

LEVEL

(13)

AD A110430

FINAL TECHNICAL SUMMARY REPORT

for the period

1 October 1980 - 30 September 1981

THERMODYNAMICS OF ORGANIC COMPOUNDS

DTIC
SELECTED
FEB 3 1982
H

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Research sponsored by:

Air Force Office of Scientific Research (NA)
Department of the Air Force

Contract No. AFOSR-ISSA 81-00013
Project No. 2308/31

Approved for public release;
distribution unlimited.

REF ID: A110430

88 03 02 048

FINAL TECHNICAL SUMMARY REPORT

for the period

1 October 1980 - 30 September 1981

THERMODYNAMICS OF ORGANIC COMPOUNDS

DTIC
ELECTE
FEB 3 1982
S D H

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Research sponsored by:

Air Force Office of Scientific Research (NA)
Department of the Air Force

Contract No. AFOSR-ISSA 81-00013
Project No. 2308/B1

Approved for public release;
distribution unlimited.

410743

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR. 82-0023	2. GOVT ACCESSION NO. AD-A110430	3. RECIPIENT'S CATALOG NUMBER 430
4. TITLE (and Subtitle) THERMODYNAMICS OF ORGANIC COMPOUNDS		5. TYPE OF REPORT & PERIOD COVERED FINAL 1 Oct 80 - 30 Sept 81
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) N K Smith B E Gammon W D Good		8. CONTRACT OR GRANT NUMBER(s) AFOSR-ISSA 81-00013
9. PERFORMING ORGANIZATION NAME AND ADDRESS BARTLESVILLE ENERGY TECHNOLOGY CENTER DEPARTMENT OF ENERGY BARTLESVILLE, OK 74005-1398		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2308/B1 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA, BLDG 410 BOLLING AIR FORCE BASE, D C 20332		12. REPORT DATE 1981
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 21
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) RAMJET FUELS ENTHALPY OF COMBUSTION VAPOR PRESSURE HEAT CAPACITY ALKYLINDANS ALKYLNAPHTHALENES HEPTACYCLOTETRADECANE		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The research effort continues to be focussed on high density/high energy hydrocarbons. In cooperation with researchers at Wright-Patterson Air Force Base, heats of combustion are measured for constituents of current ramjet fuels and for finished fuels; meanwhile, pure hydrocarbons are synthesized for heat-of-combustion measurement whose unusual steric or strain energies may contribute to design of high energy/high density fuels of the future. → (over)		

20. Abstract -- continued

Four pure hydrocarbons were studied during the current reporting period that were selected among the alkylnaphthalenes and indans that may exhibit unusual steric energies. One unusual hydrocarbon, with very high density and a "cage-like" molecular structure, was also studied during this period. This substance is undergoing preliminary testing as an experimental fuel. Synthesis and purification of hydrocarbons for future study are in progress at Oklahoma State University. New equipment and procedures were developed for application of the differential scanning calorimeter on measurements of heat capacity of fuels and their constituents.

Preparation is underway to study the heat of combustion of several special liquid hydrocarbon fuels in cooperation with researchers at Wright-Patterson Air Force Base.

Results of past and present research done under AFOSR sponsorship were prepared for publication, and two journal articles were published.

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFOSR)
NOTICE OF TRANSMITTAL TO DTIC

This technical report has been reviewed and is approved for public release IAW AFR 190-12. Distribution is unlimited.

MATTHEW J. KIRPER

Chief, Technical Information Division

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	



FINAL TECHNICAL SUMMARY REPORT

THERMODYNAMICS OF ORGANIC COMPOUNDS

* * * * *

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Project Director: W. D. Good

Report* prepared by:

N. K. Smith
B. E. Gammon
W. D. Good

W. D. Good, Division Director
H. R. Johnson, Director

* Synthesis and purification of research samples were provided by Professor E. J. Eisenbraun, Oklahoma State University. Samples were produced by purchase agreement for this project.

Qualified requestors may obtain additional copies from the Defense Documentation Center, all others should apply to the National Technical Information Service.

Approved for public release; distribution unlimited.

