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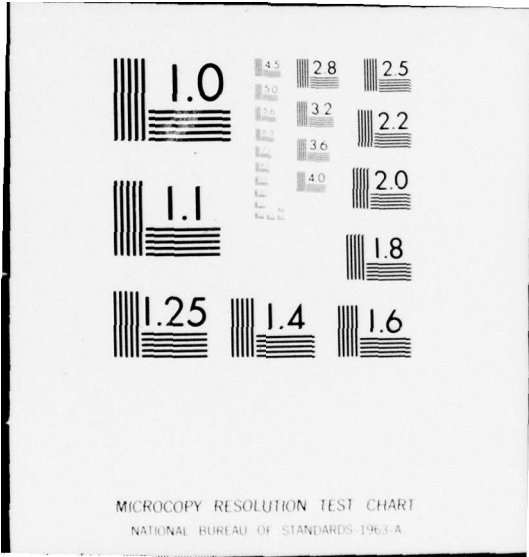
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# DAVID W. TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER



Bethesda, Md. 20084

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THE ENTHALPIES OF DISTILLATE FUELS  
BY A  
DIFFERENTIAL SCANNING CALORIMETRIC METHOD

by  
John G. Zimmerman  
Professor, United States Naval Academy

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MATERIALS DEPARTMENT  
RESEARCH AND DEVELOPMENT REPORT

The Enthalpies of Distillate Fuels by a Differential Scanning Calorimetric Method

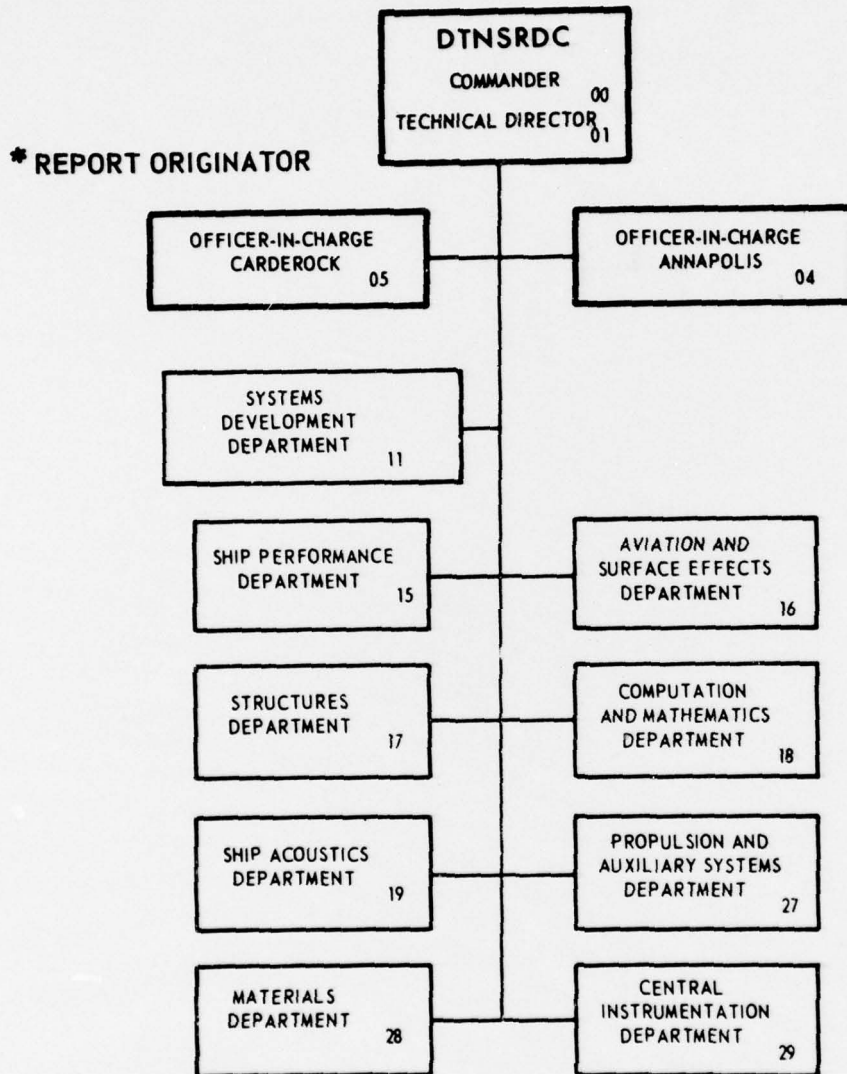
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## ADMINISTRATIVE INFORMATION

This report is a milestone for fiscal year 1976 of the Multipurpose Fuel for Navy Ships Program (Task Area SF 54 593 502, Task 19517, Work Unit 2831-155). This program, which is being conducted at the David W. Taylor Naval Ship Research and Development Center under sponsorship of the Naval Sea Systems Command, is described in reference (a).

## ADMINISTRATIVE REFERENCE

- (a) DTNSRDC Program Summary SF 54 593 502, Task 19517, Work Unit 2831-155 of 15 Feb 1976

## LIST OF ABBREVIATIONS

API	- American Petroleum Institute
ASTM	- American Society for Testing and Materials
Btu/gal	- British thermal units per gallon
° C	- degrees Celsius
cSt	- centistokes
DFM	- Diesel Fuel Marine
DSC	- differential scanning calorimeter
DTA	- differential thermal analysis
e.g.	- for example
ENDO	- endothermic (process)
EXO	- exothermic (process)
° F	- degrees Fahrenheit
g	- gram
gal	- gallon
i.e.	- that is
in.	- inches
J	- Joules
mg	- milligrams
min	- minutes
ml	- millilitres
µl	- microlitres
NBS	- National Bureau of Standards
ND	- Navy Distillate
No.	- number
pub.	- publication
ref	- reference
SDR	- Standard Distillate Reference
sec	- seconds
WAP	- Wax appearance point
WFT	- Wax formation temperature
wt	- weight

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LIST OF SYMBOLS

- a - heating rate, ° C/min
- "a" - upper inflection point in DSC B-trace
- A - area, in<sup>2</sup>
- Al - aluminum
- "b" - lower inflection point in DSC B-trace
- c - heat capacity (specific heat), J/g ° C
- C<sub>H</sub> - heat capacity of the reference and its holder, J/° C
- C<sub>R</sub> - heat capacity of the sample and its holder, J/° C
- E - DSC calibration constant, J/° C min
- Ga - gallium
- H - energy of process occurring in sample, J
- $\bar{H}$  - absolute enthalpy, J/g
- $\Delta H$  -  $\bar{H}(T_2) - \bar{H}(T_1)$ , specific enthalpy difference for a substance heated from T<sub>1</sub> to T<sub>2</sub>, J/g
- $\Delta H_T$  -  $\bar{H}(25^\circ \text{ C}) - \bar{H}(T^\circ \text{ C})$ , specific enthalpy difference for substance heated from T° to 25° C, J/g
- In - Indium
- R - thermal resistance, ° C sec/J
- R - (subscript) reference
- R<sub>C</sub> - thermal resistance between sample and its holder, ° C sec/J
- R<sub>D</sub> - thermal resistance between sample holder and block, ° C sec/J
- s - specific gravity at 60°/60° F
- S - (subscript) sample
- t - time, sec
- T - temperature, ° C
- T<sub>S</sub> - temperature scale sensitivity, ° C/in

$T_R$  - reference temperature, ° C

$\Delta T$  - difference in temperatures of sample holder and reference holder; in this report,  $T_R - T_S$

$\Delta T_S$  - differential temperature scale sensitivity, ° C/in

$W$  - weight of sample, g

## ABSTRACT

The enthalpy differences and heat capacities of five Navy Distillate fuels, one Diesel Fuel Marine, and one JP-5 fuel were determined in the temperature range  $-15^{\circ}$  to  $+25^{\circ}$  C ( $5^{\circ}$  to  $77^{\circ}$  F) with a differential scanning calorimeter. Enthalpy differences and heat capacities were determined to a standard deviation of about 4%. The differential scanning calorimeter method also provided a means of estimating wax contents and wax formation temperatures to  $\pm 2^{\circ}$  C. The method is proposed as a quick and reasonably accurate means of determining the enthalpy differences of fuels over the temperature region appropriate to low-temperature fuel handling.

## INTRODUCTION

The Navy Distillate fuel specification (MIL-F-24397) permits a maximum pour point temperature of  $-4^{\circ}$  C ( $25^{\circ}$  F).<sup>\*</sup> This may lead to a handling problem at low temperatures since wax can crystallize from a fuel at temperatures above its pour point. Observed wax formation temperatures up to  $11^{\circ}$  C ( $20^{\circ}$  F) above the pour point and averaging  $4.4^{\circ}$  C ( $8^{\circ}$  F) above the pour point have been reported.<sup>1</sup> Wax can plug filters and other restricted passages in the fuel system, and this characteristic may adversely affect pumpability. Wax formation from the cooling of ND fuels has been studied by several techniques. Data from the ASTM cloud point temperature test (D2500),<sup>2</sup> the wax appearance point test,<sup>3</sup> and a wax formation temperature test,<sup>1</sup> developed in-house, have been reported.

