Flow Calorimeter and Measurement of the Enthalpy of *n*-Pentane

J. M. LENOIR and D. R. ROBINSON
University of Southern California, Los Angeles, Calif. 90007

H. G. HIPKIN
C. F. Braun & Co., Alhambra, Calif. 91802

The enthalpies of *n*-pentane, benzene, and water have been measured by a new flow calorimeter with results that differ from literature values by an average of 1.5 B.t.u. per pound. Results are presented for *n*-pentane from 100° to 700° F., with pressures up to 1400 p.s.i.a.

THE AMERICAN PETROLEUM INSTITUTE has initiated a program to measure the enthalpies of binary hydrocarbon mixtures experimentally at temperatures from ambient to incipient cracking, with pressures from atmospheric to 1400 p.s.i.a., for pentane and heavier hydrocarbons including paraffins, olefins, naphthenes, and aromatics. This paper describes the equipment used for the API project and presents data for *n*-pentane. Subsequent papers will present the results for hydrocarbon mixtures.

CALORIMETER

The calorimeter is a modification of the flow type described by Nelson and Holcomb (*11*) and Smith and coworkers (*5, 8, 9, 14*). Similar calorimeters, modified for low temperature operation, have been described by Wiener (*15*) and by Sahgal *et al.* (*13*). On passing through the calorimeter the hydrocarbon entering at a measured temperature is cooled to 75° F., giving up the enthalpy difference to saturated Freon-11. By measuring the hydrocarbon and Freon flow rates, the enthalpy difference is established by the relation

$$\Delta H = \frac{\rho_{F-11}\,\Delta H_{F-11}\,V_{F-11}}{\rho_{HC}\,V_{HC}} \qquad (1)$$

where V represents the volumetric flow rates of the Freon-11 and the hydrocarbon (HC), ρ the respective liquid densities, and ΔH_{F-11} the latent heat of Freon-11. The apparatus measures enthalpy differences without regard to phase condition. Figure 1 illustrates the basic shape and construction of the calorimeter.

Nelson and Holcomb (*11*) weighed both the hydrocarbon and Freon-11 throughputs. This new calorimeter measures both hydrocarbon and Freon flow rates volumetrically, a procedure that provides very convenient and rapid measurements. Another feature is the side inlet to introduce the hydrocarbon fluid, used to prevent dependency of the inlet temperature upon Freon liquid level. Table I shows some calorimeter inlet temperature profiles. Any of the three thermocouples closest to the Freon gives a satisfactory inlet temperature. The inlet temperature was computed as the arithmetic average of these three thermocouples to reduce random fluctuations. The details of the construction and operation of the calorimeter have been filed with the American Society for Information Science (ASIS).

The calorimeter does not require calibration, but the measurements do depend upon the densities of the fluids and the latent heat of Freon-11. At 75° F. and atmospheric pressure the latent heat of Freon-11 was selected as 78.32 B.t.u. per pound (*1, 3*). The density of Freon was 1.4783 grams per cc., with a density of 0.6224 gram per cc. for *n*-pentane. Table II estimates the sources of error caused by various measurement uncertainties, with over-all predicted uncertainty of 1.1 B.t.u. per pound.