Conditions of Reproduction

Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

TABLE OF CONTENTS

	<u>PAGE</u>
FOREWORD	i
ABSTRACT	ii
RESEARCH PROGRESS	1
1. ENTHALPY OF COMBUSTION	1
Alkylnaphthalenes and Indans	1
High Density/High Energy Hydrocarbons . .	10
2. DIFFERENTIAL SCANNING CALORIMETRY	13
4. PUBLICATIONS	14

FOREWORD

This research program consists of an integrated and inter-related effort of basic and applied research in chemical thermodynamics and thermochemistry. Knowledge of variation of physical and thermodynamic properties with molecular structure is used to select compounds for study that because of high ring strain or unusual steric effects may have good energy characteristics per unit volume or per unit mass and thus be useful in the synthesis of high energy fuels. These materials are synthesized, and their thermodynamic properties are evaluated. In cooperation with researchers at Wright-Patterson Air Force Base, ramjet fuels currently in use are subjected to careful thermodynamic evaluation by measurements of heat capacity, enthalpy of combustion and vapor pressure.

ABSTRACT

The research effort continues to be focused on high density/high energy hydrocarbons. In cooperation with researchers at Wright-Patterson Air Force Base, heats of combustion are measured for constituents of current ramjet fuels and for finished fuels; meanwhile, pure hydrocarbons are synthesized for heat-of-combustion measurement whose unusual steric or strain energies may contribute to design of high energy/high density fuels of the future.

Four pure hydrocarbons were studied during the current reporting period that were selected among the alkylnaphthalenes and indans that may exhibit unusual steric energies. One unusual hydrocarbon, with very high density and a "cage-like" molecular structure, was also studied during this period. This substance is undergoing preliminary testing as an experimental fuel. Synthesis and purification of hydrocarbons for future study are in progress at Oklahoma State University. New equipment and procedures were developed for application of the differential scanning calorimeter on measurements of heat capacity of fuels and their constituents.

Preparation is underway to study the heat of combustion of several special liquid hydrocarbon fuels in cooperation with researchers at Wright-Patterson Air Force Base.

Results of past and present research done under AFOSR sponsorship were prepared for publication, and two journal articles were published.

RESEARCH PROGRESS

1. ENTHALPY OF COMBUSTION

a. Alkyl naphthalenes and Indans

Enthalpies of combustion were measured for four compounds. Summaries of combustion experiments, pictorial formulas, combustion reactions, and molar values of enthalpy of combustion and formation are given for 1-ethyl-8-methylnaphthalene (Tables 1 and 2), 1-isopropyl-8-methylnaphthalene (Tables 3 and 4), and 1,6-dimethylindan (Tables 7 and 8). Similar measurements have been reported for 2-ethyl-6-methylnaphthalene,¹ a series of dimethylnaphthalenes,² and 1,7-dimethylindan.³

Synthesis of 2-isopropyl-6-methylnaphthalene and 1-isopropyl-7-methylindan are in progress in the laboratories of Professor E. J. Eisenbraun at Oklahoma State University. It is not yet possible to make all of the gaseous state comparisons desirable, but qualitatively it can be said that the 1,8-substituted naphthalenes are showing the expected high steric energies and that the 1,7-substituted indans are showing little or no steric effect. This may yet be found with more alkyl group substitution in the 1- position.

-
- ¹ AFOSR Final Technical Summary Report, 1976-1977.
² W. D. Good, *J. Chem. Thermodynamics*, 5, 715 (1973).
³ AFOSR Final Technical Summary Report, 1979-1980.

TABLE 1. Summary of Calorimetric Experiments with 1-Ethyl-8-methylnaphthalene^a(cal_{th} = 4.184 J)

