LEVEL II

13

FINAL TECHNICAL SUMMARY REPORT

for the period

1 October 1980 - 30 September 1981

THERMODYNAMICS OF ORGANIC COMPOUNDS

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Research sponsored by:

Air Force Office of Scientific Research (NA)
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Contract No. AFOSR-ISSA 81-00013
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ALKYLINDANS
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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)

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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.

FINAL TECHNICAL SUMMARY REPORT

THERMODYNAMICS OF ORGANIC COMPOUNDS

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Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Project Director: W. D. Good

Report* prepared by:

N. K. Smith
B. E. Gammon
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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.

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FOREWORD

This research program consists of an integrated and interrelated 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. Alkylnaphthalenes 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.

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[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	0.743330	0.744720	0.744702
m''(auxiliary oil)/g	0.067386	0.063239	0.053567	0.043203	0.053257	0.051743	0.052305	0.050792	0.050786
m'''(fuse)/g	0.001003	0.000980	0.000936	0.000959	0.000959	0.000918	0.000963	0.001001	0.000895
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
Δt_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	1.99971
ε(calor)$(-\Delta t_c)/cal_{th}$	-8046.27	-8017.85	-8016.86	-8015.43	-8017.50	-8019.80	-8018.50	-8015.36	-8013.34
ε(cont)$(-\Delta t_c)/cal_{th}$[b]	-8.94	-8.74	-8.82	-8.88	-8.82	-8.87	-8.75	-8.76	-8.83
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE(corr to std states)$/cal_{th}$[c]	3.95	3.94	3.97	3.99	3.97	3.97	3.97	3.97	3.97
$(-m''(\Delta E_c^\circ/m)$(auxiliary oil)$)/cal_{th}$	741.55	695.91	588.81	475.42	586.06	569.40	575.59	558.93	558.87
$(-m'''(\Delta E_c^\circ/m)$(fuse)$)/cal_{th}$	4.06	3.97	3.79	3.88	3.88	3.72	3.90	4.05	3.62
$(m'(\Delta E_c^\circ/m)$(compound)$)/cal_{th}$	-7305.47	-7322.58	-7428.93	-7540.83	-7432.24	-7451.39	-7443.62	-7456.99	-7455.53
$[(\Delta E_c^\circ/m)$(compound)$)/cal_{th}$ per g	-10015.77	-10014.31	-10012.74	-10015.00	-10012.66	-10015.60	-10013.88	-10013.14	-10011.43
$[(\Delta E_c^\circ/m)$(compound)$)/cal_{th}$ per g	-10013.84 ± 0.49 (mean and standard deviation of the mean)								

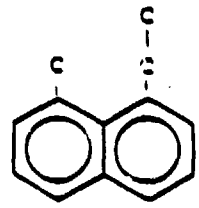
[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] ε^i(cont)$(t_i - 298.15\ K) + \varepsilon^f$(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 2. Derived Molar Thermochemical Values for 1-Ethyl-8-methylnaphthalene at 298.15 K

(cal_{th} = 4.184 J)



$$C_{13}H_{14}(l) + 33/2\ O_2(g) = 13\ CO_2(g) + 7\ H_2O(l)$$

$\Delta Ec^\circ/M$ =	-10015.77 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

ΔEc° =	-1704.92 ± 0.26 KCAL MOL^{-1}
ΔHc° =	-1707.00 ± 0.26 KCAL MOL^{-1}
ΔHf° =	+6.13 ± 0.30 KCAL MOL^{-1}
$\Delta Hf^\circ(g)$ =	+23.45 ± 0.35 KCAL MOL^{-1}

CO_2 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
$n^i(H_2O)$/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
$\{-m''(\Delta E_c^\circ/m)$(auxiliary oil)$\}/cal_{th}$	1057.29	913.90	865.73	904.45	654.67	784.33	700.30	1048.22
$\{-m'''(\Delta E_c^\circ/m)$(fuse)$\}/cal_{th}$	3.90	3.72	3.51	3.72	4.18	4.26	4.75	4.08
$\{m'(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$	-6957.29	-7106.67	-7158.65	-7117.26	-7369.63	-7235.84	-7316.07	-6974.19
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$ per g	-10101.08	-10101.76	-10101.56	-10101.86	-10101.04	-10101.36	-10101.86	-10102.02
$\{(\Delta E_c^\circ/m)$(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. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

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

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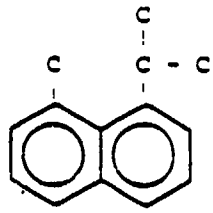
(cal_{th} = 4.184 J)