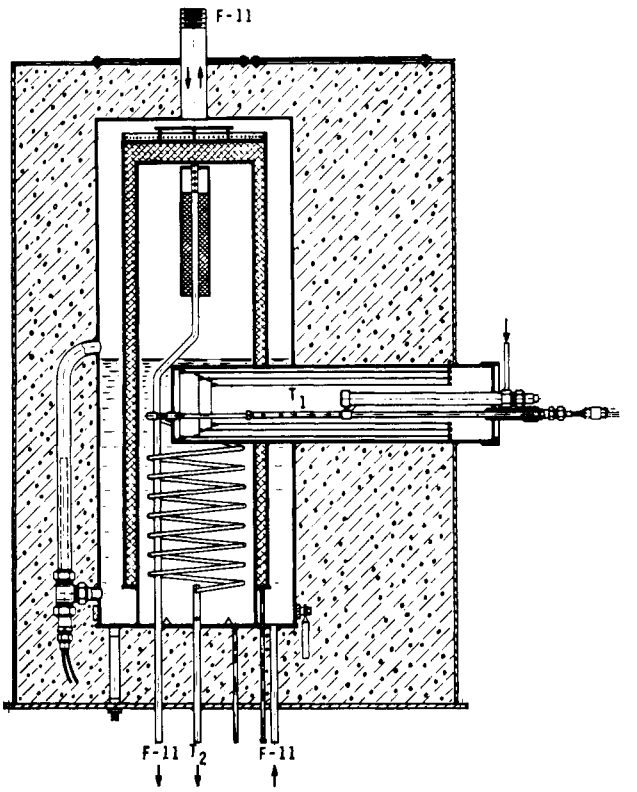

Figure 1. Detailed drawing of calorimeter

The measured enthalpy values are above a datum of liquid at 75° F. and the system pressure. The lower base value changes as the pressure rises. The relationship between enthalpy and pressure follows the relation

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \qquad (2)$$

Graphical integration shows a gradual increase in liquid

Table I. Measurements of Inlet Temperatures Showing Dependency on Position of Thermocouples as Hydrocarbon Enters Calorimeter[a]

Distance from Freon, Inches	Temp., ° F.				
6½	690.0	598.9	418.7	359.4	201.6
7½	690.6	599.4	418.7	359.4	201.7
8⅛	690.1	598.7	417.4	358.9	201.1
10⅜	695.7	603.9	421.1	361.6	202.7
12⅝	697.3	606.0	421.6	361.9	202.5

[a] Central position between inner and outer Freon containers lies 7 inches from Freon. This position should approximate correct inlet temperature position.

Table II. Estimated Accuracy of Measurement

Measured Quantity	Uncertainty, B.t.u./Pound
Inlet calorimeter temperature	0.4
Freon-11 volume in receiver	0.28
Hydrocarbon volume in receiver	0.15
Outlet calorimeter temperature	0.08
Hydrocarbon liquid density	0.06
Pressure measurement	0.05
Timing stopwatch for Freon-11	0.03
Timing stopwatch for hydrocarbon	0.03
Freon density	0.03
Calculation of pressure level correction	0.03
Estimated measurement uncertainty	1.1

