

Nomenclature

A_j = Debye-Hückel constant [see Bromley et al. (1), Table III for values]

B = constant (see Table II and Equations 3 to 5)

C_p = heat capacity of solution at constant pressure, cal/g°C

C_{sat} = heat capacity of solution at saturation, cal/g°C

$(\phi C_{p(s)})$ = apparent heat capacity of salts, cal/g salts°C

$\bar{C}_{p(s)}$ = partial heat capacity of salts in solution, cal/g salts°C

$\bar{C}_{p(s)}^\circ$ = partial heat capacity of salts at infinite dilution, cal/g salts°C

$C_{p(w)}^*$ = heat capacity of pure water at constant pressure, cal/g°C

$\bar{C}_{p(w)}$ = partial heat capacity of water in solution, cal/g water°C

I = ionic strength = $\sum m_i Z_i^2 / 2$

M_i = molecular weight of ion i

M_s = molecular weight of salt

m = molality = gram moles salt/1000 grams water

P = pressure

S = salinity in weight per cent salt

T = temperature, K

u = specific volume of saturated liquid, cm³/g

x = mass fraction of liquid in calorimeter

Z_i = charge on ion i

ν = number of ions per molecule of salt

σ = standard deviation

$$\sigma(I^{1/2})/3 = (1/I^{3/2})[1 + I^{1/2} - 1/(1 + I^{1/2}) - 2 \ln(1 + I^{1/2})]$$

Literature Cited

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Measured Enthalpies of Eight Hydrocarbon Fractions

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Measured enthalpy values are reported for five naphthas, a kerosine, a fuel oil, and a gas oil in the temperature range 155 to 640°F for pressures up to 1400 psia.

Because of the relatively unsatisfactory ability to predict accurately enthalpy values for hydrocarbon fractions, the American Petroleum Institute authorized the measurement of a series of hydrocarbon fractions with the intent of providing data for checking the accuracy of existing prediction procedures and for use in the potential development of new improved enthalpy prediction methods. The materials measured comprised a very close-boiling naphtha from the north slope of Alaska, a jet fuel naphtha, a very aromatic naphtha from a cracking furnace, two straight-run paraffinic Pennsylvania naphthas, a California kerosine, a grade number 2 fuel oil, and a gas oil.

Previously, the results for a California naphtha were reported (3). The properties of the materials measured were determined in detail, and are listed in Tables I and II. These properties include density, Watson factor, molecular weight, critical temperature and pressure, heat of combustion, refractive dispersion, ASTM and TBP distillations, and compositions.

Experimental

The mole percent of the various kinds of hydrocarbons in each material was established by use of mass spectrograph analysis. The analyses, the molecular weight, and the refractive dispersion were determined at the Union Oil Co. laboratories. The critical properties of the Alaska naphtha were measured by W. B. Kay at the Ohio State

University. The critical constants for the jet naphtha and the low-boiling naphtha were established from the enthalpy measurements. The other critical properties tabulated represent estimates obtained by using the procedures in the API data book (1).

The enthalpy measurements were made with a flow calorimeter, one in operation since 1967. This calorimeter measures the difference in enthalpy between the fluid entering the calorimeter at a relatively high temperature and a departing temperature of 75°F, at the pressure of measurement. The calorimeter operates isobarically. Repeatedly this apparatus has been shown to have an accuracy level of 1.5 Btu/lb, determined by measurements of the enthalpy of pure *n*-pentane, and liquid water, with comparison to literature values presented for these two pure components (2, 5). The calorimeter has been previously described (4).

Results and Discussion

This study represents 1013 measurements. The actual measured data have been tabulated relative to the liquid state at 75°F and the pressure of measurement, and have been deposited with the ACS Microfilm Depository Service. The measured data were converted to a base level of 75°F and the saturated liquid condition with the use of the thermodynamic equation of state as previously discussed (4). Since this correction for the change of enthalpy with pressure is computed for the liquid phase at a temperature greatly lower than the critical temperature, the conversion can be computed with a precision in excess of the accuracy of the calorimeter measurements. Following this correction for pressure level, smoothed values were obtained by cross-plotting on large scale graph paper. These smoothed results are presented in Tables III-X.