Knowledge of the energy required to heat ND fuels from below the pour point to a temperature at which fuel handling difficulty is avoided is necessary to predict fuel consumption and special handling requirements in low-temperature operation. At this Center's request, NBS, using a drop calorimeter, completed a precise determination of the enthalpies of three ND fuels in the temperature range  $-15^{\circ}$  C ( $5^{\circ}$  F) to  $25^{\circ}$  C ( $77^{\circ}$  F).<sup>4</sup> Differential scanning calorimetry is reportedly a reasonably accurate, less time-consuming, and less elaborate method of determining enthalpies and cloud points; in addition, it can reveal phase transitions, such as formation of wax crystals from

<sup>\*</sup>Definitions of abbreviations used in this report are given on page i.

<sup>1</sup>Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

solution. This report describes the use of a DSC apparatus to obtain such data on five ND-type fuels, a DFM, and a JP-5 fuel.

## TECHNICAL BACKGROUND

### CALORIMETRY

Calorimeters are devices for measuring heat, specifically heat associated with a change in temperature, a phase change, or a chemical reaction.

Every calorimeter is separable into the calorimeter cell in which the process occurs and the calorimeter jacket. The time constant of the calorimeter is the ratio of the heat capacity of the cell and its contents to the heat conduction constant between jacket and cell. The time constant is the basis of classifying calorimeters into adiabatic and isoperibol calorimeters, characterized by large time constants, and into heat conduction types, characterized by small time constants.<sup>6</sup>

In adiabatic calorimetry the heat transfer between calorimeter and jacket is minimized by holding the jacket temperature as close as possible to that of the calorimeter. In isoperibol calorimetry the jacket is maintained at a constant temperature a few degrees above or below the initial calorimeter temperature. The drop calorimeter used by NBS for fuel enthalpy determinations for the Center<sup>4</sup> is one form of isoperibol calorimeter. The theory of adiabatic and isoperibol calorimetry has been adequately presented in the technical literature.<sup>6-10</sup>

### DIFFERENTIAL THERMAL ANALYSIS AND DIFFERENTIAL SCANNING CALORIMETRY

In the last 25 years a number of heat conduction calorimeters have been developed. One, the differential scanning calorimeter, evolved from the differential thermal analysis apparatus. The DTA, which measures the temperature difference between a sample and an inert reference material as both are heated or cooled at a uniform rate, detects and identifies solid-solid, solid-liquid, liquid-liquid, and liquid-vapor transitions. The DTA technique accurately determines values of the transition temperatures but gives only rough information concerning the heats of transition. More accurate values of such heats are obtained by using the differential scanning calorimeter. A DSC produces data similar to DTA, but the area under the output curve (differential temperature versus time) is directly proportional to the total amount of energy transferred into or out of the sample.<sup>11</sup>

Basically, a DSC device measures heat flow as a function of temperature or time. Although the heat data obtained are not as accurate as those from adiabatic or isoperibol calorimeters, the technique is valuable because relatively small samples (0.1 to 100 mg) are required and because a variety of sample-handling

techniques, including open atmosphere, encapsulation, and the handling of samples in many forms and phases, can be used. Furthermore, the operation is rapid; a complete determination requires less than 30 minutes in most cases.

In a DSC cell two basic requirements must be met.<sup>12</sup> First, the temperature monitors must be removed from the sample. This frees the measured heat effect from dependence on the thermal conductivity, heat capacity, or packing of the sample. The sample and reference holders are monitored instead. Second, the path of heat transfer between the heating (or cooling) source and the detector must be fixed and reproducible to obtain good sensitivity and speed and accuracy of response (resolution).<sup>13</sup>

The Du Pont 900 thermal analyzer<sup>TM</sup> used in the current study consists of a temperature programmer-controller, an XY recorder, and a sample atmosphere control system. The apparatus can be used with various plug-in modules, e.g., the DSC and the DTA modules.

The heart of the Du Pont DSC module<sup>12</sup> is a thermoelectric disk of constantan (figure 1). This disk has two functions - first, as the major path of heat transfer to and from the sample and reference, and second, as one element of differential temperature-measuring thermocouples. It is embedded in a silver block which is heated (or cooled) at a programmed rate. Two raised platforms in the disk serve as sample and reference holders.

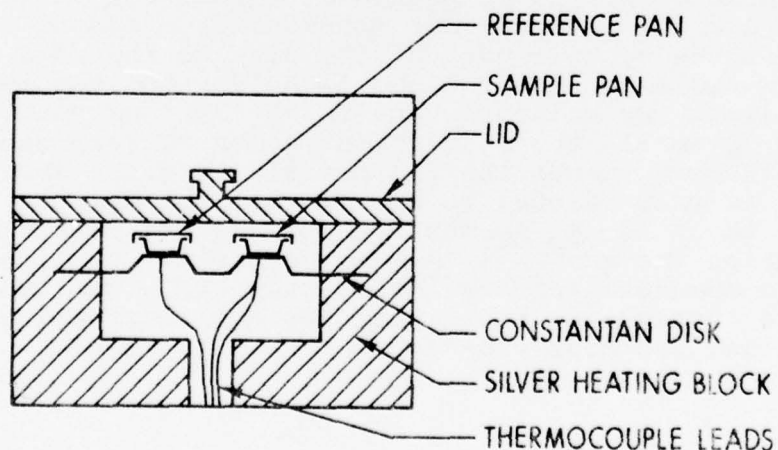


Figure 1 - DSC Cell

## THEORY OF DSC OPERATION

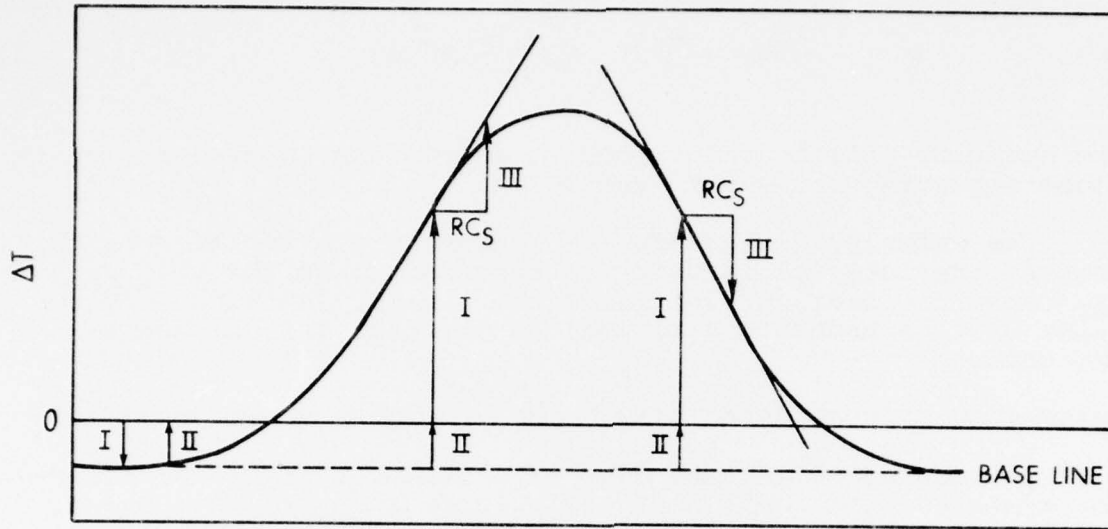
The mathematical theory of DSC calorimetry leads to the following equation:<sup>12,13</sup>

$$R_D(dH/dt) = \Delta T + R_D(C_S - C_R)(dT_R/dt) + (R_C + R_D)C_S(d\Delta T/dt) \quad (1)^*$$

$\Delta T$ , the temperature difference between the sample and reference holders, is monitored on the Y-axis of the recorder chart. In equation (1),  $R_D(dH/dt)$  is the rate of heat evolution caused by some process occurring in the sample, multiplied by the thermal resistance of the heat path between sample holder and block. The right side of equation (1) consists of three terms which are differential temperatures (figure 2) representing certain distances on the  $\Delta T$  axis of a recording of  $\Delta T$  versus  $t$  or  $T$ , obtained on the apparatus XY recorder. Term I,  $\Delta T$ , is the differential temperature recorded by the instrument. Term II,  $R_D(C_S - C_R)(dT_R/dt)$ , is the displacement of the recorder signal from the zero signal level when the instrument has reached scanning equilibrium. Term III,  $(R_C + R_D)C_S(d\Delta T/dt)$ , represents the thermal "lag" or delay of the instrument in recording the value of  $\Delta T$ . However, if  $R_C$ , the thermal resistance between the sample and its holder,  $R_D$ , the thermal resistance between the sample holder and block, and  $C_S$ , the heat capacity of the sample and its holder, are all kept as small as possible, term III may be neglected. In the Du Pont DSC the  $R_C$  value is quite small because the heat path from sample to detector is through the thin constantan disk.  $R_D$  is small but relatively large compared with  $R_C$  because the path of heat transfer from sample holder to block is from the central part of the disk to the edge of the disk.  $C_S$  is small because the sample holder and sample are kept small by design. By making  $R_C$  and  $R_D$  as small as possible and keeping  $C_S$  small, the resolution (speed of response) is increased. However, equation (1) reveals that the absolute value of  $\Delta T$  is proportional to  $R_D$ . To get the maximum signal sensitivity the ratio  $R_D/R_C$  must be as large as possible. For good resolution the sum  $R_C + R_D$  must be kept as small as possible. To compensate for any loss of signal, signal amplification must be increased. These features are incorporated in the Du Pont 900 and DSC module design.

