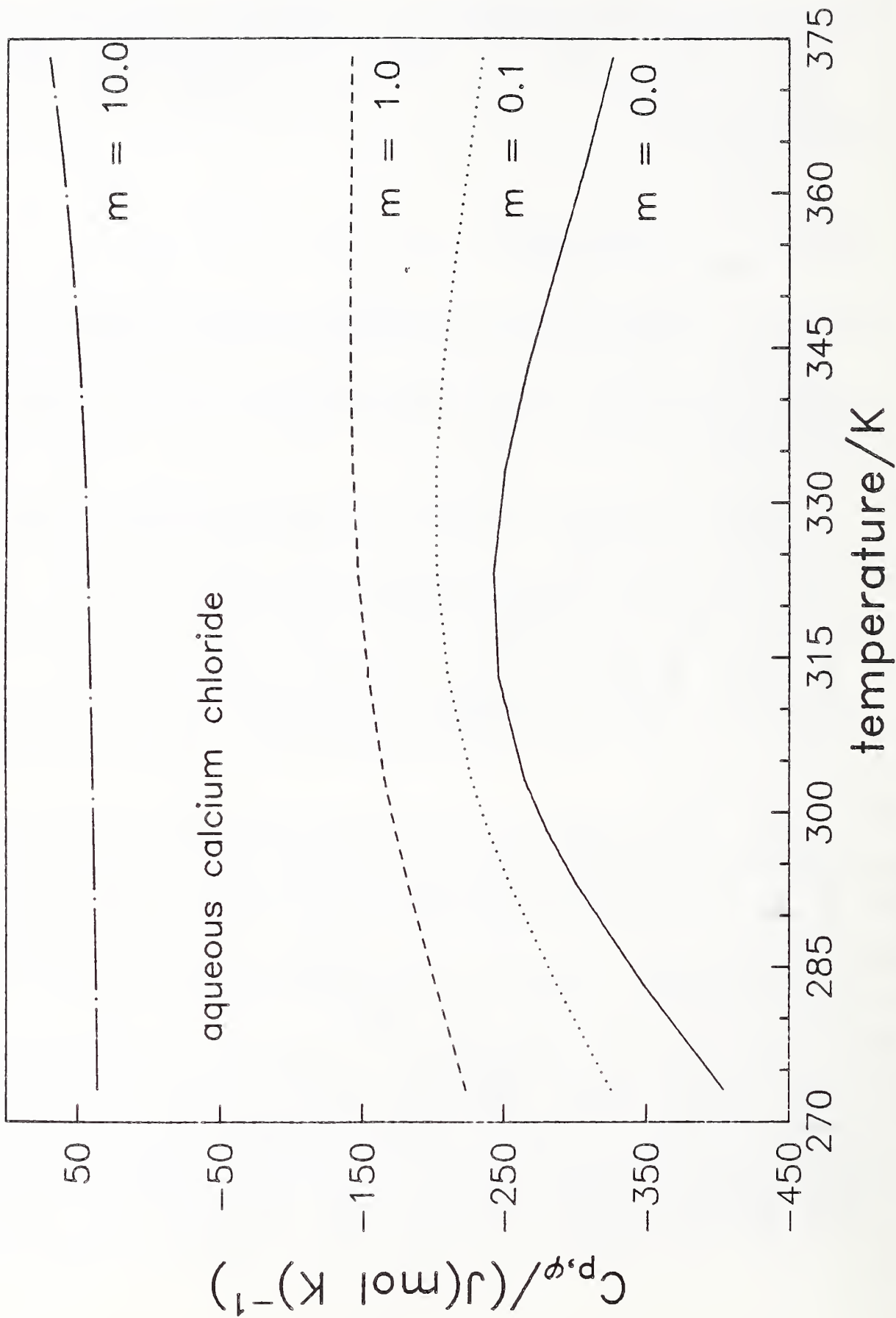
Fig. 5.3. Apparent molar heat capacity for calcium chloride-water mixtures, 273–373 K.

on a small set of measurements at 323 and 348 K. The high concentration region is important because, more often than not, the industrial applications involve concentrated solutions.

Enthalpy of dilution data are available only at or near 298.15 K. There is only one published study that covers any large range of concentrations at other temperatures (273 and 323 K). Above 298 K there are no data that reach the saturation line. Most useful would be a study at 373 K, from 0 molal to saturation, and a study at 323 K from 0 to 4 m, to validate the existing study. For both C_p and $\Delta_{dil}H$, data from 373 K to the critical line will be welcomed.

This study has also raised a significant problem for the theoretical interpretation of thermodynamic properties of electrolytes concerning the permittivity (dielectric constant) of $H_2O(l)$. It was necessary to choose a consistent formulation for the Debye-Huckel limiting law slopes A_ϕ (activities), A_H(enthalpies) and A_J (heat capacities). Later on A_V (volumes) will be required. The limiting law slopes for all properties can be calculated for any temperature or pressure provided that the density, the permittivity and their derivatives with respect to temperature and pressure are known. The Haar-Gallagher-Kell equation of state for water (NBS-NRC Steam Tables) is nearly a universal standard for the PVT properties of water. There are available, however, several formulations for the dielectric constant of water all of which represent the experimental measurements equally well, at least superficially. Our first selection was the dielectric constant correlation of Uematsu and Franck, because of the wide range of temperature and pressure at which it is applicable, the extensive data base considered, and its status as a standard.

A reviewer of the work pointed out that the formulation of Bradley and Pitzer should be used as it more accurately reproduced the measured permittivity values and derivatives at temperatures below 298.15 K. (Differences in the calculated D-H limiting law values are inconsequential for the Gibbs energy or enthalpy, but are quite dramatic, 30%, for heat capacity.) The reviewer's comment appears to be correct, and, because of our concern for fitting the lower temperature data, we have adopted his suggestion for the present.