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Table I. Properties of Hydrocarbon Fractions

	Alaska naphtha	Jet naphtha	Aromatic naphtha	Low-boiling naphtha	High-boiling naphtha	Kerosine	Fuel oil	Gas oil
Liquid density, g/cm ³ , 75°F	0.7703	0.7981	0.8449	0.7332	0.7559	0.8019	0.8553	0.8415
Enthalpy to add for -200°F basis	109	107	97	116	115	109	103	104
API gravity	50.5	44.4	34.5	59.9	54.2	43.5	33.0	35.3
Watson factor	11.63	11.48	10.5	12.1	12.1	11.8	11.68	11.8
Molecular weight	131	144	126	120	142.4	162.3	227.5	214
Critical tempera- ture, °F	626.5	665	626	605	646	739	879	868
Critical pressure, psia	414.7	440	709	463	371	361	290	280
Gross heat of combustion, Btu/lb	19500	19832	18504	20263	20178	19944	17561	19745
Refractive disper- sion	52.4		37.5	60.1		47.9	49.2	
ASTM distillation, D-86								
IBP	254	286	140	106	180	330	434	477
5	262	299	196	152	246	342	463	497
10	272	304	206	172	271	350	490	503
20	276	308	219	204	296	366	510	512
30	278	313	230	226	310	380	526	518
40	280	317	240	247	316	390	537	527
50	282	321	252	260	322	404	547	535
60	284	325	263	290	329	417	558	543
70	288	329	275	311	335	433	569	553
80	291	334	291	339	341	450	583	567
90	295	341	311	364	350	469	604	585
95	298	346	329	381	357	482	622	602
EP	308	361	340	395	366	500	634	621
Composition								
Ultimate								
Wt % C	86.3	86.05	90.1	85.1	85.4	85.8	86.9	86.5
Wt % H	13.7	13.95	9.8	14.9	14.6	14.2	13.1	13.4
Ppm S	99	132	760	376	357	58	172	261
Ppm N	0.3							3
By Component type, %								
Total paraf- fins	39.7	18.6	0.0	61.9	59.3	30.9	29.8	38.8
<i>n</i> -Paraf- fins	24.2			30.9	29.8			
<i>i</i> -Paraffins	15.5			31.0	29.5			
Total naph- thenes	39.6	69.8	0.0	30.6	30.8	64.3	45.6	41.5
Mono- naph- thenes	34.1	50.7		27.9	27.0	41.1	23.1	22.7
Dicyclo- naph- thenes	5.5	19.1		2.7	3.8	23.2	22.5	18.8
Total aro- matics	20.5	10.6	83.1	7.6	9.9	4.8	22.4	17.2
Benzene	0.2		12.8	0.2				
Toluene	1.6		38.0	0.8				
C ₈	14.7		17.7	2.1	1.8	} 2.3	} 2.6	} 2.6
C ₉	3.8		8.1	2.3	4.7			
C ₁₀	0.1		0.7	1.1	2.7			
C ₁₁				0.6	0.5			
C ₁₂				0.2				
Indane-	0.1	1.2	5.8	0.3	0.2	2.5	6.6	2.5
tetralins								
Dinaph- thene- ben- zenes							7.2	2.5

Table I. Continued

	Alaska naphtha	Jet naphtha	Aromatic naphtha	Low-boiling naphtha	High-boiling naphtha	Kerosine	Fuel oil	Gas oil
Diaromatics							5.2	4.9
Phenanthrenes							0.8	0.7
Total olefins			16.9					
Monoolefins			4.1					
Cycloolefins			8.8					
Cyclo-diolefins			4.0					
Sulfur compounds		1.0					1.3	2.4
Thiophenes		0.1					0.7	1.5
Alkyl sulfides		0.9					0.5	0.9
Aromatic sulfides							0.1	

