with iodine or bromine as solutes. Therefore, one must be cautious in using these correlations meant for infinite dilution and be assured that such abnormal behavior as found in methyl alcohol–benzene is not present in the system for which diffusion coefficient is required. We would also like to point out that we have taken viscosity of solvent which is easily available, whereas Wilke and Chang have used viscosity of solution in their equation.

The average percentage error remains within [illegible]13% for the proposed equation which is the same for Wilke and Chang equation. In the latter case, the diffsuion values for water as solute were not included in calculating the average because the Wilke and Chang equation does not hold good.

NOMENCLATURE

D = diffusion coefficient, sq. cm./sec.
η = viscosity of solvent in Equation 2 and viscosity of solution in Equation 1, cp.
V_m = molecular volume, cc./gram mole
M_s = molecular weight of solvent
X = association parameter
L_s = latent heat of vaporization of solvent, at normal boiling point, cal./gram
L = latent heat of vaporization of solute, at normal boiling point, cal./gram
D_T = diffusion coefficient calculated by Equation 2
D_E = experimental diffusion coefficient
D_W = diffusion coefficient calculated by Equation 1

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Specific Heat Measurements of Complex Saturated Hydrocarbons

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Specific heats of complex saturated hydrocarbons were measured from 100° to 400° F. Major hydrocarbon groups investigated were cyclohexanes, bicyclohexyls, tercyclohexyls, decalins, and hydrindans. A differential heating method employing twin thermal cells was used. The cells were charged with 25 ml. of test fluid and 25 ml. reference fluid (diphenyl ether), respectively, and suspended in air in identical bronze cylinders. These cylinders were, in turn, welded in place to the circular metallic cover of a silicone fluid bath regulated to ±0.02° F. from 80 to 420° F. The samples were stirred magnetically and the rate of heating of each was followed using Chromel-Alumel thermocouples connected to a precision potentiometer. Calorimetric cell constants were previously obtained with fluids of known specific heats. The over-all accuracy of the method at two temperatures, 104° and 212° F., was determined by measuring fluids of known specific heats. Density and viscosity data obtained by standard techniques are included for each fluid.

RECENTLY, greater emphasis has been placed on the physical properties of complex saturated hydrocarbons as potential fuels for supersonic aircraft and advanced missile power plants. In addition to density-temperature, viscosity-temperature, and vapor pressure–temperature relationships, and heat of combustion, boiling range, freezing point, and thermal stability data, the heat transfer properties of these organics have been examined more closely in the past several years. It is increasingly evident that heat capacity and thermal conductivity information at higher temperatures is of paramount importance in fully evaluating the potential of any hydrocarbon as a fuel in high performance aircraft and missile vehicles.

This article summarized experimentally determined specific heat results for many new complex saturated hydrocarbons.

EXPERIMENTAL

A differential heating method was chosen for determining the specific heats of hydrocarbon fuels over a wide temperature range. In recent years, more emphasis has been placed on differential heating techniques. For evaluating the specific heat of hydrocarbon fuels over the desired 100° to 400° F. temperature range, a small-sample calorimeter using twin tubes was selected. The apparatus constructed for this fuels program is very similar to that described in the literature by Porter *et. al.* (*7*), Spear (*8*), and Thompson

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Table I.

Reference Fluid	Test Fluid	Test Temp., ° F.	Specific Heat, Btu./Lb./° F. Lit. Value	Found	Deviation, %
Diphenyl ether	Water	104	0.998(*4*)	1.010	+1.20
				1.011	+1.30
				0.986	-1.20
				0.985	-1.30
Diphenyl ether	Aniline	104	0.505(*2, 5*)	0.499	-1.19
				0.518	+2.50
				0.509	+0.79
Water	Aniline	104	0.505(*2, 5*)	0.491	-2.78
Diphenyl ether	*n*-Decane	104	0.540(*6*)	0.527	-2.41
				0.555	+2.78
Water	*n*-Decane	104	0.540	0.524	-2.97
Diphenyl ether	Ethylbenzene	104	0.435(*2*)	0.421	-3.22
				0.417	-4.14
Water	*n*-Heptane	104	0.549(*6*)	0.538	-1.83
				0.533	-2.91
Diphenyl ether	Diphenyl ether	212	0.424(*3, 4*)	0.409	-3.36
				0.424	0.00
				0.427	+0.83
				0.429	+1.20
Diphenyl ether	Aniline	212	0.539(*2, 5*)	0.542	+1.01
				0.535	-0.75
				0.529	-1.86
				0.538	-0.20
				0.524	-2.79
				0.545	+1.11
				0.558	+3.52

Products, Inc. (*9*). However, some modifications have been incorporated.