An ensuing examination of the available experimental permittivity data, however, indicated they are not accurate enough for our purposes especially below 298.15 K. There are several detailed studies that show similar trends with temperature, but the studies disagree in absolute value. Thus it is difficult to establish the second derivative. The data are compared in Figure 5.4. The trend with temperature (below 298.15 K) in the Bradley-Pitzer formulation is steeper than in the Uemetsu-Franck treatment, and is closer to the trends in the principal studies. It is clear, however, that this important property of an important substance needs to be redetermined.
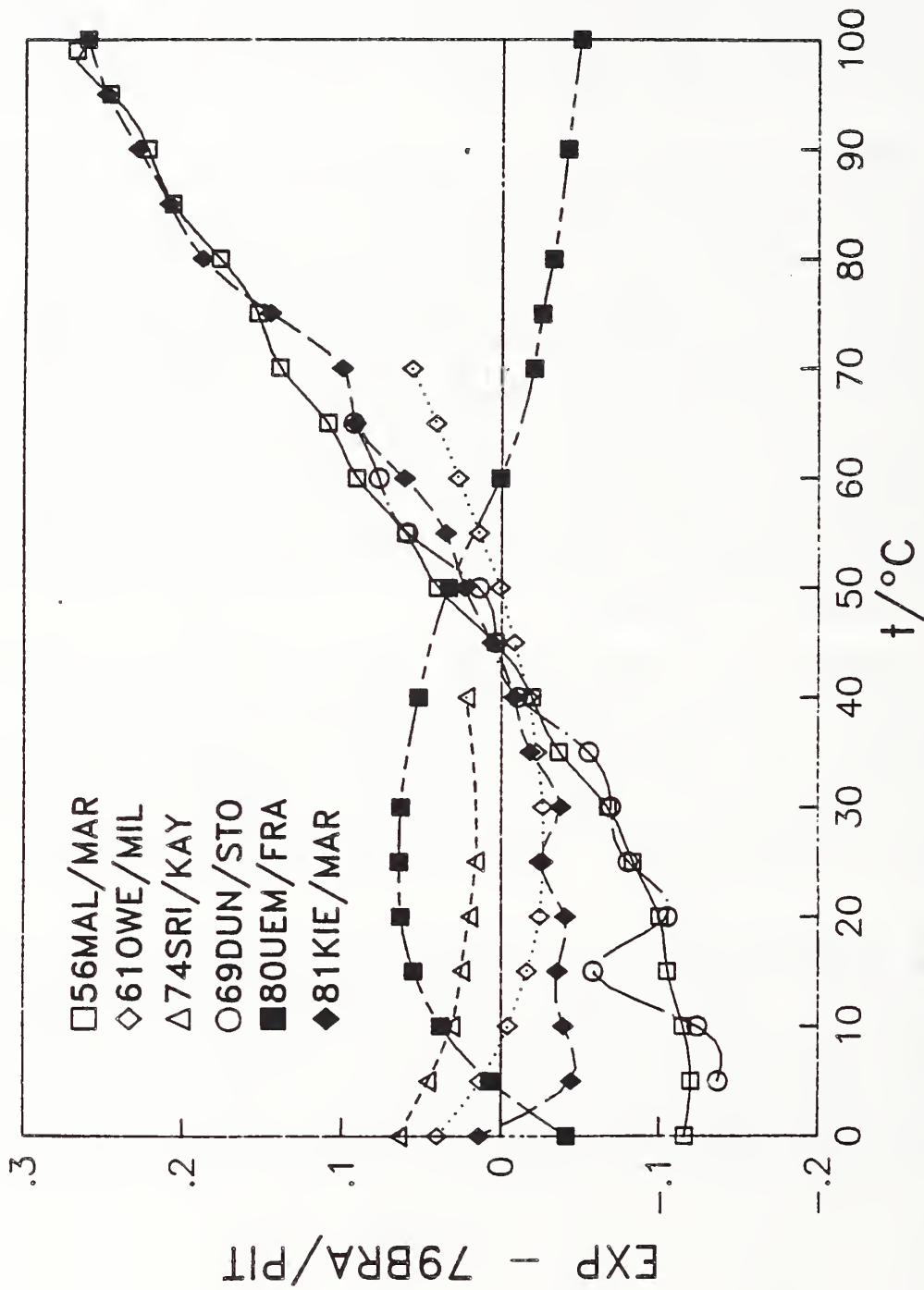
Fig 5.4 The two correlations represented by solid points are compared to the 79 BRA/PIT correlation. Four experimental data sets represented by open points are compared to the BRA/PIT correlation.

2.   Krebs Cycle Thermodynamics
      (D. Smith-Magowan)

        The thermochemical analysis of the reactions comprising the Krebs
cycle has continued during the year. The value of the network method for
obtaining thermochemical properties for metabolic substrates has been shown
in several aspects of the work thus far.

        Inconsistencies in the results for several reactions suggested, after some
thought, that the value of the reduction potential for the Nicotinamide
Adenine Dinucleotide/Nicotinamide Adenine Dinucleotide (NAD/NADH) couple
(0.311 ± 0.006 V from potentiometric measurements), which is widely adopted
and was input to the network, must be in error. This is indeed the case as
our subsequent investigation revealed. It was discovered that an error in
the formation data for the reduction of acetaldehyde to ethanol obtained from
the compilation by Stull, Westrum and Sinke leads to an error in the
interpretation of equilibrium measurements for alcohol dehydrogenases from
which this potential has been deduced. Recent equilibrium measurements for
the acealdehyde/ethanol system have been used to obtain a more reliable value
for the NAD/NADH potential (0.3165 ± 0.001 V) that is more consistent with
the other reactions of the Krebs cycle.

        For many of the substances involved in the Krebs cycle it is virtually
impossible to obtain an estimate of the Gibbs energy of formation in solution
by the more traditional approach of combining enthalpy of reaction and heat
capacity determinations (to get entropies) for the pure substance with
measurements of the solubilities (to get $\Delta_{sol}G$), because the necessary data
are lacking. Lactic acid, for example undergoes polymerization in aqueous
solution, making it impossible to measure its solubility accurately. Using
the power of the network analysis, which includes reactions linking lactate
with pyruvate, oxaloacetate, and acetate, a value for Gibbs energy of
formation (-519.77 kJ/mol) has been obtained that is accurate to ±0.4
kJ/mol. Similar situations can be quoted for other substances.

        The Krebs cycle is common to almost all aerobic respiration pathways, which
implies, at least in principle, that the network can be extended to encompass
metabolic substances of unlimited complexity. If this is indeed possible,
it could be the most reliable way to quantify and relate the subtle effects
of changes in structure, in solution, of the complex substances that
biotechnology seeks to exploit.

3.   Electrolyte Solution Properties Data Base
      (D. Smith-Magowan)

        A computer database of thermodynamic properties for electrolytes
is being developed for the Design Institute for Physical Property Research
(DIPPR). DIPPR is sponsored by AIChE and is a consortium of about 50 major
chemical companies that support various research projects depending upon
their individual interests. The database will consist of a collection of the
activity, enthalpy, heat capacity and volume properties for electrolyte
solutions supplemented by computational utilities to aid the engineering
application of these properties. These utilities will provide the ability to
calculate values of properties for simple binary solutions using several
different models for extrapolation, prediction, or comparison; the

calculation of properties for ternary or more complex mixtures; and methods for integrating these properties to obtain consistent sets of properties for a range of temperature, pressure and composition.