Table II. True Boiling Point and Density at Percent Distilled

Material		IBP	5%	10%	20%	30%	50%	70%	90%	95%
Alaska naphtha	$t^{\circ}\text{F}$	198	246	258	267	274	284	297	310	...
Jet naphtha, g/cm ³	$t^{\circ}\text{F}$	242	259	273	288	307	329	341	357	367
	ρ		0.762	0.799	0.807	0.791	0.803	0.810	0.811	0.820
Aromatic naphtha, g/cm ³	$t^{\circ}\text{F}$	164	170	173	217	226	251	279	325	335
	ρ		0.778	0.841	0.845	0.858	0.841	0.855	0.856	0.857
Low-boiling naphtha, g/cm ³	$t^{\circ}\text{F}$	50	125	168	205	226	279	326	382	402
	ρ		0.654	0.689	0.719	0.739	0.765	0.775	0.775	0.785
High-boiling naphtha, g/cm ³	$t^{\circ}\text{F}$	100	223	262	296	313	340	356	381	390
	ρ		0.738	0.747	0.753	0.755	0.773	0.762	0.776	0.773
Kerosine, g/cm ³	$t^{\circ}\text{F}$	258	295	312	337	358	402	442	486	499
	ρ		0.772	0.778	0.787	0.795	0.817	0.824	0.829	0.830
Fuel oil	$t^{\circ}\text{F}$	360	430	465	497	520	554	585
	ρ		0.835	0.849	0.860	0.861	0.861	0.854
Gas oil	$t^{\circ}\text{F}$	420	451	470	495	514	544	580	604	621
	ρ		0.828	0.835	0.843	0.847	0.851	0.855	0.856	...

Table III. Enthalpy of an Alaska Naphtha

Units: Btu/lb
Base level: 75°F, saturated liquid

Temp. °F	Psia										
	0	30	60	100	200	300	400	415	600	800	1400
75		0.0	0.2	0.3	0.6	0.9	1.1	1.1	1.6	2.2	3.7
280		108.5									111.0
300		120.9									123.0
320		133.2									135.1
330.6		140.0 ^a									
340		236.5	146.0								147.4
342.3		264.6 ^a									
360		273.7	158.8								159.8
380		284.2	171.6								172.2
384.7			174.5 ^a								
395.6			289.8 ^a								
400		295.1	292.0	184.6							185.0
420	309.5	306.4	303.2	197.6							197.7
440	320.2	317.5	314.6	211.0							210.9
442				212.3 ^a							
451.6				316.2 ^a							
460	331.4	328.7	325.2	321.0	224.9						224.2
480	342.9	340.0	336.9	332.9	238.9						238.0

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Table III. Continued

Units: Btu/lb
Base level: 75°F, saturated liquid

Temp. °F	Psia										
	0	30	60	100	200	300	400	415	600	800	1400
500	354.1	351.2	348.7	344.9	253.6					252.6	251.8
520	365.9	363.1	360.6	357.0	268.2					266.7	265.9
521.6					269.3 ^a						
530.3					352.2 ^a						
540	378.0	375.3	372.9	369.1	358.6	283.3				281.3	280.0
560	390.9	388.1	385.6	382.0	372.0	299.1				296.0	294.5
576						312.0 ^a					
580	403.7	401.0	398.3	394.9	385.4	343.3	315.1		312.3	311.0	309.0
583.8						375.0 ^a					
600	416.6	413.9	411.1	407.7	399.0	385.4	331.4		328.5	326.2	323.5
610	423.1			414.0	405.9	391.9	340.4		336.8	333.9	330.9
615.1							345.7 ^a				
620	429.9			420.2	412.8	398.2	384.0 ^a	352.9	345.0	341.6	338.1
624							388.0	361.0	348.2	344.8	341.8
626							389.2	369.0 ^b	350.0	346.1	342.5

^a On saturated locus. ^b Critical point.
Cricondentherm temperature 626.3°F, $h = 371.9$.