Table III. Measured Values of Pentane Enthalpy in Gas Phase

Pressure, P.S.I.A.	Temp., ° F.	ΔH as Measured, B.t.u./Lb.[a]	ΔH_a, B.t.u./Lb.[a]	$\Delta H - \Delta H_a$, B.t.u./Lb.	$\frac{\Delta H_a}{\Delta H'}$
25	211.4	218.0	217.8	0.2	1.0009
	252.5	235.2	237.0	−1.8	0.9924
	275.8	249.8	249.1	0.7	1.0028
	299.4	263.6	262.9	0.7	1.0027
	300.1	262.2	262.5	−0.3	1.0011
	300.6	263.6	263.0	0.6	1.0023
	326.2	276.5	276.4	0.1	1.0003
	350.4	289.4	290.0	−0.6	0.9979
	375.3	304.7	304.5	0.2	1.0007
	400.5	321.6	319.1	1.5	1.0047
	405.1	321.8	323.0	−1.2	0.9963
	450.2	349.0	349.0	0.0	1.0000
	477.2	367.0	365.5	1.5	1.0041
	498.9	380.2	379.8	0.4	1.0011
	502.6	380.7	381.3	−0.6	0.9984
	525.0	396.3	395.6	0.7	1.0018
	549.2	411.6	411.4	0.2	1.0005
	574.0	426.9	428.0	−1.1	0.9974
	598.4	444.7	444.1	0.6	1.0014
	624.6	462.7	462.0	0.7	1.0015
	672.6	496.0	495.0	1.0	1.0020
	697.8	514.4	515.0	−0.6	0.9988
200	294.4	243.9	242.3	1.6	1.0066
	295.0	243.7	242.5	1.2	1.0050
	295.3	244.9	243.0	1.9	1.0078
	298.1	243.4	244.7	−1.7	0.9930
	298.6	243.6	245.0	−1.4	0.9943
	299.4	244.5	245.4	−0.9	0.9963
	303.8	248.2	248.7	−0.5	0.9980
	310.1	252.9	252.6	0.3	1.0012
	319.7	256.5	258.2	−1.7	0.9934
	333.9	267.6	266.3	1.3	1.0045
	335.2	268.2	267.4	0.8	1.0030
	340.5	270.0	270.5	−0.5	0.9981
	341.0	271.8	270.7	1.1	1.0040
	348.4	277.2	275.8	1.4	1.0051
	385.1	297.6	297.7	−0.1	0.9997
	385.7	298.3	297.9	0.4	1.0014
	403.8	308.7	309.0	−0.3	0.9987
	404.2	308.6	309.3	−0.7	0.9977
	499.5	368.0	370.1	−2.1	0.9941
	499.7	370.3	370.2	0.1	1.0003
	499.9	368.5	370.3	−1.9	0.9949
	499.9	369.1	370.3	−1.2	0.9965
	499.9	369.1	370.3	−1.2	0.9965
	499.9	370.5	370.3	0.2	1.0005
	500.6	372.6	371.3	1.7	1.0050
	500.9	371.5	371.5	0.0	1.0000
	523.6	386.0	385.8	0.2	1.0008
	589.9	433.4	429.1	4.3	1.0095
	593.9	430.0	431.4	−1.4	0.9968
	599.8	438.1	435.5	2.7	1.0060
400	366.6	259.8	262.6	−2.8	0.9894
	368.2	262.7	263.6	−1.1	0.9958
	369.2	263.5	264.5	−1.0	0.9962
	373.6	266.9	267.2	−0.3	0.9989
	378.5	272.7	271.4	1.3	1.0048
	378.9	273.1	271.5	1.6	1.0059
	383.5	277.0	274.3	2.7	1.0098
	388.5	279.8	279.2	0.6	1.0021
	388.5	281.0	279.2	1.8	1.0064
	397.3	288.3	286.1	2.2	1.0077
	401.4	290.3	288.3	2.0	1.0070
	417.7	303.5	301.3	2.2	1.0073
	417.9	301.5	301.6	−0.1	0.9997
	418.6	300.7	302.1	−1.4	0.9954
	437.2	316.1	315.6	0.5	1.0016
	437.2	318.3	315.6	2.7	1.0086
	440.4	318.0	317.1	0.9	1.0030
	441.7	319.5	317.7	1.8	1.0057
	457.7	333.4	330.2	3.2	1.0096
	476.5	343.9	343.3	0.6	1.0017
	476.9	345.1	343.5	1.6	1.0047
	496.4	355.0	356.1	−1.1	0.9966
	496.7	358.7	357.0	1.7	1.0048
	497.9	357.5	357.8	−0.3	0.9992
600	403.6	235.0	237.2	−2.2	0.9908
	403.7	235.5	237.2	−1.7	0.9929
	406.0	243.0	241.3	1.7	1.0071
	426.0	276.0	273.2	2.8	1.0102
	441.0	299.7	294.2	2.5	1.0084
	473.7	325.2	323.2	2.0	1.0062
	475.9	326.9	324.9	2.0	1.0061
	500.0	346.8	343.9	2.9	1.0084
	501.3	345.8	344.9	0.9	1.0026
1000	400.4	216.9	217.2	−0.3	0.9986
	405.9	220.3	219.6	0.7	1.0032
	450.0	263.2	263.1	0.1	1.0004
	506.9	318.2	318.2	0.0	1.0000
	506.9	318.7	318.2	0.5	1.0016
	695.2	480.2	480.0	0.2	1.0004
	695.4	479.7	480.0	−0.3	0.9994
1400	402.5	213.6	211.6	2.0	1.0093
	402.8	212.7	211.7	1.0	1.0046
	500.3	296.4	297.3	−0.9	0.9960
	500.6	294.3	297.6	−2.3	0.9924
	531.5	325.9	324.1	1.8	1.0046

[a] Base value liquid phase at 75° F. and pressure of measurement.