4.   Temperature-Density-Composition Correlations of Excess Properties (D. Smith-Magowan)

The correlation of thermodynamic properties of electroytes as a function of temperature, pressure and composition is underway using an algorithm that simultaneously treats temperature, density and composition as independent variables. The experimental data for calcium chloride are being used as a test case so that comparison with the CODATA skeleton table can provide an indication of the quality of the performance of this algorithm. The choice of density as an independent variable instead of pressure is made because of the PVT behavior of water at elevated temperatures. As the critical point is approached, the compressibility of water increases greatly and the excess thermodynamic properties of binary electrolytes appear to show corresponding trends. For example, the apparent molar heat capacity (at constant pressure) of aqueous NaCl seems to diverge to a value of negative infinity as the temperature of the critical point (674 K) of water is approached. A polynomial in temperature to fit such behavior requires terms of very high order. The heat capacity at constant density (or volume) on the other hand, is not divergent and can be fitted with a less complicated expression.

C.   Thermodynamic Properties of Organic Compounds (E.S. Domalski, E.D. Hearing, J.F. Liebman, D. Garvin)

1.   Prediction of Properties

An estimation method developed by S.W. Benson and coworkers for calculating thermodynamic properties for gas phase organic compounds from structural group parameters has been extended to the liquid and solid phases for hydrocarbons. The work is in the process of being reviewed for publication in the Journal of Physical and Chemical Reference Data.

The group parameters for hydrocarbons in gas, liquid and solid phases at 298.15 K have been tested in 1267 comparisons with experimental data. For 527 comparisons with enthalpy of formation data, the average difference is ± 2.8 kJ/mol. The average differences for 396 comparisons for heat capacity and 344 comparisons for entropy in all three phases are ±2.6 and 3.1 J/(mol.K), respectively. The publication will include examples of the method of calculation, total symmetry numbers and methyl corrections for hydrocarbons plus a bibliography on the development of estimation methods since 1932.

This estimation procedure is now being extended to C-H-O compounds in the gas, liquid and solid phases at 298.15 K, and it is planned to apply it to C-H-N and C-H-N-O compounds.

2.   Thermochemistry of Organic Compounds of Interest in Biotechnology.

A preliminary machine-readable data base has been compiled for evaluated data on the chemical thermodynamic properties of a thousand organic compounds at 298.15 K. Four general classes of compounds are covered, all of

interest to researchers in biotechnology, namely: (1) amino acids, peptides and related compounds, (2) heterocyclic nitrogen compounds, (3) heterocyclic oxygen compounds, and (4) heterocyclic sulfur compounds. The properties covered are enthalpy of combustion, enthalpy of formation, heat capacity, entropy, Gibbs energy of formation and the logarithm of the equilibrium constant of the formation reaction. The data base is now being annotated. Publications are planned for each section.

3. Enthalpies of Combustion of Components of Natural Gas.

Recommended values have been prepared and published for the enthalpies of combustion of the C_1 -C_6 alkanes, C_2 - C_3 alkenes, acetylene, benzene and C_3 - C_6 cyclolkanes. In addition to the thermochemical data, corrections are given for non-ideal behavior of the gases. This work has been incorporated in a handbook on properties of natural gas for use in the liquified natural gas industry (prepared for the International Group of Importers of Liquified Natural Gas, GIIGNL), included in the Gas Producer Association standards, recommended to ASTM, discussed withan ISO Task Group, and reported on at an industry conference on "Gas Quality". In the course of this work it has been noted that thermochemical data for the hexanes are conflicting. Predicted enthalpies of combustion (and formation) of 2,2-dimethyl and 2,3-dimethyl alkanes tend to be outliers in estimation schemes. That is true for the hexanes 2,2-dimethylbutane and 2,3-dimethyl butane. Their enthalpies of combustion also are the least well defined of those for the lower molecular weight hydrocarbons. Calorimetric, isomerization equilibrium and correlation results spread by 2.5 kJ/mol. Combustion calorimetry on these two hexanes (now known only from relative measurements) could lead to a solution of the general problem of how to treat such isomers.

D. Automating Data Center Procedures
     (D.B. Neumann, D.M. Bickham)

Automation efforts in the Chemical Thermodynamics Data Centers are oriented toward providing for the following needs: (a) data analysis, (b) on-line access to data and bibliography, (c) transfer of data to other media or other data bases, (d) re-formatting data for publication, and (e) graphical presentation of data.

This year, three generic solutions to data center problems have been developed. The problems are: search for and retrieval of chemical data, bibliographic data management, and, printing and publication of results. The solutions are applicable to the work of all the CCP Data Centers.

1. Search and retrieval systems.

A general keyed access search-retrieval system called SETKY-GETKY has been written and implemented on the HP-1000. It is suitable for indexed material containing either text or tabular material.

SETKY-GETKY provides rapid access to free formatted textual or tabular material stored in large data files on the mini-computer. As a "keyed access" system it permits the user to create editable files with the usual system editor. Index commands, or "keys", are placed into the file by the user.

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SETKY is then invoked. It reads the original file and creates a file of keys that will be searched. The key file contains only the keys and the physical disc positions of the text in the original file to which the keys refer.

In its on-line mode the user invokes GETKY with a key or an approximate key. The GETKY program rapidly searches for the key in the key file. Using the physical disc position retrieved from the key file, GETKY retrieves, by direct access in the original file, the indexed item of text and displays it. If the key cannot be found, Getky returns the 20 keys alphabetically nearest to it and prompts the user to select one.

There are several aspects of the system that has made it unique and highly useful for Data Center work:

Text related to a key may be obtained from within programs, i.e. the GETKY functions are callable from user programs. This has been used to build retrieval systems for the JANAF Thermochemical Tables and the CTDC abstract files.

The original text files can be used for text processing as well as for on-line or programmatic retrieval. This has been accomplished by choosing the syntax of the index commands in the original files to be compatible with the TEXED system currently used for text formatting of reports and papers. This feature has been used in building a system for printing the CODATA Thermodynamic Tables.

The original file remains accessible, may be corrected or expanded by its owner. (This is much easier than when a Data Base Management System is used.)

The number of index items per entry is unlimited.

SETKY-GETKY is written in FORTRAN 77.

It is expected that these programs will be transferable to other systems such as the NBS Cyber or micro-computers such as the IBM-PC/XT, or AT. It may prove advantageous to use it as the search system for data distributed on floppy discs.

A users guide for SETKY-GETKY is being published in the proceedings of the 1986 International Users Group for Hewlett-Packard minicomputers. The applications of the system to date are (1) in printing a large section of the CODATA Task Group on Chemical Thermodynamic Tables, (2) a combined users manual and on-line help system for the HP-1000 was created, (3) a retrieval system for the JANAF Tables, (4) the NBS Telephone Book on-line, and (5) a retrieval system for abstracts of thermochemical data.