	2	3	4	5	6	7	8	9
m'(compound)/g	0.729397	0.731212	0.741948	0.752954	0.742284	0.743978	0.744330	0.744720
m''(auxiliary oil)/g	0.067386	0.063239	0.053507	0.043203	0.053257	0.051743	0.052305	0.050786
m'''(fuse)/g	0.001003	0.000980	0.000936	0.000959	0.000959	0.000918	0.000963	0.001001
n ⁱ (H ₂ O)/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/k = (t_f - t_i + \Delta t_{corr})/K$	2.00793	2.00084	2.00059	2.00024	2.00075	2.00132	2.00100	2.00022
$\epsilon(\text{calor})(-\Delta t_c)/\text{cal}_{th}$	-8046.27	-8017.85	-8016.86	-8015.43	-8017.50	-8019.80	-8018.50	-8013.34
$\epsilon(\text{cont})(-\Delta t_c)/\text{cal}_{th}^b$	-8.94	-8.74	-8.82	-8.88	-8.82	-8.87	-8.75	-8.83
$\Delta \epsilon_{igr}/\text{cal}_{th}$	0.18	0.18	0.18	0.16	0.18	0.18	0.18	0.18
$\Delta \epsilon(\text{corr to std states})/\text{cal}_{th}^c$	3.95	3.94	3.97	3.99	3.97	3.97	3.97	3.97
$(-m''(\Delta \epsilon_c^2/m)(\text{auxiliary oil}))/\text{cal}_{th}$	741.55	695.91	588.81	475.42	506.06	569.40	575.59	558.87
$(-m'''(\Delta \epsilon_c^2/m)(\text{fuse}))/\text{cal}_{th}$	4.06	3.97	3.79	3.88	3.88	3.72	3.90	3.62
$(m'(\Delta \epsilon_c^2/m)(\text{compound}))/\text{cal}_{th}$	-7305.47	-7322.58	-7428.93	-7540.83	-7432.24	-7451.39	-7443.62	-7455.53
$(\Delta \epsilon_c^2/m)(\text{compound}))/\text{cal}_{th}$ per g	-10015.77	-10014.31	-10012.74	-10015.00	-10012.66	-10015.60	-10013.80	-10011.43
$(\Delta \epsilon_c^2/m)(\text{compound}))/\text{cal}_{th}$ per g	-10013.84 ± 0.49 (mean and standard deviation of the mean)							

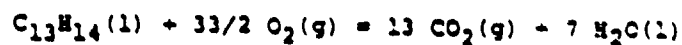
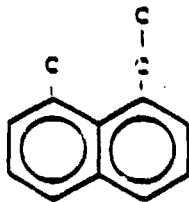
^a The symbols and abbreviations of this table are those of M. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

^b $\epsilon^i(\text{cont})(t_i - 298.15 K) + \epsilon^f(\text{cont})(298.15 K - t_f + \Delta t_{corr})$.

^c Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 2. Derived Molar Thermochemical Values for
1-Ethyl-8-methylnaphthalene at 298.15 K

(calch = 4.184 J)



$$\Delta \text{Ec}^\circ/\text{M} = -10015.77 \text{ CAL G}^{-1}$$

-10014.31

-10012.74

-10015.00

-10012.66

-10015.60

-10013.88

-10013.14

-10011.43

MEAN -10013.84

STD. DEV. OF MEAN ±0.49

$$\Delta \text{Ec}^\circ = -1704.92 \pm 0.26 \text{ KCAL MOL}^{-1}$$

$$\Delta \text{Hc}^\circ = -1707.00 \pm 0.26 \text{ KCAL MOL}^{-1}$$

$$\Delta \text{Hf}^\circ = -6.13 \pm 0.30 \text{ KCAL MOL}^{-1}$$

$$\Delta \text{Hf}^\circ(\text{g}) = +23.45 \pm 0.35 \text{ KCAL MOL}^{-1}$$

CO₂ RECOVERY 99.991 ± 0.005% (MEAN AND SDM)

TABLE 3. Summary of Calorimetric Experiments with 1-Isopropyl-8-methylnaphthalene^a(cal_{th} = 4.184 J)