Table IV. Enthalpy of a Jet Fuel Naphtha

Units: Btu/lb
Base level: 75°F, saturated liquid

Temp. °F	Psia									
	0	20	30	60	100	150	200	300	400	1400
75		0.0	0.1	0.2	0.3	0.4	0.5	0.8	1.1	3.7
160		40.1								43.9
180		50.6								54.1
200		61.1								64.4
220		72.1								75.2
240		83.3								86.6
260		94.8								98.0
280		106.1								109.2
300		117.6								120.6
320		129.8								132.5
332.2		137.2 ^a								
340		160.0	142.0							144.4
360		265.0	154.1							156.2
361.6		269.4 ^a								
362			155.3 ^a							
380		279.0	247.9	166.5						168.5
388.7			281.5 ^a							
400	292.0	299.5	287.5	179.2						180.6
420	302.1	300.2	298.5	192.6						193.0
426				196.8 ^a						
440	312.9	311.0	309.5	274.5	206.0					205.6
447.6				309.2 ^a						
460	324.0		321.0	317.0	219.5					218.6
480	335.8		332.5	329.4	233.1					231.8
480.6					233.7 ^a					
500	347.7		344.2	341.1	332.6	246.7				245.4
501					337.0 ^a					
520	360.0		357.0	354.0	350.3	260.4				259.9
527.8						265.9 ^a				
540	372.7		369.8	366.8	363.1	306.0	274.3		273.6	273.0
550						362.8 ^a				
560	385.2		382.3	379.5	375.9	369.7	288.9		287.9	286.9
567.6							294.8 ^a			
570	391.6		388.8	386.0	382.2	376.9	304.9	296.7	295.0	294.0
580	397.9		395.1	392.3	388.9	384.0	367.0	304.4	302.3	301.0
584.6							382.3 ^a			
590	404.1		401.5	398.8	395.4	391.0	386.2	312.5	310.0	308.0
600	410.3		407.7	405.0	401.9	398.0	393.2	321.0	318.1	315.2

^a On saturated locus.

Table V. Enthalpy of a Highly Aromatic Naphtha

Units: Btu/lb
Base level: 75°F, saturated liquid

Temp, °F	Psia									
	0	30	100	200	300	375	500	600	1000	1400
75		0.0	0.2	0.5	0.7	0.9	1.2	1.5	2.5	3.4
270		92.8 ^a								93.8
300		180.3	109.0							109.8
320		242.9	120.0							120.4
324		256.5 ^a								
340		263.2	131.1							131.2
360		272.4	142.5							142.1
373.7			149.7 ^a							
380		281.7	169.1	154.0						153.1
400	293.7	290.9	229.3	165.3						164.3
420	303.0	300.2	291.0	177.0						175.8
421			294.4 ^a							
440	312.4	309.8	303.7	189.0					188.0	187.4
450				195.0 ^a						
460	321.9	319.3	313.5	221.2	201.2				200.4	199.8
480	331.5	329.0	323.2	277.9	213.9				213.0	212.0
495				322.1 ^a						
500	341.7	339.1	333.4	324.8	226.8				225.8	224.4
514					236.0 ^a					
520	351.8	349.2	343.8	335.8	249.5	240.0			245.1	243.6
540		359.6	354.4	346.6	302.4	254.2			251.9	250.1
546.7					317.8	259.0 ^a				
560			365.3	357.9	342.9	291.8	268.4		265.2	263.7
563.3					347.8 ^a					
580				369.2	361.0	332.1	283.3		279.0	277.1
589				374.4	367.3	349.5	290.1 ^a		285.2	283.5
593				376.8	370.0	356.3	299.4	293.3	288.1	286.2
600				380.8	374.1	363.8	314.4	299.6	293.1	291.2

^a On saturated locus.

Table VI. Enthalpy of a Low-Boiling Straight Run Paraffinic Naphtha

Units: Btu/lb
Base level: 75°F, saturated liquid

Temp, °F	Psia							
	0	30	100	150	200	300	1000	1400
75		0.0	0.3	0.4	0.6	0.8	2.8	3.9
220		76.9						
240		89.6						
260		102.5						
263.4		104.5 ^a						
280		130						
300		163	124.8				127.0	
320		197.5	137.3				139.4	
340		237.6	150.8				152.1	
360		269.0	164.1				165.1	
368.1		283.0 ^a						
377			175.8 ^a					
380		288.4	180.8	177.7			178.4	
400		300.7	216.2	191.5			191.9	
420		312.1	254.1	205.9			205.3	
427				210.9 ^a				
440		323.7	290.0	231.9	220.6		219.9	219.1
457					232.7 ^a			
460	337.9	335.7	318.0		237.0	234.6	233.6	233.1
480	349.8	347.9	341.6		267.7	249.0	247.8	247.0
481.2			343.2 ^a					
500	361.7	360.0	355.0	337.3	303.9	263.6	262.0	261.1
511.6						272.1 ^a		
515				358.1 ^a				