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\*Definitions of symbols used in this report are given on page v.



t OR T

Figure 2 - Relationship of  $R_D(dH/dt)$  to  
Experimental DSC Curve  
(adapted from Gray)<sup>1,3</sup>

#### TYPES OF MEASUREMENTS IN DSC CALORIMETRY

Most physical and chemical phenomena are accompanied by thermal effects which are functions of the temperature. The DSC is ideally suited for quantitative measurements of many of these thermal effects. Two such effects of particular interest in fuel studies are heats of transition and enthalpies.

A heat of transition is the heat associated with a change of state occurring in a substance or mixture. The heat may be determined by measuring the area of a time-based plot of  $\Delta T$  lying between the DSC recorder curve and the baseline obtained from the curve just before and just after the transition peak. The normal procedure is to calibrate the instrument with a material of a known heat of transition that occurs at a temperature about the same as that for the material under study.

The numerical value of the absolute enthalpy or heat content,  $H$ , of a material at a given temperature is unknown, so it is customary to measure enthalpy differences,  $\Delta H_T$ , between some reference temperature such as  $25^\circ \text{C}$  and  $T$ , the temperature of interest.  $\Delta H_T$  in this report will represent the heat required to raise the temperature of 1 gram of fuel at constant pressure from  $T^\circ$  to  $25^\circ \text{C}$  and is the specific enthalpy difference\* for the specified range:

\*For brevity, in this report  $\Delta H_T$  will often be referred to as simply the specific enthalpy of the fuel at  $T^\circ \text{C}$ .

$$\Delta H_T = \bar{H}(25^\circ \text{ C}) - \bar{H}(T^\circ \text{ C}) \quad (2)$$

The quantity will be understood to include any heats of transitions occurring between  $T^\circ$  and  $25^\circ \text{ C}$ .

The enthalpy difference for 1 gram of a material when the temperature interval is unity is referred to as the heat capacity (specific heat) of the material. Again, in this study the value will be understood to include any transitional heats encountered.

#### ESTIMATION OF HEAT CAPACITIES

Methods of estimating heat capacities of liquid hydrocarbon mixtures from certain of their properties are well known. One method (ASTM D 2890)<sup>14</sup> utilizes the API gravity,\* distillation data, and the temperature at which the heat capacity is to be measured. With the nomographs provided and some practice it is possible to determine the values with a repeatability of about 2%, a reproducibility of 4%, and an accuracy of 4% for straight-run\*\* petroleum fractions and 8% for pure olefins.

Other methods of estimating heat capacity usually involve interpolation of values in a table<sup>15,16</sup> using only the API gravity and the temperature. However, interpolation is often awkward and may be inaccurate. Use of an analytical function overcomes these disadvantages, e.g., equation (3) adapted from Cragoe:<sup>15</sup>

$$c = (1.684 + 0.00339T)/s^{1/2} \quad (3)$$

yields accurate values of the heat capacity of petroleum liquids.

#### MATERIALS AND PROCEDURES

##### GENERAL

The heat capacities and enthalpy differences referred to  $25^\circ \text{ C}$  were determined from levels as low as  $-15^\circ \text{ C}$  in replicate differential scanning calorimeter runs on each of seven distillate fuels. The fuels, fuel handling procedures, experimental details, and data-handling techniques are described in this section.

\*The API gravity may be calculated from the specific gravity by:  $\text{API} = 141.5/\text{sp gr} - 131.5$ .

\*\*A straight-run product is one produced by the primary distillation of crude oil.

## FUELS STUDIED

Five ND-type fuels conforming to either MIL-F-24397 (ND fuel requirements) or to MIL-F-24376A (SDR fuel requirements) plus two fuels included for comparison purposes, a DFM and a JP-5 jet fuel satisfying the specifications MIL-F-16884G and MIL-T-5624G, respectively, were used in these tests. For identification purposes in this report, the ND-type fuels have been designated by the symbols A through E, the DFM by F, and the JP-5 by G. Table 1 lists the more pertinent properties of these fuels.

TABLE 1  
PHYSICAL PROPERTIES OF FUELS STUDIED BY DSC

	Fuel							
	A	B	C		D	E	F	G
	Type and Specification							
	ND MIL-F-24397	SDR MIL-F-24376	ND MIL-F-24397	ND MIL-F-24397	SDR MIL-F-24376	DFM MIL-F-16884G	JP-5 MIL-T-5624G	
Gravity, °API at 60° F	32.2	30.6	35.8	36.7	28.9	37.5	43.0	
Specific gravity, 60°/60° F	0.864	0.873	0.846	0.841	0.882	0.837	0.811	
Viscosity, cSt at 100° F	4.83	6.04	3.74	2.34	6.07	2.45	-	
Pour point, ° F	20	15	25	-	25	0	-	
Cloud point, °C <sup>(1)</sup>	2	3	-3	-21	2	-13	-	
Freezing point, ° C	-	-	-	-	-	-	-51	
Distillation data								
10% point, ° F	-	508	430	406	472	410	372	
50% point, ° F	564	623	536	469	593	482	396	
90% point, ° F	644 <sup>(2)</sup>	719	618	589	726	575	434	

<sup>(1)</sup> Cloud points were measured in ° F and converted to nearest ° C.  
<sup>(2)</sup> 87% distilled.

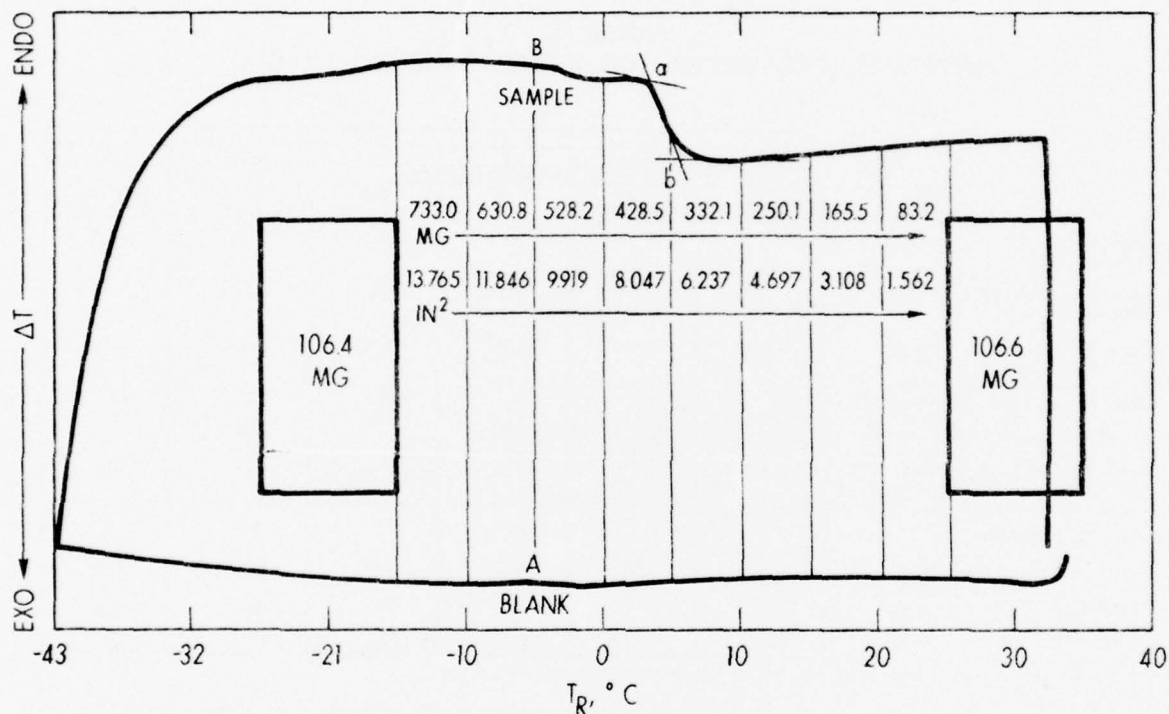
## HANDLING AND PREPARATION OF SAMPLES

Primary samples of fuels are stored in 55-gallon drums at the Annapolis site of DTNSRDC. Secondary samples are drawn in 1-gallon bottles or stainless steel safety cans as required for laboratory use. Tertiary samples of the seven fuels were decanted from the secondary sample containers into 125-ml brown glass bottles containing 6 grams each of anhydrous sodium sulfate, a drying agent. After vigorous agitation to secure adequate fuel/desiccant contact, each bottle was left undisturbed for at least 24 hours to permit the desiccant particles to settle.