The motivation to create the SETKY-GETKY system was to automate CTDC's large data base of literature extracts, some 50,000 in number. In FY86 a section of this data base was re-formatted for this application. Using this section as a test we expect to remove remaining problems from the retrieval system and put the entire data base on line in early FY1987. At that point retrieval by substance formula, property, name, Wisswesser line notation, and registry number will be possible.

2. Common Bibliographic System.

A bibliographic system for CTDC and the other Data Centers, DB-BIB, was placed on-line and is being tested. Initial test applications are with a small Ion-Energetics bibliography and a bibliography of sputtering data (Surface Chemistry Division). The goal of this effort is to load, as an on-line searchable data base, all 60,000 -70,000 CTDC bibliographic citations. This is necessary to permit the more efficient preparation and publication of reaction catalogs such as that for rubidium thermochemistry, which is now in press.

3. Printing and Text Formatting Utilities. A program utility, (called PTTL), for printing using the OSRD laser printer was written by CTDC. This system is now in use by the Atomic Spectra Data Center, the Kinetics Data Center, and is used heavily by CTDC. Its function is to provide for sub- and super-scripts, Greek and math symbols, italics, bold, various line spacing needs, as well as a general and consistent input technique for Data Center staff. OSRD staff have made a number of improvements to this utility.

A utility for formatting reports containing text as well as tabular material, called TEXDA, was implemented by CTDC on the OSRD and CTDC mini-computers. It is an expansion of TEXED distributed by the International HP Users Group. A User's Guide covering both these utilities is in preparation by OSRD.

4. CTDC Abstracts Data Base.

Twenty six hundred current articles on thermodynamics were abstracted during the ten months Nov 1985 through Aug 1986. The process for doing this has been refined to make use of the Chemical Abstracts Data Base. Articles of interest are selected by inspection of CA or of high-yield journals. This is done by a contractor and by CTDC staff. The abstracts of the articles are retrieved from CA and then a decision is made by CTDC staff about the usefulness of each article and how it is to be abstracted. Copies of the articles to be retained are obtained, if possible, and microfilmed. Each article is indexed for its thermodynamic data content (in terms of substance and property studied), either from the article or its abstract, depending upon the subject and on the availability of the original. This material becomes part of the computerized CTDC Abstracts Data Base.

This data base is the ready reference used in the Center when evaluations of data are made. In addition, it is used to answer questions from the public.

All of the Abstracts Data Base since 1970 is machine-readable. During the year new programs have been written for processing the input. The programs have been tested extensively and are being used in a production mode. They have also been used to prepare indexes for the Bulletin of Chemical Thermodynamics. CTDC has processed the material for the inorganic index (prepared here), the organic index (prepared at Texam A&M Univ.), and the organic mixture index (prepared at Univ. Paris) into a form that can be handled by the index formatting programs of the Bulletin. The programs used here have also been supplied to the editor of the Bulletin who plans to do the entire processing task next year.

6. PUBLICATIONS

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Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions", University of Newcastle-upon-Tyne, United Kingdom, July 9, 1986.

Goldberg, R.N., "GAMPHI-A Database of Activity and Osmotic Coefficients", University of Newcastle-upon-Tyne, United Kingdom, July 10, 1986.

Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions", University of Glasgow, United Kingdom, July 11, 1986.

Goldberg, R.N., "Thermodynamics of the Conversion of L-Aspartate to Fumarate and Ammonia", 9th IUPAC Thermodynamics conference, Lisbon, Portugal, July 18, 1986.

Goldberg, R.N., "The Enthalpy of Hydrolysis of Adenosine 5'-Triphosphate", 9th IUPAC Thermodynamics Conference, Lisbon, Portugal, July 18, 1986.

Goldberg, R.N., "The Enthalpy of Hydrolysis of Adenosine 5'-Triphosphate", 41st Calorimetry Conference, Somerset, NJ, August 21, 1986.

Goldberg, R.N., "Thermodynamics of the Conversion L-Plenylalanine to Trans-Cinnamic Acid and Ammonia", ACS Middle Atlantic Regional Meeting, Baltimore, MD, September 2, 1986.

Goldberg, R.N., "Thermodynamics of the Hydrolysis of Adenosine 5'-Triphosphate", ACS Middle Atlantic Regional Meeting, Baltimore, MD, September 2, 1986.

Harrison, R., "A Common Sense Guide to Maximum Entropy", Mid-Atlantic Protein Cystallography Workshop, NBS, May 15-17, 1986.

Kirchhoff, W.H., "An Analysis Program for the Characterization of Interface Profile Shapes", 8th Symposium on Applied Surface Analysis, University of Dayton, Dayton, OH, June 4, 1986.

Kirchhoff, W.H., "A Computer Program for Describing the Denaturation of Biopolymers, as Measured by Differential Scanning Calorimetry, in Terms of a Two State Model", 41st Calorimetry Conference, Somerset, NJ, August 22, 1986.

Kirklin, D.R., "Estimation Methods and Combustion Calorimetry on Organic Phosphorus Compounds", 1985 Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, November 22, 1985.

Kirklin, D.R., "Enthalpies of Formation of Organic Phosphorus Compounds", 41st Annual Calorimetry Conference, Somerset, NJ, August 21, 1986.

Miller, M., "Oligomers of DNA", Mid-Atlantic Protein Crystallography Workshop, NBS, May 15-17, 1986.

Newmann, D.B., "The Chemical Thermodynamics Data Center Bibliographic Data Base System", Chemical Thermodynamics Division Seminar, April, 1986.

Newmann, D.B., "The Application of the IMAGE/1000 Database Management System to Scientific Data", Baltimore-Washington HP-1000 Users Group, Baltimore, MD, November 15, 1985.

Parker, V.B., "CODATA Chemical Thermodynamic Data Bases for Science and Technology", Tenth International CODATA Conference, July 15, 1986, Ottawa, Canada.

Smith-Magowan, D., "A Database of Thermodynamic Properties of Aqueous Electrolyte Solutions with Computational Procedures for Industrial Applications", AIChE National Meeting, Chicago, IL, November 1985.

Smith-Magowan, D., "Effects of Temperature, Pressure and Composition on the Thermodynammic Properties of Electrolytes", International Association for Properties of Steam, Dusseldorf, W. Germany, Sept 22-26, 1986.

Tewari, Y.B., "Thermodynamic Investigations of Reactions Catalyzed by Glucose Isomerase", Indian Institute of Technology, New Delhi, India, October 29, 1985.

Tewari, Y.B., "Thermodynamic Investigations of Enzyme Catalyzed Reactions", Indian Institute of Technology, Bombay, India, November, 21, 1985.

Tewari, Y.B., "Thermodynamics of Carbohydrate Isomerization Reactions: Conversion of Aqueous Allose to Psicose", 41st Calorimetry Conference, Somerset, NJ, August 21, 1986.