APPARATUS

The basic parts of the calorimeter are shown in Figure 1. The apparatus is designed to give simultaneous heating curves for a test liquid and a reference liquid contained in identical sample tubes. These sample tubes, *A*, are fabricated from yellow brass tubing (24-gage), 1-inch o.d., and 6.5 inches long. The bottom is closed with a brass plug (24-gage), and the top is capped with a tight-fitting, one-piece cover of the same material. The tubes and their caps are nickel plated.

The sample and reference tubes are charged with 25 ml. of test and reference fluids, respectively, weighed, and then centrally suspended in air by rigid thermal insulation in identical bronze cylinders, *B*, 2 inches in diameter and 8.5 inches long. These bronze cylinders are welded rigidly in place to the circular metallic cover, *E*, of the silicone fluid bath. The bottoms of the cylinders are closed with bronze plates and the tops with removable, tight-fitting, machined disks, *C*, as indicated in the diagrams. When the bath cover is placed in position, the bronze cylinders are suspended in an insulated stainless steel beaker, 8 inches in diameter and 9 inches high, containing Dow Corning 710 silicone fluid as the bath liquid.

This fluid is stirred by an electric motor driven steel blade stirrer, *D*. A 1000-watt, stainless steel, sheathed immersion heater, *L*, is used to obtain the desired temperatures, with the bath temperature controlled by a Thermotrol temperature regulator, *M* (Hallikainen Instruments). Bath temperature regulation is ±0.01° C. from 25° to 220° C.

Magnetic electrical stirrers, *J*, are centrally located 0.75 inch beneath each cylinder and preset to provide constant stirring speeds. The magnetic mixers rotate small iron bar magnets, *H*, in the sample tubes and thereby stir the test and reference fluids. This prevents temperature gradients from developing within the liquids during test. Magnetic stirring action is determined by a pronounced, audible, pinging sound caused by the rotating magnets which is indicative of proper stirring. Chromel-Alumel thermocouples, *K*, enter through small holes in each well cover, *C*, and tube cap. Their voltages are measured alternately to the nearest microvolt with a Leeds and Northrup K-3 potentiometer.

The method of operation is adequately described (*7, 8*). The thermal capacities of the cells were obtained by calibration with liquids of known specific heats; these were reportedly determined by methods accurate to ±1% or better. Table I shows the over-all accuracy of the method as noted by the results for fluids of known specific heat at 104° and 212° F. Each value reported is the average of three determinations showing % deviation from the

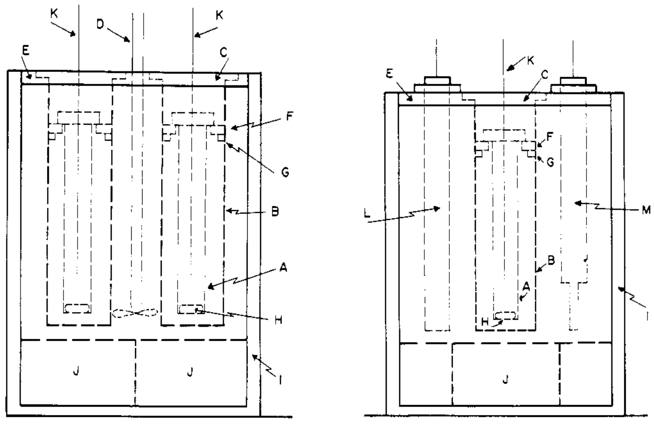

Figure 1. Front (left) and side (right) view schematics of comparison calorimeter

A. Sample tube
B. Bronze cylinder
C. Well cover
D. Electric stirrer
E. Bath cover
F. Insulating spacer
G. Sample tube support
H. Magnetic stirring bar
I. Insulation
J. Magnetic stirrer (electric)
K. Thermocouple
L. Immersion heater
M. Thermotrol probe