(Continued on page 200)

Table VI. Continued

Units: Btu/lb
Base level: 75°F, saturated liquid

Temp, °F	Psia							
	0	30	100	150	200	300	1000	1400
520	373.9	372.3	367.9	361.8	337.3	284.3	276.7	275.5
540	386.4	384.9	380.9	376.0	365.8	315.0	292.0	290.4
545					372.3 ^a			
560	399.0	397.6	394.0	389.5	384.0	355.5	307.8	305.9
580	412.0	410.5	406.9	402.9	398.7	384.9	323.0	321.0
582.3						387.4 ^a		
600	425.1	423.7	419.9	416.3	412.8	401.6	338.4	336.1
620	438.9	437.3	433.5	430.2	426.8	417.1		351.4
640	452.7	451.1	447.7	444.4	441.0	432.2		367.0
650	459.9	458.3	454.8	451.3	448.2	439.8		375.0
	Psia							
	350	400	450	475	500	550	600	800
520	279.0							277.2
540	296.2 ^a							293.1
560	328.6	314.3					311.8	309.3
566.5		320.5 ^a						
580		344.5	333.8	332.0	330.8	329.4	328.3	325.0
590	382	365.3	344.7	342.2	340.5	338.1	336.6	333.1
593.4			349.0 ^a					
594.6	389.7 ^a							
597		378.8						
600	394.8	383.9	359.2	354.8	352.0	347.1	345.0	341.1
603.1		388.8 ^a	366.2	359.1	355.7			
607.4		391.9	380.2 ^a	367.1				
610	403.6	395.3	383.4	372.7	365.8	357.0	353.8	349.1
620	411.7	404.6	396.0	390.7	382.1	368.2	363.0	357.0
630	419.4	413.0	406.0	401.8	396.0	383.2	373.5	366.0
640	427.0	421.1	414.8	411.2	407.2	398.4	386.4	375.1
650		429.1	422.8	420.1	417.2	411.0		

^a On saturated locus. Critical point 605°F, 462 psia, $h = 366.8$. Cricondentherm 607.5°F, 453 psia, $h = 378.4$.

Table VII. Enthalpy of a High-Bolling Straight Run Paraffinic Naphtha

Units: Btu/lb
Base level: 75°F, saturated liquid

Temp, °F	Psia											
	0	30	50	70	100	150	200	240	300	600	1000	1400
75		0.0	0.1	0.2	0.3	0.4	0.6	0.7	0.8	1.6	2.8	3.8
220		74.6										78.0
240		86.6										89.5
260		98.8										101.2
280		111.2										113.2
300		124.1										125.6
320		136.6										138.2
340		149.5										151.1
358		162.1 ^a										
360		164.3	162.8									164.3
380		238.0	176.1									177.9
390		289.2 ^a										
400		295.4	189.9									190.8
400.7			190.2 ^a									
420		308.1	247.0	202.8								202.9
434.9				212.6 ^a								
440		320.2	315.6 ^a	226.0	216.0							215.7
460		332.1	328.2	300.0	229.9							229.1

Table VII. *Continued*
 Units: Btu/lb
 Base level: 75°F, saturated liquid

Temp, °F	Psia											
	0	30	50	70	100	150	200	240	300	600	1000	1400
473.4				332.9 ^a								
476					241.2 ^a							
480	346.2	343.8	340.7	337.6	253.0	244.1						243.0
500	357.5	355.2	353.0	350.3	333.9	258.9						257.2
506.4					350.0 ^a							
520	369.3	367.0		363.1	360.1	274.0						271.2
524.5						277.8 ^a						
540	381.6	379.3		375.8	373.2	332.0	289.7					285.0
550.2						372.6 ^a						
560	394.9	392.7		389.2	386.5	380.6	305.0			302.7	301.0	299.4
562.4							307.0 ^a					
580	408.6	406.4		403.0	400.1	394.5	377.1	320.5		318.2	316.4	314.9
584.1							388.8 ^a					
589							391.8	327.9 ^a				
594	418.9	416.8		413.0	410.0	404.3	396.9	347.0	332.0	329.3	327.4	326.0
600					413.8	407.9	401.0	374.0	337.1	334.2	332.1	330.7

^a On saturated locus.