Tewari, Y.B., "Thermodynamics of the Conversion of L-phenylalanine to Trans-Cinnamic Acid and Ammonia", 41st Calorimetry Conference, Somerset, NJ, August 21, 1986.

Tewari, Y.B., "Thermodynamics of Carbohydrate Isomerization Reactions: The Conversion of Aqueous Allose to Psicose", ACS Middle Atlantic Regional Meeting, Baltimore, MD, September 2, 1986.

Weber, I.T., "The Analysis of Protein Structure from Crystallographic Data". The Structure of Catabolite Gene Activator Protein and its Complex with DNA", Course on Protein Structure and Function, Les Diablerets, Switzerland, September 30 to October 3, 1985.

Weber, I.T., "Model for the Complex of Catabolite Gene Activator Protein and Its Site in Lac Operon", Series on the Relation between DNA Structures and their Interactions, NIH, Bethesda, MD, March 19, 1986.

Weber, I.T., "The Structure of a Mutant of Catabolite Gene Activator Protein.", Mid-Atlantic Protein Crystallography Workshop, NBS, Gaithersburg, MD, May 15-17, 1986.

Weber, I.T., "The Crystal Structure of a Mutant of Catabolite Gene Activator Protein.", Gordon Conference: Diffraction Methods in Molecular Biology, New Hampshire, June 30-July 4, 1986.

Wlodawer, A., "A Novel Method for the Determination of Solvent Structure in Protein Crystals", Max-Planck-Institut, Munich, West Germany, January 28, 1986.

Wlodawer, A., "High Resolution Studies of Proteins Using X-ray and Neutron Diffraction", University of Washington, Seattle, WA, June, 3, 1986.

Wlodawer, A., "Bound Solvent in Proteins: Improvement of Fourier Maps by Protein Averaging Combined with Flattening of the Solvent", Gordon Research Conference, Andover, NH, June 30, 1986.

Wlodawer, A., "Bound Solvent in Proteins - a Novel Technique for its Analysis", Tenth European Crystallographic Meeting, Wroclaw, Poland, August 5, 1986.

Wlodawer, A., "High Resolution Refinement of BPTI and Ribonulcease", Department of Crystallography, Birkbeck College, University of London, England, August 15, 1986.

Wlodawer, A., "X-ray and Neutron Diffraction Studies of Proteins and Nucleic Acids", NBS Staff Research Seminar, September 5, 1986.

8. Chemical Thermodynamics Division Seminars

Kamlet, M.J., Navel Surface Weapons Center, Silver Spring, MD, "A General Equation for Correlation and Prediction of Solute---Solvent Interaction in Chemical and Biological Systems", October 1, 1985.

* Bott, R., Genentech, Inc. South San Franciso, CA, "Protein Engineering, Modification of the Oxidative Stability of Subtilisin", October 18, 1985.

Ditmars, D.A., NBS, Gaithersburg, MD, "Heat Capacity of Solid Calcium: a Tour de Force of Macrocalorimetry", September 30, 1986.

* O'Leary, T.J., NIH, Bethesda, MD, "Spectroscopic and Calorimetric Studies of Biomembranes", October 24, 1985.

* Osman, R., Department of Physiology and Biophysics, New York, NY, "A New Mechanism of Action of Superoxide Dismutase", November 7, 1985.

* Rein, R., Department of Biophysics, Roswell Park Memorial Institute Buffalo, NY, "Multistep Modeling of Bioactive polypeptides in 3-Dimensions", November 14, 1985.

* Hyde, C., NIH, Bethesda, MD, "Three Dimensional Structure of Aspartate Aminotransferase and Substrate Complexes", December 18, 1985.

Thompson, P.T., Chemistry Department, Swarthmore College, Swarthmore, PA, "Progress Towards the Development of Simple Potential Functions for Solute-Solute Interactions in Non-electrolyte Aqueous Solution", January 13, 1986.

* Goldberg, R.N., NBS, Gaithersburg, MD, "Thermodynamics of Enzyme Catalyzed Reactions", February 21, 1986.

* Wlodawer, A., NBS, Gaithersburg, MD, "Structure of a 'Standard' Protein Bovine Pancreatic Trypsin Inhibitor at High Resolution", February 28, 1986.

Neumann, D., NBS, Gaithersburg, MD, "A Bibliographic Database for the HP-1000 Mini-Computer", March 5, 1986.

Roy, R., Drury College, Springfield, MO, "Thermodynamics of Mixtures of Strong Electrolytes: Applications of Pitzer's Equations", March 20, 1986.

* Gitomer, W., NIH, Bethesda, MD, "The Estimation of the Free Mitochondrial Ca^{2+} Concentration in Vivo", April 15, 1986.

* Zeyfus, M., Department of Biological Chemistry, Pennsylvania State University, University Park, PA, "Compact Domains of Proteins", April 17, 1986.

* Pember, S., Department of Chemistry, Pennsylvania State University, University Park, PA, "Mechanism and Structure of Chromobacterium Violaceum Phenyl Alanine Hydroxylase", April 22, 1986.

* Harman, J.G., NIH, Bethesda, MD, "Structure - Function Analysis of Cylic AMP Receptor Protein", May 12, 1986.

* McKenney, K., NIH, Bethesda, MD, "Protein Structure Function Studies Using Synthetic Oligonucleotides", May 14, 1986.

* Tweedy, N.B., Department of Chemistry, Pennsylvania State University, University Park, PA, "Effects of Point Mutations on Protein Folding", May 21, 1986.

* Biotechnology Seminars

9. TECHNICAL AND PROFESSIONAL
COMMITTEE PARTICIPATION AND LEADERSHIP

Abramowitz, S.
    Member, ASTM Commitee E-38 on Resource Recovery, Subcommittee E38.01
    Energy

Bickham, D.
    Member, Baltimore-Washington HP-1000 Users Group

Chase, M.
    Vice-chairman, ASTM Committee E-27 on Hazard Potential of Chemicals

    Consultant, CODATA Task Group on Chemical Thermodynamic Tables,

    Corresponding member, Engineering Science Data Unit - Physical Data
    and Reaction Committee

Churney, K.L.
    Member, ASTM Committee E-37 on Thermal Measurements

    Member, ASTM Committee on Hazard Potential of Chemicals, Subcommittee
    E-27.02 on Thermal Stability

    Member, ASTM Committee E-38 on Resource Recovery

Colbert, J.C.
    Member, ASTM Committee E-38 on Resource Recovery, Subcommittee E38.01
    Energy

    Member, ASTM Committee D-05 on Coal and Coke

Ditmars, D.A.
    Member, ASTM Committee E37.05 on Thermal Measurements/Thermophysical
    Properties working group I (Thermodynamics) Task Group 1.5 (Drop
    Calorimetry), 1.6 (Adiabatic Calorimetry)

    Division Safety Officer

    Member, Standards Committee, U.S. Calorimetry Conference

Domalski, E.S.
    Member, ASTM Committee E-27 on Hazard Potential of Chemicals, Subcommittee
    E-27.07 Computational Methods

    Member, ASME Research Committee for Industrial and Municipal Wastes

    Member, ASTM Committee E-38 on Resource Recovery, Subcommittee
    3-38.01 Energy

Garvin, D.