$C_{14}H_{16}(l) + 18\ O_2(g) = 14\ CO_2(g) + 8\ H_2O(l)$

$\Delta Ec^\circ/M$ =	-10101.08 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

ΔEc° = -1861.55 ± 0.24 KCAL MOL^{-1}

ΔHc° = -1863.92 ± 0.24 KCAL MOL^{-1}

ΔHf° = +0.69 ± 0.30 KCAL MOL^{-1}

CO_2 RECOVERY 99.96 ± 0.01% (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
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.99461	1.99280	2.00063	2.03585	2.02654	2.00320
ε(calor)$(-\Delta t_c)/cal_{th}$	-7993.36	-7986.10	-8017.49	-8158.64	-8121.30	-8027.78
ε(cont)$(-\Delta t_c)/cal_{th}$[b]	-8.69	-8.69	-8.66	-9.67	-9.60	-9.49
$\Delta E_{ign}/cal_{th}$	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
$\{-m''(\Delta E_c^\circ/m)$(auxiliary oil)$\}/cal_{th}$	693.68	625.57	771.33	405.87	292.85	322.32
$\{-m'''(\Delta E_c^\circ/m)$(fuse)$\}/cal_{th}$	5.04	4.07	5.15	4.84	4.19	4.45
$\{m'(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$	-7299.76	-7361.56	-7246.12	-7753.92	-7830.18	-7706.87
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$ per g	-10371.44	-10372.34	-10372.39	-10373.50	-10373.46	-10372.66
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$ per g	-10372.63 ± 0.32 (mean and standard deviation of the mean)					

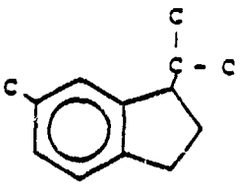
[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] ε^i(cont)$(t_i - 298.15\ K) + \varepsilon^f$(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 6. Derived Molar Thermochemical Values for 1-Isopropyl-6-methylindan at 298.15 K

(cal_{th} = 4.184 J)



$C_{13}H_{18}(l) + 35/2\ O_2(g) = 13\ CO_2(g) + 9\ H_2O(l)$

$\Delta Ec^\circ/M$ =	-10371.44 CAL G^{-1}
	-10372.34
	-10372.39
	-10373.50
	-10373.46
	-10372.66
MEAN	-10372.63
STD. DEV. OF MEAN	±0.32

ΔEc° = -1807.83 ± 0.26 KCAL MOL^{-1}

ΔHc° = -1810.50 ± 0.26 KCAL MOL^{-1}

ΔHf° = -27.00 ± 0.30 KCAL MOL^{-1}

CO_2 RECOVERY 99.98 ± 0.03% (MEAN AND SDM)

TABLE 7. Summary of Calorimetric Experiments with 1,6-Dimethylindan[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
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.99688	1.99940	2.00004	2.00129	2.00030	1.99987	2.00127	1.98779
ϵ(calor)$(-\Delta t_c)/cal_{th}$	-8001.99	-8012.08	-8014.66	-8019.65	-8015.71	-8013.98	-8019.56	-7965.56
ϵ(cont)$(-\Delta t_c)/cal_{th}$[b]	-8.82	-8.69	-8.88	-8.81	-8.86	-8.89	-8.83	-8.72
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE(corr to std states)$/cal_{th}$[c]	3.56	3.58	3.59	3.61	3.58	3.58	3.56	3.52
$\{-m''(\Delta E_c^\circ/m)$(auxiliary oil)$\}/cal_{th}$	795.24	718.74	660.71	517.36	727.32	700.21	839.64	887.71
$\{-m'''(\Delta E_c^\circ/m)$(fuse)$\}/cal_{th}$	4.66	3.93	4.32	4.86	3.56	3.94	3.79	4.07
$\{m'(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$	-7207.17	-7294.35	-7354.74	-7502.45	-7289.93	-7314.96	-7181.23	-7078.79
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$ per g	-10242.83	-10242.42	-10241.26	-10244.35	-10241.33	-10242.82	-10243.40	-10243.11
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$ per g	-10242.69 ± 0.36 (mean and standard deviation of the mean)							

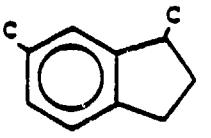
[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] 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 8. Derived Molar Thermochemical Values for 1,6-Dimethylindan at 298.15 K

(cal_{th} = 4.184 J)