Table VIII. Enthalpy of Kerosine

 Units: Btu/lb
 Base level: 75°F and saturated liquid

Temp, °F	Psia									
	0	20	30	50	70	80	100	150	1400	
75		0.0	0.1	0.1	0.2	0.2	0.3	0.4	3.8	
300		120.0							123.1	
320		132.3							135.3	
340		144.9							147.8	
360		157.6							160.4	
380		170.2							173.0	
400			183.2						185.9	
420			196.5						199.0	
435			206.5 ^a							
440			219.1	209.8					211.8	
455		318.3 ^a								
460		320.7	269.0	223.2					224.8	
480	336.1	333.5	320.9	237.1					237.9	
481				238.0 ^a						
485.5			335.0 ^a							
500	348.5	346.0	344.4	280.0	250.9				250.9	
516.1					262.2 ^a					
520	361.0	358.6	357.1	331.3	271.0	265.0			265.0	
532.5				361.9 ^a		274.1 ^a				
540	373.7		370.0	367.1	318.1	291.0	279.6		279.1	
560	386.3		382.8	380.7	368.3	340.4	294.5		293.9	
562.6							296.3 ^a			
566.8					382.7 ^a					
580	399.3		396.0	394.1	392.3	389.5	340.3	309.5	308.3	
580.6						390.9 ^a				
590	405.8		402.7	400.7	398.8	397.5	366.2	317.2	315.7	
600	412.2		409.2	407.2	405.1	404.1	392.3	324.8	323.0	
605	415.4		412.4	410.5	408.4	407.2	405.1 ^a	328.7	326.6	

^a On saturated locus.

Table IX. Enthalpy of Fuel Oil, Grade No. 2

Units: Btu/lb
Base level: 75°F and saturated liquid

Temp, °F	Psia			
	20	25	100	1400
75	0.0		0.3	3.8
300	115.8	0.1		119.2
320	127.8			131.2
340	139.9			133.1
360	152.1			155.1
380	164.5			167.1
400	176.9			179.2
420	189.4			191.9
440	202.0			204.5
460	215.0			217.2
480	228.1			230.0
500	241.2			243.1
520	254.9			256.3
540	268.7			270.0
560	282.8 ^a			283.8
570	304.8	290.1		290.9
580	328.9	298.1 ^a		298.2
590	353.0	321.2	306.0	305.9
600	378.4	346.0	313.8	313.1

^a On saturated locus.

When the values could be established from the measurements, the enthalpy values for the critical point and for the cricondentherm temperature were presented. The enthalpy values listed at 75°F represent the computed values needed to correct from the pressure level of measurement to the low liquid saturation pressure. It is observed that these corrections are small, never exceeding 3.9 Btu/lb. In accordance with the procedures of the API data book, it is customary to present the results relative to a base level of -200°F and the saturated liquid state. Since the calorimeter can only measure enthalpy differences for inlet temperatures over 100°F, the difference in enthalpy along the saturated liquid state between -200 and 75°F must be predicted to use the -200°F basis. Table I shows the estimated value needed to add to the results shown on Tables III through X to convert to this low -200°F basis. These estimates were made through the use of the API data book.

Table X. Enthalpy of Gas Oil

Units: Btu/lb
Base level: 75°F, saturated liquid

Temp, °F	Psia		
	40	700	1400
75	0.0	2.0	3.9
140	30.2	32.2	33.9
160	40.2	42.3	43.9
180	50.4	52.5	54.1
200	61.0	63.3	64.8
220	71.6	73.9	75.6
240	82.3	84.9	86.8
260	93.8	96.3	98.0
280	105.4	107.6	109.4
300	117.1	119.1	121.1
320	129.1	131.1	132.9
340	141.2	143.3	144.9
360	153.6	155.6	157.0
380	166.0	168.0	169.0
400	178.7	180.7	181.0
420	191.6	193.6	194.0
440	204.8	206.5	206.9
460	217.9	219.4	220.1
480	231.1	232.7	233.4
500	244.3	245.9	246.9
520	257.9	259.2	260.0
540	272.2	272.7	273.1
560	287.1	286.9	286.8
580	302.8	301.5	301.0
600			315.9

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