OUTLINE OF PROCEDURE

Determining the enthalpy of a fuel between two specified temperatures requires two DSC runs. The first is a blank run in which the XY recorder trace of T versus  $\Delta T$  (curve A in figure 3) is obtained with empty sample and reference pans.

Curve A - Blank Run  
 Curve B - Sample Run



NOTE: CUMULATIVE CHART PAPER WEIGHTS FOR 5° C INTERVALS AND THE CORRESPONDING AREAS ARE SHOWN. (THE TWO 2-IN<sup>2</sup> CALIBRATION AREAS YIELDED THE PAPER CALIBRATION OF 53.25 MG/IN<sup>2</sup> NECESSARY TO DETERMINE THE AREAS. SEE SECTION INTERPRETING THE RESULTS.)

Figure 3  
 A Typical DSC Record  
 $\Delta T$  Versus  $T_R$  for a Blank and  
 a Sample Run

The second is a run for which the trace (curve B in figure 3) is obtained with the sample pan containing a weighed fuel sample while the reference pan remains empty. The respective traces will be referred to herein as the "A-trace" and the "B-trace." The enthalpy difference between any two temperatures is

proportional to the area enclosed by the two curves and the ordinates corresponding to the two temperatures. The proportionality constant is obtained in a calibration run from an A-trace followed by a B-trace for a sample of known enthalpy in the same temperature range.

The legend on the  $\Delta T$  axis in figure 3 requires some comment. On the actual recorder chart, as received, the  $\Delta T$  axis is labelled



However, since the positions of sample and reference in the apparatus are reversed (see the next section), the legend must be changed to



This has been done in figure 3. The terms "ENDO" and "EXO" do not here represent positions on the chart but rather simply directions. Thus, upward movement of the pen (toward ENDO) indicates that the sample temperature,  $T_S$ , is lagging behind the reference temperature,  $T_R$ , because of an endothermic process occurring in the sample. That is,  $\Delta T = T_R - T_S$  is increasing. As the process terminates,  $T_S$  approaches  $T_R$  and  $\Delta T$  approaches zero, so the pen moves down. The curve traced in the whole process is then an upward bulge termed, simply, an "endotherm."

#### OBTAINING THE BLANK OR A-TRACE

Two aluminum sample pans of 0.05-ml volume, with covers, were matched within 0.1 mg, marked for identification as sample and reference pans, and weighed with a precision of  $\pm 0.01$  mg on an electrobalance. The covered empty sample pan was placed in the DSC cell on the reference raised platform (the "R" position), while the covered empty reference pan was placed on the sample raised platform (the "S" position). In figure 1 the R and S positions are identified by the labels "reference pan" and "sample pan," respectively. (The reason for this reversal of the indicated placement is explained in the section on the B-trace.)

With the empty pans positioned, the DSC cell was cooled to  $-50^{\circ}\text{C}$  by a dry ice-acetone mixture in a cooling accessory mounted over the cell block (figure 4). This device, a stainless steel cylinder, fits snugly around the cell block while the coolant chamber in its upper end makes direct contact with the block.

The temperature of  $-50^{\circ}\text{C}$  was chosen as the starting temperature for a heating run so that there would be ample time for the apparatus to stabilize at the programmed heating rate before reaching the onset temperature of  $-15^{\circ}\text{C}$  at which energy measurements were to begin.

When the cell had cooled to  $-50^{\circ}\text{C}$ , the apparatus was allowed to equilibrate for several minutes at that temperature, i.e., the cooling produced by the cooling accessory was exactly balanced by a heat input to the cell. The control was then switched to heat at a programmed rate. A rate of  $10^{\circ}\text{C}/\text{min}$  was generally used because it is fast enough to give good sensitivity yet slow enough to give good resolution. At slower heating rates the area between the A- and B-traces is too small; at faster rates the temperature indication is too inaccurate.<sup>17</sup>

On the XY recorder the reference holder temperature,  $T_{RH}$ , was recorded on the X-axis and the differential temperature,  $\Delta T = T_R - T_S$ , on the Y-axis (figure 3). The chart range and scale for each axis can be preselected by appropriate control panel settings. For the  $T_R$  axis the selected range was generally  $-50^{\circ}$  to  $+50^{\circ}\text{C}$ . For the  $\Delta T$  axis the range was set to position the A-trace near the bottom of the chart, and the scale selected was the most sensitive setting.

When the temperature reached  $30^{\circ}\text{C}$ , the apparatus was allowed to equilibrate for several minutes before switching off. The pen was then lifted from the paper preparatory to obtaining the B-trace on the same record sheet.

#### OBTAINING THE SAMPLE OR B-TRACE

Following the blank run, both pans were retrieved from the DSC cell in order to charge the sample pan with 8 to 10  $\mu\text{g}$  of fuel and to seal both covers onto their respective pans. The run sample was transferred from its bottle to the sample pan by means of a microsyringe filled to the 10  $\mu\text{l}$  (0.01-ml) mark. The sample pan and reference pan covers were sealed onto their respective pans by means of an encapsulating press, and the sample pan with

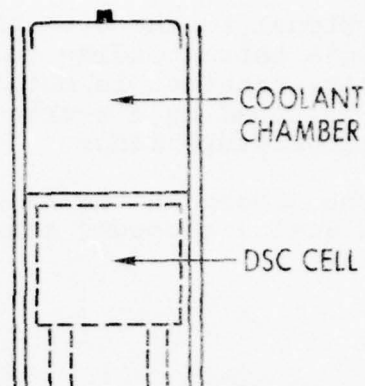


Figure 4  
Cooling Accessory

its contents was weighed to  $\pm 0.01$  mg. To obtain the B-trace the sealed pans were reinserted in the DSC cell with the sample pan again in the R position and the reference pan in the S position. The unit was cooled and the run executed exactly as for the blank run.

The reversal of placement of sample and reference is required if the apparatus recorder rather than an external recorder is to be used for area (energy) measurements. A time-based plot of  $\Delta T$  is needed if the area between the blank and sample curves is to be proportional to the associated sample energy. The temperature of the S position of the cell is monitored and fed back to the temperature controller. If the sample were placed in the S position, the transitions occurring in the sample would affect the rate of heat input to the cell, and, although the trace would give a faithful representation of the sample holder temperature, the recorded temperature would not be proportional to time. If, however, the empty reference pan is placed in the S position, the resulting trace follows the reference temperature which is a linear function of time. This is equivalent to a time-based record. Some accuracy in identification of the temperature of the transitions occurring in the sample is sacrificed to substantially improve the accuracy of energy measurement. The reversal of position means that upward motion of the recorder pen indicates endothermic transitions in the sample, and this is so shown in figure 3 in the legend for the  $\Delta T$  axis.

#### INTERPRETING THE RESULTS

To convert the record on the chart paper into usable energy data, areas bounded by the two curves and ordinates corresponding to pairs of selected temperatures were determined with fair accuracy and in reasonable time by the cut-and-weigh technique. (The method involves cutting out the area to be measured and weighing the paper; proportionality of the area cut out and the corresponding mass of the paper is assumed.) The accuracy of the procedure depends not only on the care used in cutting but also on the constancy of the paper density and thickness. For this purpose the use of a Xerox copy provides a measurable increase in accuracy and precision because it has a higher density and greater homogeneity than the chart paper. Also, it has another advantage: the original trace is preserved. A reported relative standard deviation of 1.7% for the cut-and-weigh technique contrasts with one of 4.1% for the planimeter,<sup>16</sup> although there is some disagreement about this.<sup>17</sup>

After determining the areas from the weights and paper calibration constant, the following formula was used to convert each area to the corresponding specific enthalpy difference,  $\Delta H_T$ , in j/g:

$$\Delta H_T = \frac{E \cdot A \cdot \Delta T_s \cdot T_s}{W \cdot a} \quad (4)$$

Heat capacity (specific heat) is proportional to the distance between the A-trace and the B-trace at the temperature in question. However, since readings on the chart X-axis are actual reference temperatures rather than sample temperatures, the heat capacity was obtained as an average over a 10° interval rather than at any single temperature. For example, the heat capacity at 20° C for a given sample was calculated as the specific enthalpy difference for the interval 15° to 25° C, divided by 10.

#### CALIBRATION

The constant, E, in equation (4) is unique to each DSC cell and must be determined experimentally through the use of substances of known enthalpy characteristics in the temperature range of interest. In the current work E was evaluated by using three liquid petroleum fuels whose enthalpy properties had been determined by drop calorimetry.<sup>4</sup> Values of E were calculated from the experimental data and a rearrangement of equation (4):

$$E = \frac{\Delta H_T \cdot W \cdot a}{A \cdot \Delta T_S \cdot T_S} \quad (4a)$$

In order to verify the calibration independently of the fuel studies, values of E were also found in DSC runs involving the fusion of indium and gallium and the heating of aluminum from 25° to 250° C. For the fusion runs no A-trace was required; the area above the base line under the B-trace was determined and the value inserted in equation (4a) along with the known value,  $\Delta H$ , of the heat of fusion of indium or gallium. In the heating runs on aluminum, E was calculated from

$$E = \frac{c \cdot W \cdot a}{\Delta T_{A-B}} \quad (4b)$$

in which c (the specific heat) is the known value for aluminum at any given temperature, and  $\Delta T_{A-B}$  is the absolute difference in temperature between the A- and B-traces at the same temperature.