$C_{11}H_{14}(l) + 29/2\ O_2(g) = 11\ CO_2(g) + 7\ H_2O(l)$

$\Delta Ec^\circ/M$ =	-10242.83 CAL G^{-1}
	-10242.42
	-10241.26
	-10244.35
	-10241.33
	-10242.82
	-10243.40
	-10243.11
MEAN	-10242.69
STD. DEV. OF MEAN	±0.36

ΔEc° = -1497.83 ± 0.20 KCAL MOL^{-1}

ΔHc° = -1499.91 ± 0.20 KCAL MOL^{-1}

ΔHf° = -12.86 ± 0.25 KCAL MOL^{-1}

CO_2 RECOVERY 99.96 ± 0.01% (MEAN AND SOM)

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
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.88629	1.9 537	1.99098	2.00102	2.00785	2.01057	2.00139	2.00442
ϵ(calor)$(-\Delta t_c)/cal_{th}$	-7559.28	-7996.39	-7978.82	-8019.04	-8046.41	-8057.32	-8020.54	-8032.68
ϵ(cont)$(-\Delta t_c)/cal_{th}$[b]	-8.11	-8.63	-8.61	-8.65	-8.68	-8.74	-8.68	-8.69
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
ΔE(corr to std states)$/cal_{th}$[c]	3.73	3.98	3.97	4.00	4.01	4.02	4.00	4.00
$\{-m'''(\Delta E_C^\circ/m)$(fuse)$\}/cal_{th}$	7.06	7.80	7.63	7.34	6.45	7.84	7.34	7.96
$\{m'(\Delta E_C^\circ/m)$(compound)$\}/cal_{th}$	-7556.42	-7993.07	-7975.65	-8016.17	-8044.45	-8054.03	-8017.71	-8029.23
$\{(\Delta E_C^\circ/m)$(compound)$\}/cal_{th}$ per g	-10019.42	-10020.00	-10020.47	-10019.35	-10019.68	-10019.50	-10019.2[illegible]	-10019.79
$\{(\Delta E_C^\circ/m)$(compound)$\}/cal_{th}$ per g	-10019.68 ± 0.14 (mean and standard deviation of the mean)							

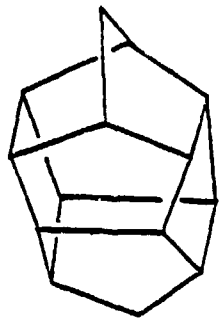
[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] 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 10. Derived Molar Thermochemical Values for Heptacyclotetradecane at 298.15 K

(cal_{th} = 4.184 J)



$C_{14}H_{16}(c) + 18\ O_2(g) = 14\ CO_2(g) + 8\ H_2O(l)$

$\Delta Ec°/M$	=	-10019.42 CAL/G
		-10020.00
		-10020.47
		-10019.35
		-10019.68
		-10019.50
		-10019.20
		-10019.79
MEAN		-10019.68 CAL/G
STD. DEV. OF MEAN		±0.15 CAL/G
$\Delta Ec°$	=	-1846.46 ± 0.24 KCAL/MOL
$\Delta Hc°$	=	-1848.83 ± 0.24 KCAL/MOL
$\Delta Hf°$	=	-14.40 ± 0.30 KCAL/MOL
CO_2 RECOVERY		(99.90 ± 0.01)% (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^T, available to the total number of moles of the sample, n^T, of a pure substance.

$$nC_v^{II} = n^{\ell}C_{\sigma}^{\ell} + n^{g}C_{\sigma}^{g} - T\gamma_{\sigma}\left(\frac{n^{\ell}}{\rho^{\ell}}\alpha_{\sigma}^{\ell} + \frac{n^{g}}{\rho^{g}}\alpha_{\sigma}^{g}\right)$$

$$C_v^{II} = \left(C_{\sigma}^{\ell} - T\gamma_{\sigma}\alpha_{\sigma}^{\ell}/\rho^{\ell}\right) + \left(\frac{V^T}{n^T} - \frac{1}{\rho^{\ell}}\right)T\left(\frac{d^2\rho}{dT^2}\right)_{\sigma}$$

$$C_p^{\ell} = C_{\sigma}^{\ell} + T\alpha_p^{\ell}\,\gamma_{\sigma}/\rho^{\ell} \qquad (1)$$

$$\gamma_{\sigma} = \left(\frac{d\rho}{dT}\right)_{\sigma}$$

$$\alpha_{\sigma} = -\left(\frac{d\ln(\rho^{\ell})}{dT}\right)_{\sigma}$$

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, Cyclpentylamine 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).

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