Table II. Specific Heat Data for Hydrocarbon Fuels

Compound	Specific Heat, Btu./Lb./° F.				Viscosity at 100° F. Centistokes	Density at 100° F. Grams/Ml.
	104	212	302	410		
Cyclohexanes						
Diethylcyclohexane	0.446	0.511	0.564	. . .	1.07	0.7844
1,4-Diethylcyclohexane						
70% *cis*-30% trans	0.445	0.487	0.538	. . .	1.11	0.7878
80% *cis*-	0.457	0.475	0.530	. . .	1.11	0.7949
Hexaethylcyclohexane	0.502	0.575	0.609	0.650	11.19	0.8627
t-Butylcyclohexane	0.451	0.530	0.603	. . .	1.59	0.7945
Bis(cyclohexylmethyl)cyclohexane	. . .	0.522	0.574	0.649	56.07	0.9067
Bicyclohexyls						
Bicyclohexyl	0.431	0.471	0.540	0.636	3.12	0.8710
2-Methylbicyclohexyl	0.439	0.504	0.583	0.661	3.10	0.8715
2-Ethylbicyclohexyl	0.454	0.512	0.570	0.653	4.68	0.8731
Isopropylbicyclohexyl	0.480	0.531	0.567	0.616	6.27	0.8739
Cyclopentylbicyclohexyl	0.442	0.510	0.547	0.622	14.50	0.9169
4-*n*-Heptylbicyclohexyl	0.438	0.500	0.543	0.604	12.23	0.8601
4-*n*-Nonylbicyclohexyl	0.468	0.503	0.552	0.604	16.04	0.8727
Tercyclohexyls						
o-Tercyclohexyl	0.411	0.471	0.538	0.608	44.17	0.9404
m-Tercyclohexyl	. . .	0.483	0.525	0.624	. . .	. . .
p-Tercyclohexyl	. . .	. . .	0.543	. . .	. . .	. . .
4-*n*-Heptyltercyclohexyl	. . .	0.519	0.547	0.619	246.90	0.9001
4-*n*-Nonyltercyclohexyl	. . .	0.523	0.562	0.620	220.10	0.9048
Decalins						
Decalin	0.384	0.440	0.498	. . .	2.37	0.8846
cis-Decalin	0.434	0.483	0.546	. . .	2.63	0.8813
trans-Decalin	0.433	0.485	0.524	. . .	1.81	0.8545
α-Methyldecalin	0.418	0.495	0.537	. . .	2.21	0.8695
β-Methyldecalin	0.406	0.465	0.538	. . .	1.82	0.8536
Dimethyldecalin	0.436	0.494	0.526	0.667	2.36	0.8710
Dimethanodecalin	0.403	0.473	0.502	. . .	2.37	0.9942
α-Ethyldecalin	0.439	0.493	0.545	0.664	2.37	0.8713
β-Ethyldecalin	0.420	0.480	0.534	0.664	2.37	0.8663
Ethyldecalin	0.428	0.496	0.540	0.665	2.32	0.8797
α-*n*-Propyldecalin	0.447	0.472	0.555	0.640	2.86	0.8680
α-Isopropyldecalin	0.422	0.486	0.545	0.610	3.24	0.8772
Isopropyldecalin	. . .	0.495	0.533	0.639	3.21	0.8678
α-*n*-Butyldecalin	0.445	0.506	0.563	0.629	3.81	0.8724
α-*sec*-Butyldecalin	0.433	0.495	0.533	0.632	3.93	0.8776
α-Isobutyldecalin	0.441	0.484	0.524	0.627	3.32	0.8637
t-Butyldecalin	0.433	0.496	0.544	0.608	4.60	0.8687
Hydrindans						
Hydrindan	0.425	0.480	0.571	. . .	1.92	0.8645
Methylhydrindan	0.457	0.500	0.561	. . .	1.68	0.8587
Ethylhydrindan	0.445	0.506	0.554	. . .	1.78	0.8524
Isopropylhydrindan	0.476	0.519	0.542	. . .	2.11	0.8745
1-Cyclohexyl-3-methylhydrindan	0.438	0.505	0.533	0.614	9.35	0.9127
1-Cyclohexyl-1,3,3-trimethylhydrindan	0.443	0.516	0.571	0.644	31.69	0.9360
Miscellaneous structures						
Dicyclohexylmethane	0.424	0.517	0.563	0.650	4.10	0.8630
2-Methylbicyclohexylmethane	0.444	0.484	0.523	0.640	5.32	0.8746
2-Ethylbicyclohexylmethane	0.473	0.517	0.566	0.653	5.23	0.8722
Bis(2,4,6-*tri*-methylcyclohexyl)methane	. . .	0.534	0.568	0.627	20.18	0.8764
Cyclohexyl(ethylcyclohexyl)methane	0.462	0.513	0.564	0.635	5.84	0.8591
Bis(Ethylcyclohexyl)methane	0.471	0.523	0.572	0.616	7.40	0.8600
Cyclohexyl(isopropylcyclohexyl)methane	0.461	0.522	0.564	0.632	8.40	0.8708
1,1-Dicyclohexylethane	0.428	0.516	0.561	0.633	5.89	0.8804
1,2-Dicyclohexylethane	0.452	0.516	0.561	0.625	5.37	0.8616
1,1-Bis(dimethylcyclohexyl)ethane	0.440	0.527	0.582	0.644	16.20	0.8810
1,1-Bis(ethylcyclohexyl)ethane	0.456	0.523	0.576	0.623	11.19	0.8670
1-Cyclohexyl-1-isopropylcyclohexylethane	0.472	0.535	0.584	0.647	13.65	0.8830
1,2-Dicyclohexylpropane	0.457	0.515	0.577	0.635	6.50	0.8760
1,1,3-Tricyclohexylpropane	. . .	0.525	0.577	0.629	266.36	0.9264
1,3-Dicyclohexylbutane	0.431	0.496	0.547	0.616	8.76	0.8751
1,1-Dicyclohexylheptane	0.483	0.543	0.586	0.646	18.95	0.8918
Bicyclopentyl with 0.01% cyclopentyl bromide	0.401	0.434	0.500	. . .	1.36	0.8511
Bicyclopentyl with 0.10% cyclopentyl bromide	0.392	0.435	0.501	. . .	1.29	0.8578
1,3-Dicylopentylcyclopentane	0.421	0.484	0.520	0.585	3.45	0.9005
Perhydrophenathrene	0.409	0.472	0.526	0.575	5.47	0.9301
2-Ethylperhydrophenanthrene	0.437	0.473	0.538	0.600	7.83	0.9230
Perhydromethylcyclopentadiene dimer	0.426	0.471	0.584	. . .	4.72	0.9167
Diethylperhydropyrene	0.448	0.480	0.523	0.614	17.23	0.9679
9-Methylperhydrofluorene	0.402	0.481	0.527	0.598	4.56	0.9202
9-(2′-Ethylhexyl)perhydrofluorene	0.502	0.538	0.596	0.646	26.39	0.8948
Pinane	0.401	0.456	0.529	. . .	1.89	0.8398