    Secretary, CODATA Task Group on Chemical Thermodynamic Tables

    Member, ASTM Committee E-38 on Resource Recovery

    Member, ASTM Committee E-27 Hazard Potential of Chemicals

Kirchoff, W.H.

    Immediate Past Chairman, ASTM Committee E-47 on Biological Effects and Environmental Fate

    Member, ASTM Committee E-48 on Biotechnology

    Titular member, IUPAC Commission I.1. on Physicochemical Symbols, Terminology and Units

Kirklin, D.R.

    Member, ASTM Committee E-38 on Resource Recovery, Subcommittee E-38.01 on Energy, Subcommittee E-38.02 on Research

    Director, U.S. Calorimetry Conference

Neumann, D.

    Member, Hewlett-Packard HP-1000 International Users Group

    Member, Baltimore-Washington HP-1000 Users Group

Parker, V. B.

    Consultant, IAEA Committee on Chemical Thermodynamics of Actinide Elements and Compounds,

    Member, Subcommittee IAEA.WG.01 Actinide Halide Thermodynamics.

    Corresponding member, CODATA Task Group on Chemical Thermodynamic Tables

    Member, Chemical Thermodynamimcs Advisory Committee on Aqueous Solutions Data Base, (Lawrence Berkeley Laboratories, Sidney Phillips)

Smith-Magowan, D.

    Organizing Committee of the 'International Conference on Thermodynamics of Aqueous Solutions with Industrial Applications', Airlie House, May 1987.,

    Member, International Association for the Properties of Steam

Wlodawer, A.

    Treasurer, Neutron Special Interest Group of the American Crystallographic Association

    Member, Apparatus and Standards Committee, American Crystallographic Association

10. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Abramowitz, S.

Collaborated with I.W. Levin, National Institute of Arthritis and Metabolic Disease, NIH, on vibrational analysis of small molecules and some biological species.

Formulated cooperative research program on high temperature thermodynamics with AFOSR.

Interacted with the following agencies and organizations regarding the NBS program in Biotechnology: National Aeronautic and Space Administration (NASA), National Academy of Science (NAS), National Science Foundation (NSF), Office of Technology Assessment (OTA).

Chase, M.

Reviewed and planned for physical property data issued by Engineering Science Data Unit.

Participated in the development of ASTM Standard on "Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials" prepared by ASTM. Committee E-27 on Hazard Potential for Chemicals.

Supplied thermal functions to the Therdynamic Research Center, Texas A & M University, for inclusion in the TRC Hydrocarbon and Non-hydrocarbon Tables.

Collaborated with AIP on the design and publication of the JANAF Tables, 3rd edition.

Prepared tables of thermal functions for the CODATA Thermodynamic Tables and for CODATA Key Values for Thermodynamics, and participated in meetings of the CODATA Task Group on Chemical Thermodynamic Tables.

Interacted to obtain data needed for development of theoretical concepts used in the JANAF Tables with J.L. Haas, Jr, United States Geological Survey (USGS), T. Chart, & A. Dinsdale, NPL, U.K., M.H. Rand, AERE, Harwell, U.K., L. Brewer, U. CA, Berkley, P.F. Bernath, AZ State U., and D.O. Harris, U. CA, Santa Barbara, CA.

Reviewed an extensive series of articles on Isomer Group Thermodynamics (R.A. Alberty, MIT).

Churney, K.L.

Interacted with R. Wingender of the Analytical Chemistry Lab of Argonne National Laboratory, Argonne, IL on analysis of effluent fractions from combustion measurements for chlorinated dioxins and related compounds.

Colbert, J.C.

Interacted with ASTM Committee D-05 on Coal and Coke and its Subcommittee 21.02 on Methods of Analysis. Membership and active participation with subcommittee members on the evaluation of calorimetric procedures for determining the calorific value of coal and coke.

Cooperated in research with B. Coxon of the NBS Organic Analytical Research Division on bomb calorimetric and NMR studies of D-ribose and 2-deoxy-D-ribose.

Ditmars, D.

Cooperated with R.A. Robie of the U.S. Geological Survey, Reston, VA, on preparing a sample of pure calcium and measuring the heat capacity of the solid phases from 4K to the melting point, 1112K.

Interacted with Commission on Standardization of Thermophysical Preperty Measurements of the European Thermophysical Properties Union. This Commission is sponsoring and coordinating the assembly of a two-volume compendium of apparatuses and techniques for the measurement of thermophysical properties. One chapter has appeared in press on a survey of high temperature drop calorimetry. Another chapter on hardware design is in preparation.

Cooperated with C.A. Plint, Physics Department, Brock University, Ontario, Canada, on measurement of the high-temperature heat capacity of pure copper.

Cooperated with the investigator on U.S.-Yugoslav cooperative research project being carried out at NBS (Chemical Thermodynamics Division) and at Boris Kidric Institute, Belgrade (Institute for Thermal Engineering and Energy Research).

Provided advisory service to U.S. Naval Weapons Ordinance Center, Crane, Indiana on calorimetry hardware, techniques for studying low-level degrading reactions in solid propellants and explosives.

Domalski, E.S.

Cooperated with engineers involved in solid waste disposal, solid waste processing, and resource recovery from the ASTM Committee E-38 on Resource Recovery and The ASME Research Committee on Industrial and Municipal Wastes concerning combustion characteristics of waste materials.

Participated in the USUK collaboration for Waste Combustion. Areas of interest are : (1) chlorine content analysis of municipal solid waste, (2) calorific value data derived from U.S. and U.K. one kilogram-capacity calorimeters, and (3) combustion studies on threshold conditions for the formation/destruction of chlorinated species.

Interacted with the U.S. Department of the Army, Chemical Research and Development (CRDC), Aberdeen Proving Ground, Maryland to carry out combustion calorimetry and develop estimation methods for organic phosphorus compounds (CRDC) has continued in FY 1986.

Negotiated for the publication of a compilation entitled:
"Thermodynamics Data for Biomass Conversion and Waste Incineration",
prepared at NBS, compiled at the Solar Energy Research Institute, and
funded by DoE, as an ASME document.

Interacted with engineers from Combustion Engineering (J. Orcutt and
D. Borio) during a visit to the large sample flow calorimeter
facility and through discussion of plans for future research on
monitoring chlorine during MSW combustion.

Gajewski, E.
    Interacted with Anne Plant, Center for Analytical Chemistry,
    purification of monoclonal antibodies.