	1	2	3	4	5	6	7	8
m' (compound)/g	0.688767	0.703508	0.708668	0.704550	0.729591	0.716324	0.724230	0.690375
m'' (auxiliary oil)/g	0.096079	0.083049	0.078671	0.082190	0.059492	0.071274	0.063638	0.095237
m''' (fuse)/g	0.000963	0.000918	0.000868	0.000920	0.001033	0.001053	0.001173	0.001008
n ⁱ (H ₂ O)/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.99968	2.00115	2.00205	2.00142	2.00219	2.00119	2.00037	2.00164
ϵ (calor) $(-\Delta t_c)/cal_{th}$	-8013.69	-8019.56	-8023.17	-8020.65	-8023.75	-8019.72	-8016.43	-8021.51
ϵ (cont) $(-\Delta t_c)/cal_{th}$ ^b	-8.71	-8.70	-8.69	-8.75	-8.74	-8.70	-8.68	-8.71
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE (corr to std states)/cal _{th} ^c	3.75	3.78	3.79	3.78	3.83	3.80	3.81	3.75
$(-m''(\Delta E_c^0/m)(auxiliary\ oil))/cal_{th}$	1057.29	913.90	865.73	904.45	654.67	784.33	700.30	1040.22
$(-m''(\Delta E_c^0/m)(fuse))/cal_{th}$	3.90	3.72	3.51	3.72	4.18	4.26	4.75	4.08
$(m'(\Delta E_c^0/m)(compound))/cal_{th}$	-6957.29	-7106.67	-7158.65	-7117.26	-7369.63	-7235.84	-7316.07	-6974.19
$(\Delta E_c^0/m)(compound))/cal_{th}$ per g	-10101.08	-10101.76	-10101.56	-10101.86	-10101.04	-10101.36	-10101.86	-10102.02
$(\Delta E_c^0/m)(compound))/cal_{th}$ per g	-10101.57 ± 0.13	(mean and standard deviation of the mean)						

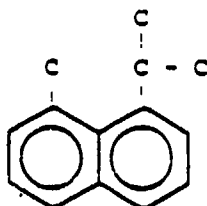
^a The symbols and abbreviations of this table are those of W. M. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. P. D. Rossini, editor. Interscience: 1956.

^b ϵ^i (cont) $(t_i - 298.15\ K) + \epsilon^f$ (cont) $(298.15\ K - t_f + \Delta t_{corr})$.

^c Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 4. Derived Molar Thermochemical Values for
1-Isopropyl-8-methylnaphthalene at 298.15 K

(cal_{th} = 4.184 J)



$$\Delta \text{Ec}^*/\text{M} = -10101.08 \text{ CAL G}^{-1}$$

-10101.76

-10101.56

-10101.86

-10101.04

-10101.36

-10101.86

-10102.02

MEAN -10101.57

STD. DEV. OF MEAN ±0.13

$$\Delta \text{Ec}^* = -1861.55 \pm 0.24 \text{ KCAL MOL}^{-1}$$

$$\Delta \text{Hc}^* = -1863.92 \pm 0.24 \text{ KCAL MOL}^{-1}$$

$$\Delta \text{Hf}^* = +0.69 \pm 0.30 \text{ KCAL MOL}^{-1}$$

$$\text{CO}_2 \text{ RECOVERY} \quad 99.96 \pm 0.014 \text{ (MEAN AND SDM)}$$

TABLE 5. Summary of Calorimetric Experiments with 1-Isopropyl-6-methylindan^a

(cal_{th} = 4.184 J)

	1	2	3	4	5	6
m' (compound)/g	0.703833	0.709730	0.698597	0.747474	0.754828	0.742998
m'' (auxiliary oil)/g	0.063037	0.056848	0.070093	0.036883	0.026612	0.029290
m''' (fuse)/g	0.001245	0.001006	0.001271	0.001196	0.001036	0.001101
n ⁱ (H ₂ O)/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
Δt _c /K = (t _f - t _i + Δt _{corr})/K	1.99461	1.99280	2.00063	2.03585	2.02654	2.00320
ε (calor) (-Δt _c)/cal _{th}	-7993.36	-7986.10	-8017.49	-8158.64	-8121.30	-8027.78
ε (cont) (-Δt _c)/cal _{th} ^b	-8.69	-8.69	-8.66	-9.67	-9.60	-9.49
ΔE _{ign} /cal _{th}	0.18	0.18	0.18	0.18	0.18	0.18
ΔE (corr to std states)/cal _{th} ^c	3.38	3.38	3.38	3.50	3.50	3.40
{-m'' (ΔE _c ^o /m) (auxiliary oil) }/cal _{th}	693.68	625.57	771.33	405.87	292.85	322.32
{-m''' (ΔE _c ^o /m) (fuse) }/cal _{th}	5.04	4.07	5.15	4.84	4.19	4.45
{m' (ΔE _c ^o /m) (compound) }/cal _{th}	-7299.76	-7361.56	-7246.12	-7753.92	-7830.18	-7706.87
{ (ΔE _c ^o /m) (compound) }/cal _{th} per g	-10371.44	-10372.34	-10372.39	-10373.50	-10373.46	-10372.66
{ (ΔE _c ^o /m) (compound) }/cal _{th} per g	-10372.63 ± 0.32	(mean and standard deviation of the mean)				