#### RESULTS AND DISCUSSION

##### CALIBRATION

Values of the cell constant E obtained by the use of NBS enthalpy data on fuels A, B, and E are shown in table 2. The range of temperature was -15° to +25° C in both the NBS study and the DSC runs. The mean value of E was found to be 0.534

J/° C min, with a standard deviation of  $\pm 0.005$  J/° C min. Values of E from the fusion runs on indium (melting point 155° C) and gallium (melting point 30° C) plus three values from the specific heat determinations on aluminum (at 50°, 127°, and 227° C) vary from 0.669 (at 227°) to 0.559 (at 30°). When extrapolated to 5° C these values yield  $E = 0.54 \pm 0.01$  J/° C min. Within the experimental error this is the same as the fuel calibration value reported above for the temperature range -15° to +25° C.

TABLE 2  
DETERMINATION OF CALIBRATION CONSTANT E

From Enthalpy Data on Fuels A, B, and E						
Fuel	$\Delta H_{-15}^{(1)}$ J/g	Run	E J/° C min			
A	82.63	1	0.533			
		2	0.536			
B	77.92	1	0.531			
		2	0.526			
E	76.27	1	0.538			
		2	0.539			
		Mean	0.534			
		Standard Deviation	0.005			
From Known Heats of Fusion and Specific Heats of Metals						
Temperature ° C	Metal	Type of Run	No. of Runs	$\Delta H_{\text{fusion}}$ J/g	Specific Heat Capacity J/g ° C	E J/° C min
155	In	$\Delta H_{\text{fusion}}$	5	28.42	-	0.642
30	Ga	$\Delta H_{\text{fusion}}$	2	79.93	-	0.559
227	Al	Specific heat	1	-	0.9960	0.669
127	Al	Specific heat		-	0.9492	0.618
50	Al	Specific heat		-	0.9140	0.575
				Extrapolation to 5° C:		0.54 $\pm$ 0.01

(1) The values are the specific enthalpy differences  
 $\Delta H_{-15} = H(25^\circ \text{ C}) - H(-15^\circ \text{ C})$  from the NBS determinations.<sup>4</sup>

PRECISION OF ENTHALPY MEASUREMENT

The specific enthalpy difference defined by the equation

$$\Delta H = \bar{H}(T_2) - \bar{H}(T_1) \quad (5)$$

represents the heat required to raise the temperature of 1 gram of fuel from temperature  $T_1$  to temperature  $T_2$ . Two or three individual DSC runs on each of the seven fuels yielded the values of  $\Delta H$  given in table 3 for the temperature intervals indicated, i.e.,  $15^\circ$  to  $20^\circ$  C and  $-15^\circ$  to  $25^\circ$  C.

TABLE 3  
PRECISION OF DSC SPECIFIC ENTHALPY RUNS  
( $\Delta H = \bar{H}(T_2) - \bar{H}(T_1)$ )

Fuel	$T_2 = 20^\circ$ C, $T_1 = 15^\circ$ C	$T_2 = 25^\circ$ C, $T_1 = -15^\circ$ C
A	8.99, 9.30, 9.49	83.2, 82.8, 82.3
B	9.29, 9.41	79.1, 78.3
C	9.55, 8.97, 8.83	81.6, 77.8, 77.4
D	8.55, 9.62, 8.89	66.6, 74.9, 70.0
E	9.03, 8.89	75.6, 75.5
F	10.44, 9.73, 9.05	79.7, 77.6, 71.0
G	10.46, 9.57	83.8, 76.6
Mean	9.34	77.4
Standard deviation	0.38	2.6
Standard deviation, % of mean	4.1	3.4

For these intervals the standard deviations calculated by using all 18 data points were 0.38 and 2.6 J/g, i.e., 4.1% and 3.4% of the respective mean  $\Delta H$  values. The percentage results indicate only a small increase in the precision for the larger temperature interval. The calculated standard deviations mean that the 80% confidence values of  $\Delta H$  are  $9.34 \pm 0.51$  J/g for the

15° to 20° C interval and  $77.4 \pm 3.5$  J/g for the -15° to 25° C interval. The latter value may be translated into customary U.S. units as a heating requirement of 235 Btu/gal with an uncertainty of 11 Btu/gal (80% confidence level) for heating a fuel of 35° API from 5° F (-15° C) to 77° F (25° C).<sup>15</sup>

#### SPECIFIC ENTHALPY

The specific enthalpy differences, referred to 25° C, were determined at 20°, 15°, 10°, 5°, 0°, -5°, -10°, and -15° C for each of the seven fuels. The mean results for all fuels are summarized in table 4. The three fuels used for calibration (A, B, and E) are grouped at the left and the enthalpy differences compared with the corresponding values from the NBS study.<sup>4</sup> The mean DSC value of  $\Delta H_{-15}$  for these three fuels equals the equivalent NBS value since the calibration was based on the mean performance of the three fuels over the entire 40° range.

TABLE 4  
MEAN SPECIFIC ENTHALPY,  $\Delta H_T$ <sup>(1)</sup> (J/g)

T° C	Fuel A		Fuel B		Fuel E		Fuel C	Fuel D	Fuel F	Fuel G
	DSC	NBS	DSC	NBS	DSC	NBS	DSC	DSC	DSC	DSC
25	0.	0.	0.	0.	0.	0.	0.	0.	0.	0.
20	9.2	9.77	9.5	9.90	8.9	9.71	9.3	9.0	9.4	10.0
15	18.4	19.47	18.8	19.59	17.9	19.19	18.4	18.1	19.1	20.0
10	27.8	28.86	28.4	28.91	27.0	28.34	27.8	27.0	28.8	30.0
5	37.5	37.83	38.2	38.26	36.4	37.48	36.6	35.6	38.6	40.0
0	48.5	48.01	48.5	47.81	46.0	46.92	45.8	44.5	48.1	50.2
-5	59.5	59.85	58.7	57.61	55.6	56.60	56.3	53.3	57.5	60.3
-10	71.1	71.28	68.8	67.61	65.6	66.39	67.3	61.9	66.7	70.3
-15	82.7	82.63	78.8	77.92	75.6	76.27	79.0	70.5	76.1	80.3
Standard deviation <sup>(2)</sup>	1.0%		0.8%		0.4%		4.0%	5.4%	5.5%	7.6%

(1)  $\Delta H_T = \bar{H}(25^\circ \text{C}) - \bar{H}(T^\circ \text{C})$ .

(2) Mean standard deviation as percent of enthalpy.

The standard deviations for fuels A, B, and E average under 1% of the measured value, while the corresponding deviations for fuels C, D, F, and G average about 5.6%. Since fuels A, B, and E were all run before C, D, F, and G, it appears that an increased noise level, observed when the latter fuels were run, was responsible for the loss of precision.

Enthalpy differences for each 5° C interval are presented in table 5 for fuels A, B, and E and compared with corresponding values from the NBS study.<sup>4</sup>

TABLE 5  
 ENTHALPY CHANGES OVER 5° C INTERVALS, DSC VERSUS NBS<sup>4</sup>  
 $\Delta H_T = \bar{H}(T^\circ) - \bar{H}(T^\circ - 5)$  (J/g)

T, ° C	Fuel A			Fuel B			Fuel E			
	DSC	NBS	Difference	DSC	NBS	Difference	DSC	NBS	Difference	
25	9.2	9.8	-0.6	9.5	9.9	-0.4	8.9	9.7	-0.8	
20	9.2	9.7	-0.5	9.3	9.7	-0.4	9.0	9.5	-0.5	
15	9.4	9.4	0.0	9.6	9.3	+0.3	9.1	9.2	-0.1	
10	9.7	9.0	+0.7	9.8	9.4	+0.4	9.4	9.1	+0.3	
	10.0	10.2	-0.2	10.3	9.6	+0.7	9.6	9.4	+0.2	
0	11.0	11.8	-0.8	10.2	9.8	+0.4	9.6	9.7	-0.3	
-5	11.6	11.4	+0.2	10.1	10.0	+0.1	10.0	9.8	+0.2	
-10	11.6	11.4	+0.2	10.0	10.3	-0.3	10.0	9.9	+0.1	
Mean difference, J/g			+0.40				+0.38			
Mean difference as % of mean NBS enthalpy			3.3%				3.9%			

The mean 5° C NBS enthalpy difference is 9.9 J/g. The maximum difference between the DSC and NBS values is seen to be 0.8 J/g, or about 8% of the mean. The average difference for the 24 pairs of values in the table is 0.36 J/g with a standard deviation of 0.23 J/g, yielding a range of errors of 0.13 to 0.59 J/g. The standard error is thus between 1.3% and 6.0% of the value measured and averages 3.6%.