Garvin, D.
    Worked with CODATA on the preparation of thermodynamic data bases, jointly
    with groups at AERE, Harwell, U.K., (M.H. Rand), LIPCM-ENSEEC,
    Grenoble, France (I. Ansara), Univ. of Sussex, Brighton, UK, (J.B.
    Pedley), and TERMOCENTER Akad. Nauk, Moscow, USSR (L.V. Gurvich, V.A.
    Medvedev, V. Yungman), and US Geolog. Survey, Reston, VA, USA (J.L.
    Haas, Jr.).

    Visited British Gas, London Research Station, London, U.K. (A.E.
    Humphreys) regarding calorimeter design.

    Selected values for properties of components of natural gas:
    Thermodynamic Research Center, Texas A & M Univ., College Station,
    TX, (K.N. Marsh, R. Wilhoit).

    Participated in completion of the handbook for calculation of proper-
    ties of natural gas for the International Group of Importers of
    Liquified Natural Gas (GILGNL), NBS, Boulder, CO, (D. Mann).

    Interacted with international standards (Chemical) community. Observer at
    IUPAC General Assembly, Lyons, France, Commission I.3 [Nomenclature],
    I.2 [Thermodynamics], I.4 [Chemical Kinetics], and II.3 [High
    Temperature Chemistry].

    Attended DOE Contractor's Meeting for Department of Energy on clean
    up of coal combustion stack gases, assessment of industry needs.

Goldberg, R.N.
    Met with Richard Veech, National Institutes of Health, general
    discussions on the thermodynamics of enzyme-catalyzed reactions.

    Met with Richard Virdins, University of Newcastle-upon-Tyne, United
    Kingdom, to discuss possible work in the penicillinase reaction.

    Met with Arthur Carrington, University of Newcastle-upon-Tyne, United
    Kingdom, to discuss pH Standards.

    Discussed with Yung-Chi Wu, Center of Analytical Chemistry, the
    treatment of electrochemical data.

Kirchhoff, W.H.

Collaborated with I.W. Levin, et. al. Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes and Digestive and Kidney Diseases on thermodynamic properties of lipids.

Worked with J.D. Fine, Surface Science Division, on the statistical analysis of depth profile data.

Neumann, D.B.

Collaborated with Freeman, Oklahoma State Univ. on the publication of the Bulletin of Chemical Thermodynamics.

Interacted with A. Maczynski, Institute for Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland – Protocal for the international exchange of chemical thermodynamic data – IUPAC sponsored activity.

Participated in Task Group meetings at Ottawa, July 1986. CODATA Task Group on Chemical Thermodynamics Tables.

Provided computer programs to Office of Standard Reference Data to assist in the production of camera ready documents and tables, acted as consultant for the planning of automation activities at NBS and DOC.

Consulted with J.W. Gadzuk, Division 541, on graphics for publication.

Consulted with D.J. Orser, Division 739, on presentation of topology of phase diagrams.

Consulted with G. Klopman, Dept of Commerce, on oceanographic data (Netherlands) to the NBS computer.

Parker, V.B.

Consulted with E. Busenberg and N. Plummer, USGS, Reston, VA concerning the thermochemistry of $BaCO_3(cr)$ and the selection of the "best values" for the enthalpy of formation at zero K; also concerning Ba^{+2} (aq. std. state) and values for the enthalpy of formation at 0 K and the entropy.

Consulted with John Haas, USGS Geological Survey, concerning the thermochemical behavior of iron oxides.

Discussed with V. Medvedev, Institute for High Temperatures and I. Khodakovsky, Vernadsky Institute for Geochemistry and Analytical Chemistry, Moscow, the evaluation of the thermochemistry of key iron compounds.

Held discussions on USA/USSR Science exchange: Exchange of data, calculational methods and interpretations of data between the Chemical Thermodynamics Data Center and a similar group at the Institute for High Temperatures, Moscow.

Collaborated with members of the CODATA Task Group on the preparation of Chemical Thermodynamic Tables: Preparation of thermodynamic data bases, jointly with groups at AERE, Harwell, U.K., (M.H. Rand), LIPCM-ENSEEG, Grenoble, France, (I. Ansara), and TERMOCENTER Akad. Nauk, Moscow, USSR, (L.V.Gurvich, V.A. Medvedev, V. Yungman), and USGS, Reston, VA, USA (J. Haas Jr.)

Held discussions, provided advice and guidance to Phillips, Lawrence Berkeley Lab. and M. Siegel, Sandia National Lab. on the need for and the construction of thermodynamic data bases for modelling in geothermodynamic equilibrium calculation in aqueous solutions.

Provided advice and guidance on handling uncertainties in thermodynamic data to NRC, DOE, and USGS at a panel meeting Dec. 17, 1985 at NRC Silver Spring, MD.

Collaborated with D.D Wagman, former NBS staff scientist, on chemical thermodynamic key values and thermodynamic tables.

Schwarz, F.P.
Collaborated with I.W. Levin, Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes and Digestic and Kidney Diseases on the thermal properties of lipids.

Collaborated with A. Shrake, Office of Biologics, FDA on the thermal stability of serum albumen.

Smith-Magowan, D.
Collaborated with R.H. Wood, University of Delaware, on the development of methods for the correlation and theoretical interpretation of the thermodynamic properties of aqueous solutions at elevated temperatures and pressures.

Interacted with S.L. Miller, Univ. of California, San Diego, on the correlation of equilibria comprising the Krebs (tricarboxylic acid) cycle and associated metabolic pathways. Joint manuscript is in preparation.

Interacted with J.O.M. Levelt-Sengers, Thermophysics Div, NEL, NBS; on the interpretation the properties of aqueous electrolytes near their critical points.

Interacted with P.T. Thompson, Swarthmore College, on the calculation of virial coefficients of small organic compounds in aqueous solution.

Provided advice to Dewey, Reynolds Metals Co., Richmond, Va; on the vapor pressure and enthalpy of concentrated NaOH solutions at elevated temperatures.

Provided advice to J. Erwin, SWRI, San Antonio TX, on the electrical conductivity of aqueous mixtures of CO_2.

Provided advice to R.L. Truitt, Dallas TX, on the formulation of colloidal suspensions of magnetic materials.

Provided advice to W. Kelly, Nuclear Regulatory Commission, on the data for aqueous solutions used in codes to predict the stability of nuclear waste storage deposits.

Tewari, Y.B.
Held discussion with and interacted with Dr. William Gitomer of the Laboratory of Metobilism at NIH on the equilibrium measurement for the process: hydrolysis of glucose 6-phosphate.

Weber, I.T.
Held discussions and interacted with Dr. Sancar Adhya, NIH, on the crystallization and structural studies of E. coli gal repressor.