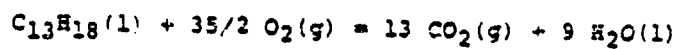
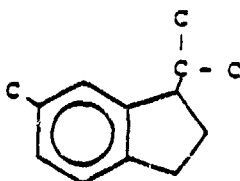
^a The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

^b εⁱ (cont) (t_i - 298.15 K) + ε^f (cont) (298.15 K - t_f + Δt_{corr}).

^c Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 6. Derived Molar Thermochemical Values for
1-Isopropyl-6-methylindan at 298.15 K

($\text{cal}_{\text{th}} = 4.184 \text{ J}$)



$$\Delta E_{\text{c}}^{\circ}/\text{M} = -10371.44 \text{ CAL G}^{-1}$$

-10372.34

-10372.39

-10373.50

-10373.46

-10372.66

MEAN -10372.63

STD. DEV. OF MEAN ± 0.32

$$\Delta E_{\text{c}}^{\circ} = -1807.83 \pm 0.26 \text{ KCAL MOL}^{-1}$$

$$\Delta H_{\text{c}}^{\circ} = -1810.50 \pm 0.26 \text{ KCAL MOL}^{-1}$$

$$\Delta H_{\text{f}}^{\circ} = -27.00 \pm 0.30 \text{ KCAL MOL}^{-1}$$

CO_2 RECOVERY $99.98 \pm 0.03\%$ (MEAN AND SDM)

TABLE 7. Summary of Calorimetric Experiments with 1,6-Dimethylindane^a

(cal_{th} = 4.184 J)

	1	2	3	4	5	6	7	8
m' (compound)/g	0.703631	0.712170	0.718148	0.732350	0.711815	0.714155	0.701059	0.691078
m'' (auxiliary oil)/g	0.072266	0.065313	0.060040	0.047014	0.066093	0.063630	0.076300	0.080669
m''' (fuse)/g	0.001150	0.000970	0.001068	0.001201	0.000880	0.000972	0.000936	0.001006
n ⁱ (H ₂ O)/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
Δt _C /K = (t _f - t _i + Δt _{corr})/K	1.99688	1.99940	2.00004	2.00129	2.00030	1.99987	2.00127	1.98779
ε (calor) (-Δt _C)/cal _{th}	-8001.99	-8012.08	-8014.66	-8019.65	-8015.71	-8013.98	-8019.56	-7965.56
ε (cont) (-Δt _C)/cal _{th} ^b	-8.82	-8.69	-8.88	-8.81	-8.86	-8.89	-8.83	-8.72
ΔE _{ign} /cal _{th}	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE (corr to std states)/cal _{th} ^c	3.56	3.58	3.59	3.61	3.58	3.58	3.56	3.52
[-m'' (ΔE _C ^o /m) (auxiliary oil)]/cal _{th}	795.24	718.74	660.71	517.36	727.32	700.21	839.64	887.71
[-m''' (ΔE _C ^o /m) (fuse)]/cal _{th}	4.66	3.93	4.32	4.86	3.56	3.94	3.79	4.97
[m' (ΔE _C ^o /m) (compound)]/cal _{th}	-7207.17	-7294.35	-7354.74	-7502.45	-7289.93	-7314.96	-7181.23	-7078.79
{(ΔE _C ^o /m) (compound)]/cal _{th} per g	-10242.83	-10242.42	-10241.26	-10244.35	-10241.33	-10242.82	-10243.40	-10243.11
{(ΔE _C ^o /m) (compound)]/cal _{th} per g	-10242.69 ± 0.36	(mean and standard deviation of the mean)						

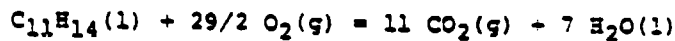
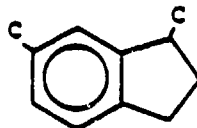
^a The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

^b εⁱ (cont) (t_i - 298.15 K) + ε^f (cont) (298.15 K - t_f + Δt_{corr}).