Table IV. Smoothed Values of Enthalpy for *n*-Pentane, Base Value Liquid Pentane at −200° F. and Low Pressure, B.t.u./Lb.

Temp., ° F.	Pressure, P.S.I.A.							
	0	200	400	500	600	800	1000	1400
700	646	637.8	631.3	629.4	625.4	620.1	611.4	599.4
680	630	623.9	618.4	614.4	610.4	604.9	597.4	583.5
660	616.5	609.8	603.4	599.4	595.4	589.2	581.2	567.8
640	602.9	595.9	588.9	584.4	580.3	572.8	564.4	551.5
620	589.4	582.1	573.9	569.8	565.5	556.7	547.4	534.9
600	575.6	568.4	559.7	555.3	550.6	540.4	530.8	518.1
580	562.4	554.4	545.5	540.4	535.6	524.4	513.9	500.0
560	549.4	540.5	531.4	525.9	520.6	508.4	497.2	481.6
540	536.2	526.6	517.3	511.4	505.4	492.4	479.4	463.4
520	523.4	513.4	503.2	497.4	490.4	475.9	461.9	445.5
500	510.9	500.4	489.0	482.4	475.4	459.4	443.4	428.7
480	497.9	487.4	475.4	467.4	459.4	442.5	424.4	412.5
460	485.4	474.2	461.5	452.4	443.4	420.0	407.0	395.9
440	473.2	461.4	447.4	437.2	425.4	395.0	395.4	378.9
420	461.4	448.4	433.4	421.2	398.7	371.5	367.4	361.3
400	449.5	436.1	419.3	401.2	365.2	353.0	348.9	344.4
390	443.9	430.3	412.3	381.3	353.2	344.0	341.0	334
380	437.9	424.3	404.8	346.3	343.2	335.0	332.4	328
360	426.3	412.2	325.9	324.4	322.4	318.9	315.9	313
340	414.9	400.3	305.6	304.6	303.9	302.4	301.4	298
320	404.0	388.1	289.4	289.2	289.0	288.3	287.4	283
300	393.4	376.1	273.5	273.3	273.0	272.7	271.5	268.7
280	383.0	260.5	258.5	258.2	258.0	257.3	256.6	254.4
260	372.5	245.4	244.7	244.4	244.0	243.4	242.6	240.9
240	362.5	231.6	231.2	230.9	230.6	230.1	229.5	228.3
220	352.6	217.6	217.3	217.1	217.0	216.6	216.3	215.6
200	343.6	204.4	204.2	204.1	204.0	203.9	203.7	203.4
75	289.2	129.8	130.3	130.5	130.7	131.2	131.6	132.5

phase enthalpy with increased pressure. Because 75° F. is far below the critical temperature, the amount of change in the liquid phase is moderate, amounting to 3.1 B.t.u. per pound between atmospheric pressure and 1400 p.s.i.a. for *n*-pentane.

MEASUREMENTS

Enthalpies of pentane, benzene, and water have been measured by this calorimeter. Table III shows the results for *n*-pentane in the gas phase, as well as pentane enthalpies in the vapor state predicted by API project 44 (*2*) in conjunction with the work of Kozicki and Sage (*7*) and Graue *et al.* (*6*). The last two columns in Table III show the difference between the measured enthalpy and API values, and the ratio of the measured to the API numbers, indicative of the percentage deviation of the measurement. The measured enthalpies deviate from the API values by an arithmetic average of 1.2 B.t.u. per pound, with a statistical deviation of 1.48 and a plus trend of 0.4. The reproducibility between sets of measurements taken at the same temperature and pressure was 0.9 B.t.u. per pound. Expressed in terms of accuracy, the measured enthalpies deviate from the API predictions by an arithmetic average of 0.41%, trending high by 0.14%.