Held discussions and interacted with Professor Herman Ammon, Department of Chemistry, University of Maryland, on structural studies of glutaminase-asparaginases from several bacterial sources.

Collaborated with Dr. Gary Gilliland, Genex Corporation, Gaithersburg, MD, on data collection from crystals of catabolite gene activator protein.

Interacted with Dr. Keith McKenny, NIH, on the crystal structures of mutants of catabolite gene activator protein.

Interacted with Dr. Alan Peterkofsky, NIH, on the crystal structures of several mutants of catabolite gene activator protein.

Interacted with Professor Thomas Steitz, Department of Molecular Biophysics and Biochemistry, Yale University, New Haven CT, on crystallization of rec A protein and on refinement of the structure of catabolite gene activator protein.

Interacted with Professor Susan Taylor, Department of Chemistry, University of California, San Diego CA, on the prediction of the structure of the regulatory subunit of mammalian cAMP-dependant protein kinase.

Interacted with Dr. Susan Wickner, NIH, on the crystallization of 'O'-protein that is required for transcription in phage λ.

Wlodawer, A.
Collaborated with Professor Robert Huber, Max Planck Institute, Martinsried, West Germany, on the comparison of two crystal forms of bovine pancreatic trypsin inhibitor.

Collaborated with Professor Lennart Sjolin, Chalmers Polytechnic, Gothenburg, Sweden, on the structural investigations of ribonuclease and bovine pancreatic trypsin inhibitor.

Collaborated with Dr. Franz Schmid, University of Regensburg, West Germany, on crystallographic studies of porcine ribonuclease.

Collaborated with Dr. David Moss, University of London, England, on comparisons of independently refined structures of bovine ribonuclease.

Collaborated with Professor Herman Ammon, University of Maryland, on crystallographic studies of glutaminase-asparaginases from several bacterial sources.

Collaborated with Dr. Giuseppe Zaccai, Institute Laue-Langevin, Grenoble, France, and Dr. Martin Gellert, NIH, Bethesda, MD, on the low-angle neutron scattering studies of gyrase and gyrase-DNA complexes.

Collaborated with Dr. Ettore Appella, NIH, Bethesda, MD, on crystallization of DNA fragments.

Collaborated with Dr. Joyce Jentoft, Case Western University, OH, on crystallographic studies of the RNA-binding protein from the phage pp12.

Collaborated with Dr. Gary Gilliland, Genex Corporation, Gaithersburg, MD, on crystallographic studies of a sweet protein, monellin, and on high resolution refinement of ribonuclease.

Collaborated with Dr. Matthew Pincus, Brooklyn Polytechnic, on crystallography of covalent complexes between ribonuclease and nucleotides.

11.   VISITING SCIENTISTS

The Thermodynamics Division has been host in the past year to the
following scientists who have worked with NBS scientists on problems of
mutual interest.

Liebman, J.F., University or Maryland-Baltimore County, Baltimore, MD,
    completed an evaluation of enthalpies of formation of amino acids,
    peptides, heterocyclic and related compounds. He is an expert on
    techniques in estimating thermodynamimc properties of organic
    compounds and on strain energies, in organic compounds.

Miller, M., University of Warsaw, Poland, Dr. Miller is working on the
    crystallographic structure of proteins and DNA fragments.

Nachmann, J., Weizmann Institute of Science, Rehovot, Israel. Dr. Nachmann
    is a protein crystallographer conducting neutron and x-ray
    diffraction measurements of macromolecules of biological importance
    in the Biomolecular Structure Group of the Division

Nuttall, R., Former NBS employee, is an expert on solution thermodynamics
    and evaluation of thermochemical data. Dr. Nuttall participated in
    developing the data for electrolyte data bases and catalogs of
    measurements of thermochemical data.

Rukkers, K., graduate student in the Department of Applied Physics, Twente
    University of Technology, Enschede, Netherlands, spent three and a
    half months (Feb-May 1986) providing assistance to the large sample
    flow calorimetry group improving the data acquisition and data
    handling procedures.

Savage, H., National Institute of Health, Bethesda, MD. Dr. Savage is
    working on neutron diffraction of protein hormones and the structure
    of bound water in biological systems.

Schumm, R.H., Former NBS employee, is an expert on the evaluation of
    thermochemical data. Mr. Schumm evaluated data on sulfur compounds
    relevant to flue gas desulfurization.

Shrake, A., Food and Drug Administration, Washington, D.C. Dr. Shrake is
    an expert in the area of thermodynamics of phase transitions in proteins
    and protein ligand complexes of biological interest.

Thompson, P.T., Swathmore College, Swathmore, PA. Dr. Thompson is an
    expert on the interaction of organic species with water in terms of
    hydrophobicity. He performed both experimental and theoretical
    research during his sabbatical at NBS during calendar year 1985.

Wagman, D.D., Former NBS employee, is an expert on the evaluation of
    thermodynamic data. Mr. Wagman has prepared the CODATA key values
    for thermodynamics.

Wasik, S.P., Former NBS employee, is an expert on the evaluations of solubility data for organic species in aqueous and mixed media. Dr. Wasik evaluated data on the thermodynamic properties of alkanes in aqueous media.

Weber, I., University of Maryland, College Park, MD. Dr. Weber is working on the molecular structure of complex biomolecules using both x-ray and neutron diffraction.

Wood, R.H., Chemistry Department, University of Delaware, Newark, DE, worked with the staff on solution thermodynamics, theory and experiment; electrolyte theory of weak electrolytes, speciation calculations, molecular interactions in solution; and the solubilities of non-electrolytes in aqueous solution as a function of concentration and temperature.

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5. AUTHOR(S)

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)* **NATIONAL BUREAU OF STANDARDS** **DEPARTMENT OF COMMERCE** **WASHINGTON, D.C. 20234**	7. Contract/Grant No.
	8. Type of Report & Period Covered Annual Report of 1986

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National Bureau of Standards
Gaithersburg, MD

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report summarizes the technical activities of the NBS Chemical Thermodynamics Division during the Fiscal Year 1986. The activities of the Division include research on: thermodynamic properties of enzyme - catalyzed reactions, DSC standards for biological systems, computer modeling of phase transitions of biomolecules, determination of the structure of proteins and nucleic acids using x-ray and neutron diffraction, combustion bomb calorimetry of pure substances, mass balances of chlorine during combustion processes, high temperature heat capacity measurements, evaluation of the thermochemistry of calcium and iron compounds, preparation of JANAF Thermochemical Tables, and automation of Data Center procedures. A listing is provided of publications and talks given by the Division staff.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

automation; biomolecular structure; biothermodynamics; bomb calorimetry; computer modeling; estimation; data evaluation; high temperature heat capacity; JANAF Thermochemical Tables; proteins; nucleic acids; thermochemistry; thermodynamics

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