^c Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 8. Derived Molar Thermochemical Values for
1,6-Dimethylindan at 298.15 K

(cal_{th} = 4.184 J)



$$\Delta \text{Ec}^\circ/\text{M} = -10242.83 \text{ CAL G}^{-1}$$

$$-10242.42$$

$$-10241.26$$

$$-10244.35$$

$$-10241.33$$

$$-10242.82$$

$$-10243.40$$

$$-10243.11$$

$$\text{MEAN} \quad -10242.69$$

$$\text{STD. DEV. OF MEAN} \quad \pm 0.36$$

$$\Delta \text{Ec}^\circ = -1497.83 \pm 0.20 \text{ KCAL MOL}^{-1}$$

$$\Delta \text{Hc}^\circ = -1499.91 \pm 0.20 \text{ KCAL MOL}^{-1}$$

$$\Delta \text{Hf}^\circ = -12.86 \pm 0.25 \text{ KCAL MOL}^{-1}$$

$$\text{CO}_2 \text{ RECOVERY} \quad 99.96 \pm 0.01\% \text{ (MEAN AND SDM)}$$

b. High Density/High Energy Hydrocarbons

An unusual hydrocarbon with cage-like molecular structure, heptacyclotetradecane, was prepared and purified in the laboratories of Professor Alan Marchand at the University of Oklahoma. This crystalline material of high density should have excellent characteristics as a solid fuel or in slurry or solution applications. Summaries of its combustion experiments, its pictorial formula, the combustion reaction, and molar values of enthalpy of combustion and formation are given in Tables 9 and 10.

TABLE 9. Summary of Calorimetric Experiments with Heptacyclotetradecane^a
(cal_{th} = 4.184 J)

	1	2	3	4	5	6	7	8
m' (compound)/g	0.754177	0.797711	0.795936	0.800069	0.802865	0.803835	0.800235	0.801337
m''' (fuse)/g	0.001743	0.001925	0.001883	0.001811	0.001593	0.001935	0.001811	0.001964
n ⁱ (H ₂ O)/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
Δt _c /K = (t _f - t _i + Δt _{corr})/K	1.88629	1.9537	1.99098	2.00102	2.00785	2.01057	2.00139	2.00442
ε (calor) (-Δt _c)/cal _{th}	-7559.28	-7996.39	-7978.82	-8019.04	-8046.41	-8057.32	-8020.54	-8032.68
ε (cont) (-Δt _c)/cal _{th} ^b	-8.11	-8.63	-8.61	-8.65	-8.68	-8.74	-8.68	-8.69
ΔE _{ign} /cal _{th}	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE (corr to std states)/cal _{th} ^c	3.73	3.98	3.97	4.00	4.01	4.02	4.00	4.00
{-m''' (ΔE _c ^o /m) (fuse) }/cal _{th}	7.06	7.80	7.63	7.34	6.45	7.84	7.34	7.96
{m' (ΔE _c ^o /m) (compound) }/cal _{th}	-7556.42	-7993.07	-7975.65	-8016.17	-8044.45	-8054.03	-8017.71	-8029.23
{(ΔE _c ^o /m) (compound) }/cal _{th} per g	-10019.42	-10020.00	-10020.47	-10019.35	-10019.68	-10019.50	-10019.20	-10019.79
{(ΔE _c ^o /m) (compound) }/cal _{th} per g	-10019.68 ± 0.14	(mean and standard deviation of the mean)						

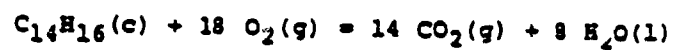
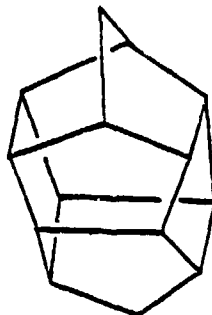
^a The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

^b εⁱ(cont) (t_i - 298.15 K) + ε^f(cont) (298.15 K - t_f + Δt_{corr}).