literature value in addition to variations for samples of the same material.

RESULTS

The heat capacities (average of two determinations) for the hydrocarbon fuels investigated with the apparatus and procedure adopted for this study are listed in Table II using diphenyl ether as the reference fluid. Included in this table are density and viscosity data for each organic liquid evaluated by accepted standard techniques. Recently, Belenyessy *et. al.*[1] reported the experimentally determined heats of combustion for many of these complex saturated hydrocarbons and demonstrated the applicability of the Handrick method for correlating such heats of combustion.

In addition to compounds of miscellaneous structures, the major hydrocarbon groups investigated were: cyclohexanes, bicyclohexyls, tercyclohexyls, decalins and hydrindans. The purity of these compounds was established by gas chromatography and reported in the literature (*1*).

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Thermodynamic Properties of Inorganic Substances

VI. The High Temperature Heat Contents of Chromel-P and Alumel

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The heat contents of Chromel-P and Alumel, contained in platinum capsules, have been determined with a copper-block drop-type calorimeter. The results are represented by two equations. Thermodynamic functions are presented at 100° K. intervals.

IT IS OF INTEREST to know the high temperature thermodynamic properties of Alumel and Chromel-P, since these alloys are now extensively used in industry both as heaters and as thermocouples. No experimental data on heat contents for these materials were previously available at high temperature.

EXPERIMENTAL

The copper-block drop-type calorimeter, described previously by Margrave and Grimley (*2, 5*), has been used to determine high temperature thermodynamic data for a variety of inorganic substances (*3, 6, 7*). The apparatus has been calibrated electrically, and, in addition, samples of synthetic sapphire from the National Bureau of Standards have been run for comparison purposes (*2, 7*).

The samples of Chromel-P and Alumel were manufactured by the Hoskins Mfg. Co., Detroit, Mich. Chromel-P contains approximately 90% Ni and 10% Cr, while the composition of Alumel is approximately 72% Ni, 25% Mn, 2% Al, and 1% Si. Platinum capsules were used as containers in all of the measurements, and no evidence of reaction was noted. Data from the calorimeter have been processed on a CDC-1604 computer with a modified version of the program developed by Tilleux (*8*).

RESULTS

The experimental results are summarized in Tables I and II. A least-squares fit of the experimental data provided the following equations for the high temperature heat content and the heat capacity for Chromel-P:

$$H_T - H_{298} = 0.08954\ T + 2.137 \times 10^{-5} T^2 - 28.60 \text{ cal./gram}$$

$$(\pm 0.8 \text{ cal./gram};\ 403^\circ < T^\circ < 1378^\circ \text{K.})$$

and

$$C_p = 0.08954 + 4.274 \times 10^{-5}\ T \text{ cal./gram/}^\circ\text{K.}$$

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