Measurements with benzene showed values that deviated from the results of Connolly and Kandalic (*4*) and Organick and Studhalter (*12*) with an average deviation of 2.2 B.t.u. per pound with a 2.60 statistical deviation and a plus 0.26 trend. The average measurement accuracy was 0.66%. The measured enthalpies for distilled water were compared with the published values of Meyer *et al.* (*10*). The measurements show an average discrepancy of 0.98 B.t.u. per pound, a statistical deviation of 1.20, and a negative trend of 0.88. The results of these accuracy studies indicate that the enthalpy measurements have an uncertainty approximating 1.5 B.t.u. per pound, representing a measurement accuracy of 0.5%. The largest difference in all the comparisons was 4.5 B.t.u. per pound.

The measured values for *n*-pentane were first graphed dependent on temperature with pressure as parameter. By cross-plotting enthalpy *vs.* pressure at fixed temperatures, smoothed values of enthalpy for *n*-pentane were visually obtained. These values are presented in Table IV placed on a zero enthalpy basis of −200° F. and the saturated liquid phase.

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NOMENCLATURE

H = enthalpy, B.t.u. per pound
ΔH = measured enthalpy difference, B.t.u. per pound
ΔH_a = enthalpy difference as shown by API 44

$\Delta H_{F\text{-}11}$ = latent heat of vaporization of Freon-11 at 75° F.
P = pressure, p.s.i.a.
T = temperature, ° F.
T_1 = inlet temperature of hydrocarbon to calorimeter, ° F.
T_2 = outlet temperature of hydrocarbon from calorimeter, ° F.
$V_{F\text{-}11}$ = volume rate of flow of Freon-11, cc. per second
V_{HC} = volume rate of flow of hydrocarbon, cc. per second
$\rho_{F\text{-}11}$ = density of liquid Freon-11, grams per cc.
ρ_{HC} = density of hydrocarbon at atmospheric pressure, grams per cc.

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Enthalpies of Mixtures of *n*-Octane and *n*-Pentane

J. M. LENOIR and D. R. ROBINSON[1]
University of Southern California, Los Angeles, Calif. 90007

H. G. HIPKIN
C. F. Braun & Co., Alhambra, Calif. 91802

Enthalpy measurements have been made with a flow calorimeter for *n*-octane and mixtures of *n*-octane with *n*-pentane. The results are presented in tabular and graphical form for pressures up to 140 p.s.i.a. and temperatures from 75° to 600° F.

EXPERIMENTAL MEASUREMENTS of enthalpy difference have been made for *n*-octane and for mixtures containing 21.8, 39.2, 59.7, and 80.9 mole % pentane. The data extend from 150° to 600° F., with pressures from 15 to 1400 p.s.i.a. The apparatus is a flow calorimeter previously described (*3*) and shown to be capable of measuring enthalpy differences of 1.5 B.t.u. per pound. Both the *n*-octane and *n*-pentane were obtained from the Phillips Petroleum Co., as the pure grade, and used as received. The *n*-octane was specified as 99% pure. The *n*-pentane was examined and found to have a purity better than 99%, containing only a trace of isopentane (2-methylbutane).

A literature search found few thermal measurements for *n*-octane and none for the pentane-octane mixtures. McKay and Sage (*4*) measured latent heat of vaporization for *n*-octane from 100° to 340° F. Das and Kuloor (*2*) summarized the available thermal data for *n*-octane and tabulated enthalpy values for the saturated loci, the superheated vapor, and subcooled liquid, based upon computations using the Benedict-Webb-Rubin equation. The enthalpy values presented here are essentially an original measurement study.

The flow calorimeter measures the difference between the enthalpy of the fluid at some temperature higher than 100° F. at the pressure of measurement, and the fluid at 75° F. in the liquid state at the same pressure. The enthalpy differences evaluated directly from the calorimeter measurements without correction have been tabulated and deposited with ASIS.

The use of the uncorrected data requires adjustment to a common base level. The enthalpy value of the liquid phase at 75° F. is different at each composition and

[1] Present address, Chevron Research Corp., Richmond, Calif. 94804