^c Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 10. Derived Molar Thermochemical Values for
Heptacyclotetradecane at 298.15 K

$$(\text{cal}_{\text{ch}} = 4.184 \text{ J})$$



$$\Delta E_{\text{c}}^{\circ}/\text{M} = -10019.42 \text{ CAL/G}$$

$$-10020.00$$

$$-10020.47$$

$$-10019.35$$

$$-10019.68$$

$$-10019.50$$

$$-10019.20$$

$$-10019.79$$

$$\text{MEAN} \quad -10019.68 \text{ CAL/G}$$

$$\text{STD. DEV. OF MEAN} \quad \pm 0.15 \text{ CAL/G}$$

$$\Delta E_{\text{c}}^{\circ} = -1846.46 \pm 0.24 \text{ KCAL/MOL}$$

$$\Delta H_{\text{c}}^{\circ} = -1848.83 \pm 0.24 \text{ KCAL/MOL}$$

$$\Delta H_{\text{f}}^{\circ} = -14.40 \pm 0.30 \text{ KCAL/MOL}$$

$$\text{CO}_2 \text{ RECOVERY} \quad (99.90 \pm 0.01)\% \text{ (MEAN AND SDM)}$$

2. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Measurements were not made on materials for this project during the past year; however, new equipment and procedures were developed for applications of the DSC to measurements on such materials. The commercial cells used for DSC have three severe limitations: (1) they cannot be filled to more than 15%, usually less, of the volume available for the sample; (2) they cannot withstand more than 2 atmospheres of internal pressure; and (3) they do not make good thermal contact with the DSC head during measurements. For these reasons, reusable screw-cap cells were designed and built to obviate these problems. These cells were used to determine results reported last year on JP-10 and RJ-6. The cells still had one deficiency which has been eliminated by a new design. In the previous version, a sheet gasket was required for sealing the cells. Upon sealing the sheet gasket was extruded to form a wrinkle into the interior volume of the cell; this led to an uncertainty in the volume available to the sample. Equation 1 shows how the observed heat capacity, C_V^{II} , along the saturation line designated by σ , depends on the total volume, V^I , available to the total number of moles of the sample, n^I , of a pure substance.

$$\begin{aligned}
 nC_V^{II} &= n^L C_\sigma^L + n^G C_\sigma^G - T \gamma_\sigma \left(\frac{n^L}{\rho^L} \alpha_\sigma^L + \frac{n^G}{\rho^G} \alpha_\sigma^G \right) \\
 C_V^{II} &= \left(C_\sigma^L - T \gamma_\sigma \alpha_\sigma^L / \rho^L \right) + \left(\frac{V^I}{n^I} - \frac{1}{\rho^L} \right) T \left(\frac{d^2 \rho}{dT^2} \right) \sigma \\
 C_p^L &= C_\sigma^L + T \alpha_p^L \gamma_\sigma / \rho^L \\
 \gamma_\sigma &= \left(\frac{d\rho}{dT} \right) \sigma \\
 \alpha_\sigma &= - \left(\frac{d \ln(\rho^L)}{dT} \right) \sigma
 \end{aligned} \tag{1}$$

If the vapor pressure is small, the volume dependence is not significant, but for pressures even near or above boiling, this term can be a significant fraction of the measured value. For this reason, the cells were redesigned with a cone-shaped seal so that only a ring gasket was required for sealing, and thereby the internal volume of the sealed cells can be determined by a simple measurement with a micrometer. Thus, appropriate corrections can be determined and made with measurements from these cells.

4. PUBLICATIONS

Thermodynamic Properties of Cyclopropylamine, Cyclopentylamine and Methylenecyclobutane by H. L. Finke, J. F. Messerly and S. H. Lee-Bechtold. *Journal of Chemical Thermodynamics*, 13, No. 4, 345-355 (1981).

Vapor Heat Capacity and Enthalpy of Vaporization of Six Miscellaneous Organic Compounds by I. A. Hossenlopp and D. W. Scott. *Journal of Chemical Thermodynamics*, 13, No. 5, 405-414 (1981).