In figure 5 the DSC specific enthalpy temperature data are plotted for fuels C and D. Fuel C has a cloud point equal to about -3° C so wax separates when the fuel is cooled below this temperature. The latent heat of crystallization of the wax adds to the heat removed in cooling the fuel. Consequently, the slope of the curve for fuel C increases as the temperature decreases. In contrast, fuel D has a cloud point close to -21° C so wax does not separate in the 25° to -15° C range of the DSC runs.

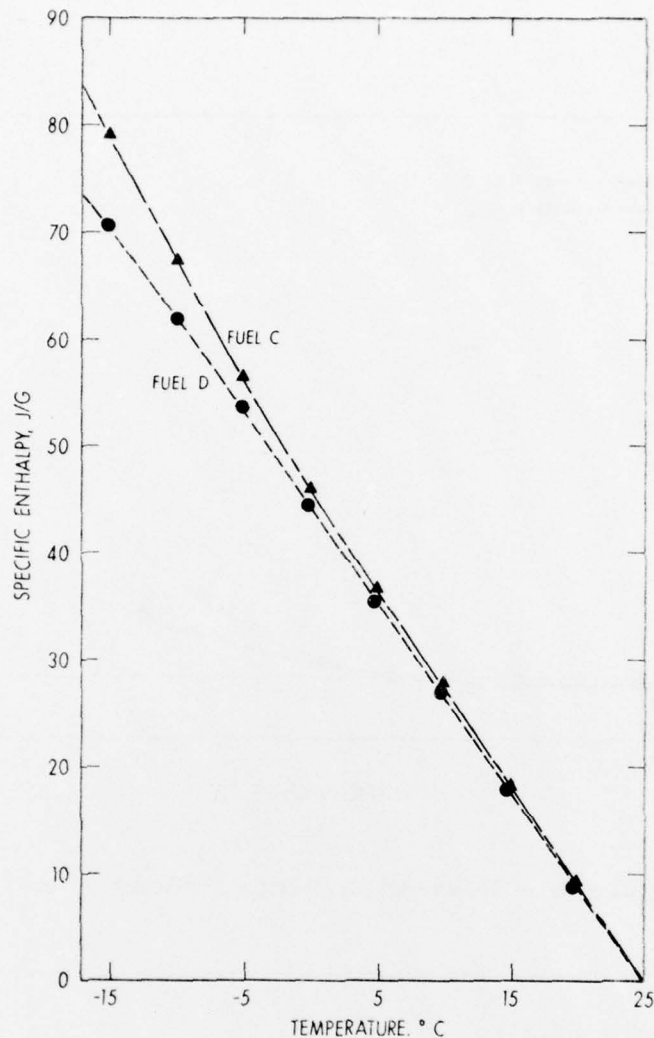


Figure 5 - Experimental DSC Specific Enthalpy of Fuels C and D versus Celsius Temperature

A more striking way to show the effect of wax separation are plots of the differences in the values of  $\bar{H}_{25} - \bar{H}_T$  from a straight line passed through the  $25^\circ\text{C}$ ,  $0\text{ J/g}$  point and the  $10^\circ\text{C}$ ,  $\Delta H_{10}$  point of a plot such as those in figure 5. Figures 6, 7, and 8 are such plots. Figures 6 and 7 for fuels A, B, C, and E (wax-containing fuels) show positive deviations from the straight line at all temperatures below their respective cloud points. At  $-15^\circ\text{C}$  these deviations are positive (8.6, 3.1, 4.9, and 3.6 J/g for fuels A, B, C, and E, respectively). The deviations of fuels D, F, and G, which show no wax separation, are smaller and mostly negative (figure 8). At  $-15^\circ\text{C}$  the deviations of fuels D and F are  $-1.5$  and  $-0.7\text{ J/g}$ , respectively. The small positive deviation of the curve for fuel G, a wax-free JP-5, is within the experimental error.