DISTRIBUTION LIST

CONTRACTORS

Aerospace Corporation
The Iv n L Gotting Laboratories
Attn: Dr Charles M Randall
P O Box 95085
Los Angeles, CA 90045

CINDAS
Purdue University Research Park
Attn: Dr H H Li
2595 Yeager Road
West Lafayette, IN 47907

Department of Energy
Bartlesville Energy Technology
Center
Attn: Mr William D Good
Bartlesville, OK 74003

Dow Chemical Company
Thermal Laboratory, Bldg 1707
Attn: Dr Malcolm Chase
Midland, MI 48640

University of Manchester/UMIST
Department of Metallurgy
Attn: Dr Roy Taylor
Grosvenor Street
Manchester M1 7HS, ENGLAND

Department of Energy
Pittsburgh Energy Technology
Center
Attn: Dr Francis E Spencer, Jr
P. O. Box 10940
Pittsburgh, PA 15236

National Bureau of Standards
Thermophysics Division
Attn: Dr Ared Cezairliyan
Washington, DC 20234

National Bureau of Standards
Chemical Thermodynamics Division
Attn: Dr Stan Abramowitz
Mr David Ditmars
Washington, DC 20234

University of Nevada
Mackay School of Mines
Attn: Prof Eugene Miller
Reno, NV 89507

Purdue University
School of Mechanical Engineering
Properties Research Laboratory
Attn: Dr R F Taylor
2595 Yeager Road
West Lafayette, IN 47907

Space Sciences, Inc
Attn: Mr Milton Farber
135 W Maple
Monrovia, CA 91016

SRI International
Physical Sciences Division
Attn: Dr D L Hildenbrand
Menlo Park, CA 94025

NON-CONTRACTORS

AFML/MXE (L Scott Theibert)
Wright-Patterson AFB, OH 45433

AFML/LP (Dr Merrill L Minges)
Wright-Patterson AFB, OH 45433

AFML/MBC (Dr W C Kessler)
Wright-Patterson AFB, OH 45433

Jet Propulsion Laboratory
Attn: Mr. Theodore W Price
4800 Oak Grove Drive
Pasadena, CA 91103

Johns Hopkins University
Applied Physics Laboratory
Attn: Dr Robert Fristrom
Johns Hopkins Road
Laurel, MD 20810

NON-CONTRACTORS--Continued

AFRPL/LKCB (Mr Curtis C Selph)
Edwards AFB, CA 93523

AFRPL/PACP (Dr David Mann)
Edwards AFB, CA 93523

AFWL/ALD (Dr Leroy Wilson)
Kirtland AFB, NM 87117

AFWL/ALD (Major David S Olson)
Kirtland AFB, NM 87117

AFAOL/RJT (Dr F D Stull)
Wright-Patterson AFB, OH 45433

U.S. Army Research Office
Attn: Dr David R Squire
P O Box 12211
Research Triangle Park, NC 27709

Atlantic Research Corporation
Attn: Dr Charles Henderson
5390 Cherokee Avenue
Alexandria, VA 22314

University of California
Department of Chemistry
Attn: Dr Leo Brewer
Berkeley, CA 94700

Cornell University
Department of Chemistry
Attn: Dr S H Bauer
Ithica, NY 14850

NSSC
Department of the Navy
Code NSEA-0331
Attn: Mr John W Murrin
Washington, DC 20360

Naval Ordnance Station
Attn: Mr Al Camp
Indian Head, MD 20640

NASA
Lewis Laboratories (Mail Stop 6-1)
Attn: Mr Sanford Gordon
Cleveland, OH 44135

NAS-NRC
Numerical Data Advisory Board
2101 Constitution Avenue, NW
Washington, DC 20418

National Bureau of Standards
OSRD
Attn: Dr David Lide
Washington, DC 20234

National Bureau of Standards
Chemical Thermodynamics Division
Attn: Mr Donald D Wagman
Washington, DC 20234

National Bureau of Standards
Office of Standard Reference
Materials
Attn: Dr Richard Kirby
Washington, DC 20234

National Bureau of Standards
Thermophysical Properties Division
Attn: Dr Jerry Hust
Boulder, CO 80302

Office of Naval Research
Attn: Mr Rudolph Marcus
1030 E Green Street
Pasadena, CA 91101

Office of Naval Research
Power Program, Code 473
Attn: Dr Richard Miller
800 North Quincy Street
Arlington, VA 22217

Rice University
Department of Chemistry
Attn: Dr John Margrave
Houston, TX 77001

United Technologies Corporation
Chemical Systems Division
Attn: Dr R O MacLaren
Sunnyvale, CA 94086

Chemical Propulsion Information
Agency
APL/JHU (2 copies)
Johns Hopkins Road
Laurel, MD 20810