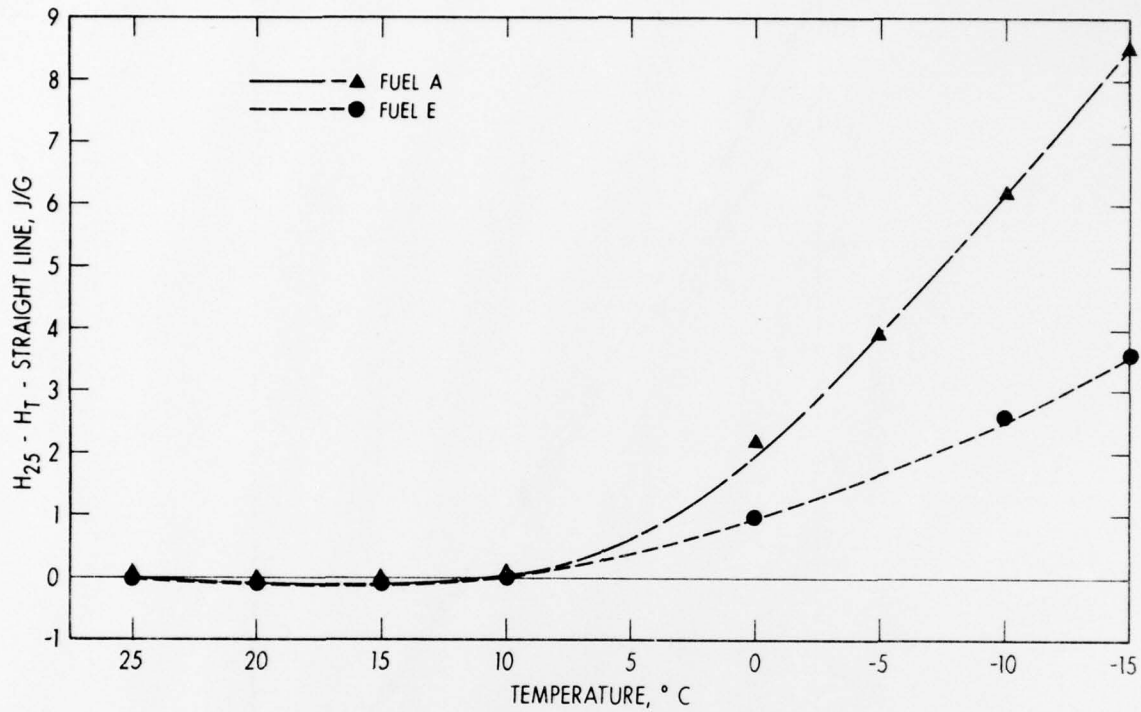


Figure 6 - Deviation Plots, Fuels A and E

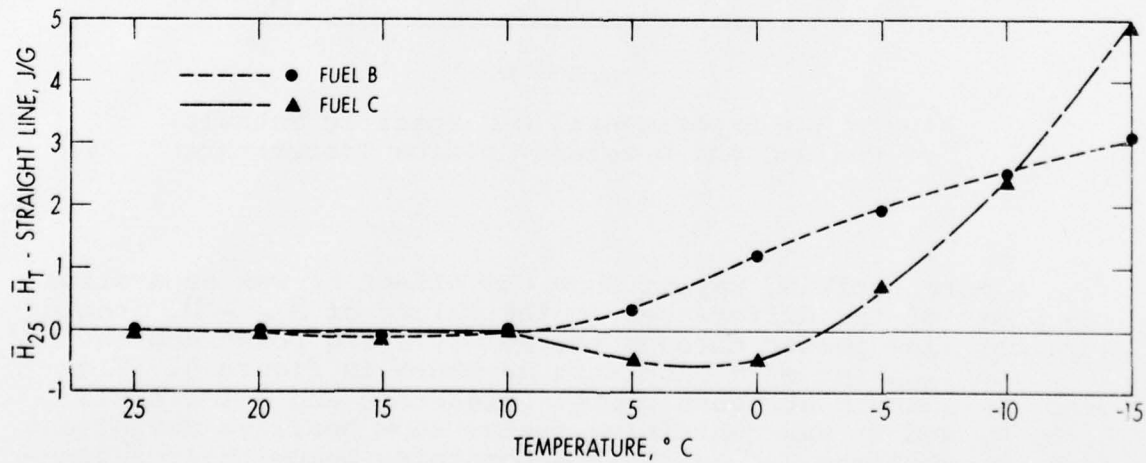


Figure 7 - Deviation Plots, Fuels B and C

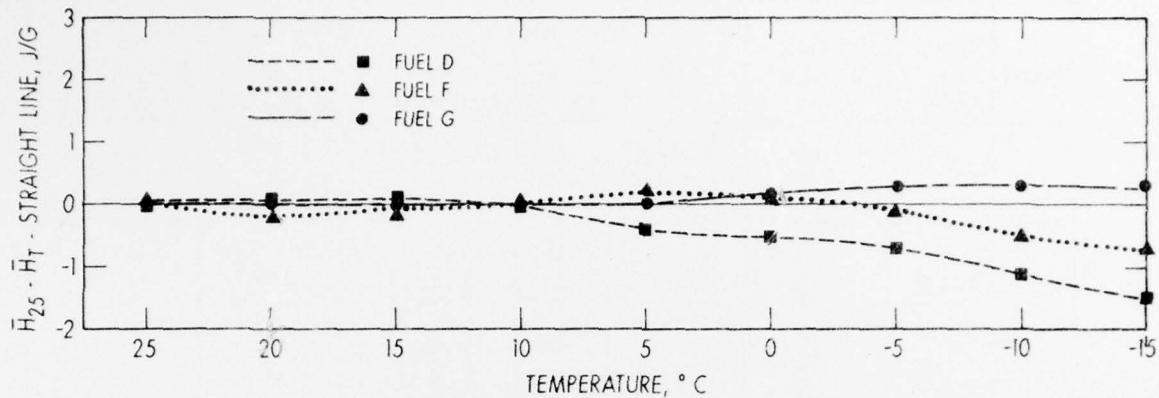


Figure 8  
Deviation Plots, Fuels D, F, and G

#### HEAT CAPACITY

"Heat capacity" (specific heat) is a term normally applied to a material undergoing heating or cooling in the absence of any transitions involving latent heat. It will be used here, however, without regard to the formation or re-resolution of wax in the fuels. Average heat capacities over 10° C intervals\* are shown in table 6 for three different values of T. The calculated heat capacities in table 6 were obtained by methods noted under Technical Background.<sup>14-16</sup> Thus, the calculated heat capacities headed ASTM D 2890 - 71 were based on the API gravity and the distillation data for the fuel. Those headed NBS pub. 97 were based on equation (3), and those headed Petroleum Engineer were interpolated from a tabulation.

\*Identified by the mid-temperature of the interval.

TABLE 6 - HEAT CAPACITIES OF FUELS  
 AT 15°, 5°, AND -10° C  
 (Heat Capacity, J/G ° C)

Fuel	°API at 60° F	Temper- ature ° C	Experimental		Calculated		
			NBS (ref 4)	This Work	ASTM D 2890-71	NBS Pub. 97	Petroleum Engineer
A	32.2	15	1.909	1.86	-(1)	1.866	1.856
		5	1.913	2.07	-(1)	1.830	1.812
		-10	2.277	2.33	-(1)	1.775	1.745
B	30.6	15	1.901	1.89	1.838	1.857	1.842
		5	1.887	2.01	1.812	1.821	1.799
		-10	2.030	2.01	1.758	1.767	1.731
C	35.8	15	-(2)	1.85	1.885	1.887	1.886
		5	-(2)	1.80	1.862	1.850	1.843
		-10	-(2)	2.27	1.808	1.795	1.776
D	36.7	15	-(2)	1.80	1.871	1.892	1.893
		5	-(2)	1.75	1.833	1.855	1.850
		-10	-(2)	1.72	1.783	1.799	1.784
E	28.9	15	1.863	1.81	1.816	1.848	1.828
		5	1.858	1.89	1.779	1.811	1.785
		-10	1.967	2.00	1.737	1.757	1.717
F	37.5	15	-(2)	1.94	1.892	1.896	1.900
		5	-(2)	1.93	1.862	1.859	1.857
		-10	-(2)	1.87	1.820	1.804	1.790
G	43.0	15	-(2)	2.00	1.932	1.927	1.933
		5	-(2)	2.02	1.890	1.889	1.890
		-10	-(2)	2.00	1.826	1.833	1.824

(1) Necessary distillation data not available.  
 (2) Not run.

ESTIMATION OF WAX CONTENT

The measured heat capacities of the waxy fuels A, B, C, and E (table 6) at -10° C are 10% to 30% greater than the calculated values. This behavior is associated with re-resolution of solid wax and provides a means of estimating the quantity of wax which separates down to -15° C. As an example, a fuel having the same gravity as fuel A should have a specific enthalpy at -15° C referred to 25° of 73.24 J/g, the value obtained when the equation  $dH = cdT$ , where  $c$  has the functional form given in equation (3), is integrated between the desired temperature limits. The calorimetric result for fuel A (table 4) is 82.63 j/g.<sup>4</sup> If the heat of mixing of the melted wax with the fuel is neglected, the 9.39 J/g difference must be attributed to the heat of fusion of the wax. If an average heat of fusion of wax of 168.6 J/g<sup>13</sup>

is assumed, this energy would melt 0.056 gram\* of wax per gram of fuel heated over the range in question. This represents 5.6% (wt) of the fuel. Fuel A may contain more wax that remains in solution below  $-15^{\circ}\text{C}$ .

At a temperature of  $5^{\circ}\text{C}$  all the wax should be in solution in fuels A, B, C, and E since the maximum cloud point of these fuels is about  $3^{\circ}\text{C}$ . In spite of this, at  $5^{\circ}\text{C}$  the calculated heat capacity for a fuel having the same gravity as the mean of these fuels is  $1.819\text{ J/g }^{\circ}\text{C}$ , whereas the mean experimental value is  $1.917\text{ J/g}$ , 5.4% larger. It may be that, even above the maximum wax re-solution temperature, the wax molecules retain some "memory" of their solid structure in the form of organized micelles in solution. Only at higher temperatures would such micelles be completely broken up. This hypothesis is supported by the fact that at  $15^{\circ}\text{C}$  the mean value of the heat capacities of fuels A, B, C, and E is  $1.85\text{ J/g }^{\circ}\text{C}$  (by DSC), within 0.5% of the predicted value of  $1.856\text{ J/g }^{\circ}\text{C}$ .

#### WAX RE-SOLUTION TEMPERATURES VERSUS WAX FORMATION TEMPERATURES

The fusion of a pure substance occurs at a definite temperature. Figure 9 shows the type of endotherm typically obtained for such a process.

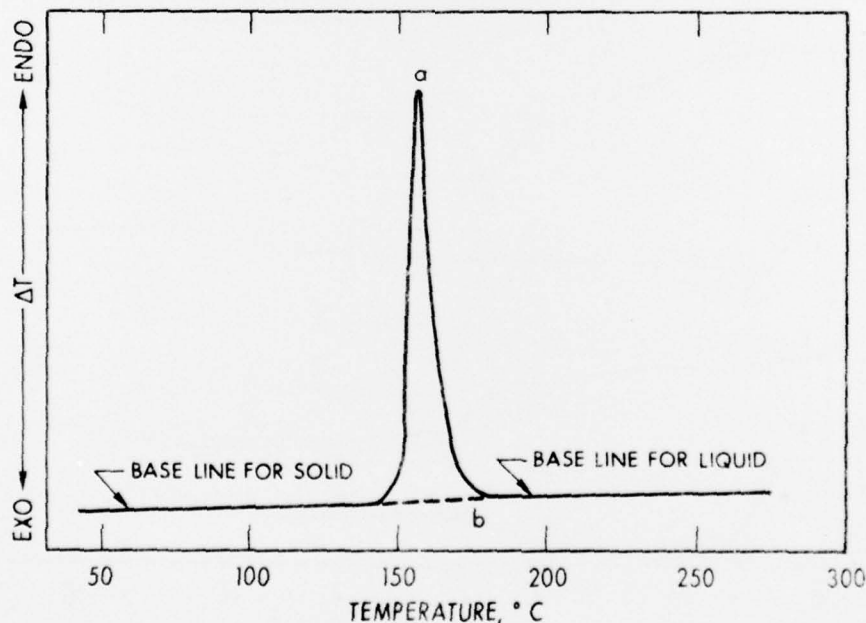
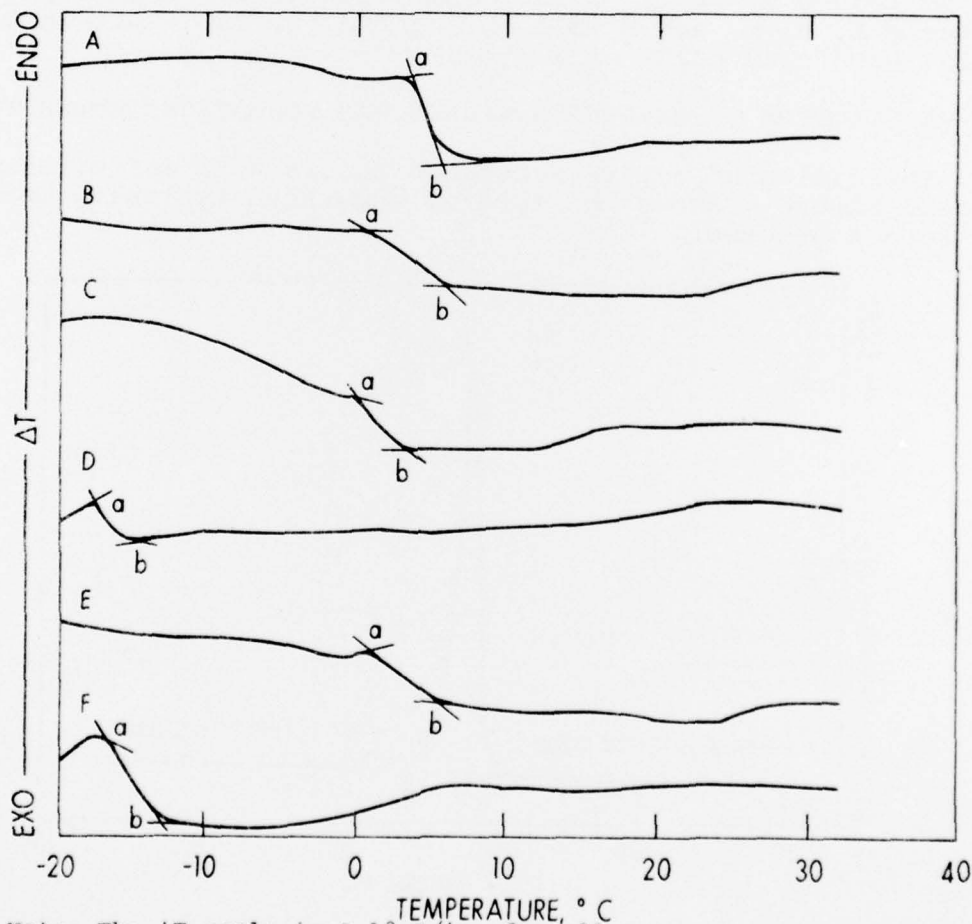


Figure 9  
DSC Fusion Endotherm for Metallic Indium

$$*(9.39/168.6) = 0.056.$$

The point of inflection which marks the peak of the endotherm (see "a" in the figure) if projected onto the base line of the endotherm yields the melting point of the substance. Similar projection of the point of inflection "b" in figure 9 marks the temperature at which the sample temperature has caught up with the programmed temperature of the calorimeter. The projections referred to here are not perpendicular to the temperature (or time) axis but slope down toward lower temperatures because the projections are determined by the general slope of both the ascending and descending portions of the endotherm.

In contrast to such fusion endotherms for pure substances, the endotherms for fuels A through F in figure 10 reflect the solution of a solid mixture (wax) in a liquid mixture, a process which occurs over a range of temperatures.



Note: The  $\Delta T$  scale is  $0.1^\circ \text{C/in.}$  for all curves.

Figure 10 - Recorder B-traces Showing Wax Re-resolution Endotherms and Inflections "a" and "b" for Fuels A through F

Correct projections of points of inflection in these cases are necessarily less accurate. In the curves of figure 10 the points "a" correspond to the beginning of the descending leg of the endotherm, while the points "b" mark the termination of the endotherm. In most cases the curve between "a" and "b" is steep enough that a vertical projection of "a" onto the temperature axis should mark with fair accuracy the completion of the re-solution process; the "a" projection so obtained may then be called the "re-solution temperature." The values of "a" for fuels A through F are recorded in table 7. Values of "b" are included to indicate the sharpness of the descending leg and the probable accuracy of the "a" values.

TABLE 7  
WAX RE-SOLUTION TEMPERATURES BY DSC  
VERSUS WAX FORMATION TEMPERATURES BY OTHER METHODS

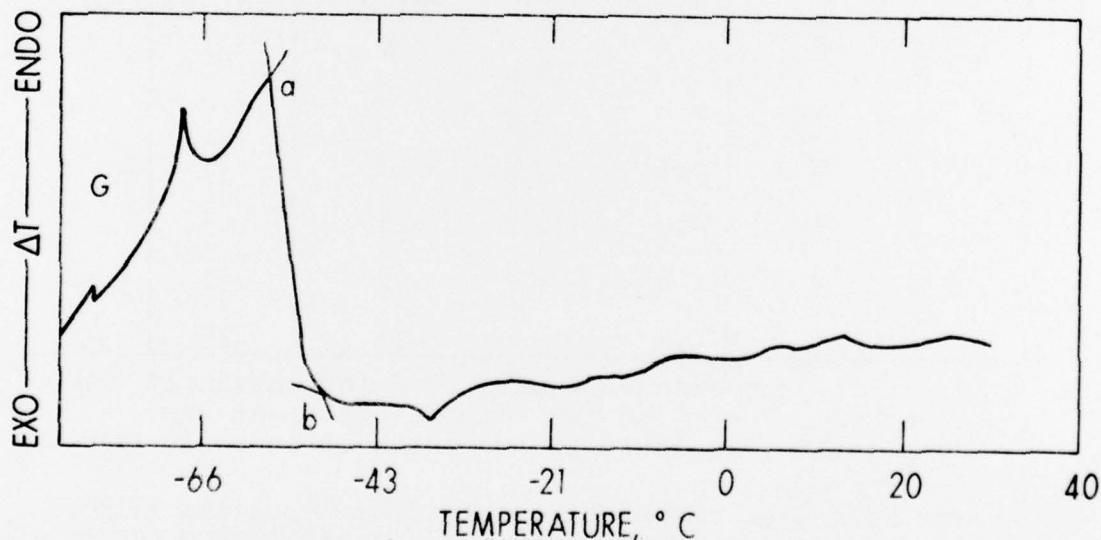
Fuel	Number of DSC Runs	Inflection Points, DSC Curve ° C <sup>(1)</sup>		Wax Formation Temperatures of Oven-Dried Fuels, ° C <sup>(2)</sup>		
		"a"	"b"	Cloud Point (ref 2)	WAP (ref 3)	WFT (ref 1)
A	7	3	5	2	1	1
B	6	2	6	3	0	0
C	4	-1	2	-3	-	-
D	3	-19	-16	-21	-	-
E	5	3	6	2	-1	-4
F	6	-18	-15	-18	-18	-16

(1) Vertical projections of points of inflection of the endothermic curve on the temperature axis; wax re-solution temperatures are taken as equal to the "a" values.

(2) Wax formation temperature data from White and Nagy<sup>1</sup> and from unpublished data obtained at DTNSRDC.

The use of three established experimental methods of estimating the temperature at which wax begins to form when a fuel is cooled (the cloud point,<sup>2</sup> the wax appearance point,<sup>3</sup> and the wax formation temperature,<sup>1</sup>) produced the other data included in table 7. In each case, the "a" value temperature determined by DSC agrees within 2° C with the cloud point temperature, the only other procedure from which data are available for all six fuels. In only 2 cases in 14 does an experimental wax formation temperature show a positive deviation with respect to the corresponding "a" value, and only 2 cases show a negative deviation greater than -2° C. Wax formation temperatures, which can be subject to supercooling error, should be lower than the re-resolution temperature indicated by "a" since this value is subject to thermal lag error which can make it too high. That the net difference (wax formation temperature minus "a") averages -1.6° C shows that these errors are not large. Thus, it is clear that DSC offers an alternate method of estimating wax formation temperatures.\*

The B-trace for fuel G (figure 11) is especially interesting because this JP-5 fuel contains little wax. The endotherm shown in figure 11 is a true fusion endotherm which was obtained by warming the sample from about -120° C (liquid nitrogen was used).



Note: The  $\Delta T$  scale is 0.1° C/in. for all curves.

Figure 11 - Recorder B-trace  
Showing Endotherm for Fuel G

\*Although cooling runs were not tried on the DSC, such runs should be no more difficult than heating runs and might afford an even closer check on the wax formation temperature.

The lower temperature peak resembles results from a crystal transformation (typical of paraffins) from orthorhombic to hexagonal which allows free rotation about the main chain axis; the higher temperature peak is the result of actual fusion.<sup>80</sup> The correct fusion temperature is not vertically under the fusion peak, but the broadness of the endotherm does not permit accurate projection to the temperature axis, so "a" is vertically projected as before. Point "a" lies vertically over  $-57^{\circ}\text{C}$  while point "b" lies vertically over  $-51^{\circ}\text{C}$ . Estimation of the melting point from these data is subject to more error than would apply if the endotherm were that of a pure substance. The value of the melting point of fuel G is listed in table 1 as  $-51^{\circ}\text{C}$ .

#### CONCLUSIONS

- Enthalpies and specific heats of fuels can be determined by DSC with a precision of about 4%.
- The differential scanning calorimeter technique has the advantage of requiring a very small sample and although the apparatus is costly, offers a considerable saving in time and manpower, compared to conventional calorimetric procedures for determining enthalpies and heat capacities of hydrocarbon fuels.
- The DSC can be used to estimate the wax formation temperature of any petroleum liquid fuel with a precision of  $\pm 2^{\circ}\text{C}$ . (This is an advantage over methods dependent on visual observation of wax crystal formation as such methods cannot be used with dark-colored fuels.)
- Wax contents can be estimated from heat capacity data.

#### RECOMMENDATIONS

- Use the DSC as a means of providing the thermal data needed as a basis for intelligent handling of fuels at low temperatures.
- Study the possibility of using the DSC record as a means of typing fuels and eliminating some currently required physical tests, such as those for pour point, cloud point, and WAP temperatures.
- Investigate the DSC cooling run as a potentially accurate means of determining the wax formation temperature of any fuel, with the aim of suggesting its use for that purpose to the ASTM Committee D2, Research and Development Division VII on Flow Properties.

● When accurate heat capacities are required in the vicinity of a fuel's cloud or wax appearance point, DSC (or standard calorimetry) should be used rather than calculations by ASTM D 2890, NBS pub. 97, or Petroleum Engineer since the error can be as high as 25%.

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