Heats of Formation, Combustion, and Vaporization of The 35 Nonanes and 75 Decanes

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GREENSHIELDS AND ROSSINI (*1*) developed relations for calculating the isomeric variation in the values of a number of physical and thermodynamic properties of the paraffin hydrocarbons. The properties so calculated included the molal volume, the molal refraction, the standard heat of formation, and the standard heat of

Table I. Standard Heats of Vaporization, ΔHv°, Formation,[a] ΔHf°, and Combustion,[b] $-\Delta Hc^\circ$, at 25° C., in Kilocalories per Mole, for the 35 Nonanes

		ΔHf°		$-\Delta Hc^\circ$	
Compound	ΔHv°	Gas	Liquid	Gas	Liquid
n-Nonane	11.10	-54.74	-65.84	1474.90	1463.80
2-Methyloctane	10.73	-56.45	-67.18	1473.19	1462.46
3-Methyloctane	10.72	-55.77	-66.49	1473.87	1463.15
4-Methyloctane	10.63	-55.77	-66.40	1473.87	1463.24
3-Ethylheptane	10.63	-55.08	-65.71	1474.56	1463.93
4-Ethylheptane	10.54	-55.08	-65.62	1474.56	1464.02
2,2-Dimethylheptane	10.11	-59.00	-69.11	1470.64	1460.53
2,3-Dimethylheptane	10.42	-56.32	-66.74	1473.32	1462.90
2,4-Dimethylheptane	10.26	-57.48	-67.74	1472.16	1461.90
2,5-Dimethylheptane	10.34	-57.48	-67.82	1472.16	1461.82
2,6-Dimethylheptane	10.35	-58.17	-68.52	1471.47	1461.12
3,3-Dimethylheptane	10.18	-57.74	-67.92	1471.90	1461.72
3,4-Dimethylheptane	10.42	-55.63	-66.05	1474.01	1463.59
3,5-Dimethylheptane	10.34	-56.79	-67.13	1422.85	1462.51
4,4-Dimethylheptane	10.09	-57.74	-67.83	1471.90	1461.81
2-Methyl-3-ethylhexane	10.33	-55.63	-65.96	1474.01	1463.68
2-Methyl-4-ethylhexane	10.25	-56.79	-67.04	1472.85	1462.60
3-Methyl-3-ethylhexane	10.25	-56.48	-66.73	1473.16	1462.91
3-Methyl-4-ethylhexane	10.41	-54.94	-65.35	1474.70	1464.29
2,2,3-Trimethylhexane	9.97	-57.65	-67.62	1471.99	1462.02
2,2,4-Trimethylhexane	9.73	-58.13	-67.86	1471.51	1461.78
2,2,5-Trimethylhexane	9.73	-60.71	-70.44	1468.93	1459.20
2,3,3-Trimethylhexane	10.05	-57.08	-67.13	1472.56	1462.51
2,3,4-Trimethylhexane	10.21	-56.18	-66.39	1473.46	1463.25
2,3,5-Trimethylhexane	10.05	-58.03	-68.08	1471.61	1461.56
2,4,4-Trimethylhexane	9.81	-57.56	-67.37	1472.08	1462.27
3,3,4-Trimethylhexane	10.13	-56.39	-66.52	1473.25	1463.12
3,3-Diethylpentane	10.41	-55.44	-65.85	1474.20	1463.79
2,2-Dimethyl-3-ethylpentane	9.96	-56.96	-66.92	1472.68	1462.72
2,3-Dimethyl-3-ethylpentane	10.20	-55.82	-66.02	1473.82	1463.62
2,4-Dimethyl-3-ethylpentane	10.12	-56.18	-66.30	1473.64	1463.34
2,2,3,3-Tetramethylpentane	9.84	-56.70	-66.54	1472.94	1463.10
2,2,3,4-Tetramethylpentane	9.76	-56.64	-66.40	1473.00	1463.24
2,2,4,4-Tetramethylpentane	9.12	-57.83	-66.95	1471.81	1462.69
2,3,3,4-Tetramethylpentane	10.00	-56.46	-66.46	1473.18	1463.18

[a] Of the given compounds in the given state, from solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard reference state (*4*).

[b] Of the given compounds in the given state, in oxygen, to form gaseous carbon dioxide and liquid water, with each substance in its thermodynamic standard reference state (*4*).

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Table II. Standard Heats of Vaporization, $\Delta Hv°$, Formation[a], $\Delta Hc°$, and Combustion[b], $-\Delta Hc°$, at 25° C. in Kilcalories per Mole, for the 75 Decanes

Compound	$\Delta Hv°$	$\Delta Hf°$		$-\Delta Hc°$	
n-Decane	12.28	-59.67	-71.95	1632.34	1620.06
2-Methylnonane	11.92	-61.38	-73.30	1630.63	1618.71
3-Methylnonane	11.92	-60.70	-72.62	1631.31	1619.39
4-Methylnonane	11.81	-60.70	-72.51	1631.31	1619.50
5-Methylnonane	11.78	-60.70	-72.48	1631.31	1619.53
3-Ethyloctane	11.81	-60.01	-71.82	1632.00	1620.19
4-Ethyloctane	11.67	-60.01	-71.68	1632.00	1620.33
2,2-Dimethyloctane	11.32	-63.93	-75.25	1628.08	1616.76
2,3-Dimethyloctane	11.62	-61.25	-72.87	1630.76	1619.14
2,4-Dimethyloctane	11.42	-62.41	-73.83	1629.60	1618.18
2,5-Dimethyloctane	11.46	-62.41	-73.87	1629.60	1618.14
2,6-Dimethyloctane	11.56	-62.41	-73.97	1629.60	1618.04
2,7-Dimethyloctane	11.57	-63.10	-74.67	1628.91	1617.34
3,3-Dimethyloctane	11.38	-62.67	-74.05	1629.34	1617.96
3,4-Dimethyloctane	11.58	-60.56	-72.14	1631.45	1619.87
3,5-Dimethyloctane	11.45	-61.72	-73.17	1630.29	1618.84
3,6-Dimethyloctane	11.55	-61.72	-73.27	1630.29	1618.74
4,4-Dimethyloctane	11.24	-62.67	-73.91	1629.34	1618.10
4,5-Dimethyloctane	11.51	-60.56	-72.07	1631.45	1619.94
4-*n*-Propylheptane	11.57	-60.01	-71.58	1632.00	1620.54
4-Isopropylheptane	11.37	-60.56	-71.39	1631.45	1620.43
2-Methyl-3-ethylheptane	11.48	-60.56	-72.04	1631.45	1619.97
2-Methyl-4-ethylheptane	11.31	-61.72	-73.03	1630.29	1618.98
2-Methyl-5-ethylheptane	11.45	-61.72	-73.17	1630.29	1618.84
3-Methyl-3-ethylheptane	11.40	-61.41	-72.81	1630.60	1619.20
3-Methyl-4-ethylheptane	11.47	-59.87	-71.34	1632.14	1620.67
3-Methyl-5-ethylheptane	11.44	-61.04	-72.48	1630.97	1619.53
4-Methyl-3-ethylheptane	11.50	-59.87	-71.37	1632.14	1620.64
4-Methyl-4-ethylheptane	11.29	-61.41	-72.70	1630.60	1619.31
2,2,3-Trimethylheptane	11.15	-62.58	-73.73	1629.43	1618.28
2,2,4-Trimethylheptane	10.86	-63.06	-73.92	1628.95	1618.09
2,2,5-Trimethylheptane	10.96	-64.95	-75.91	1627.06	1616.10
2,2,6-Trimethylheptane	10.97	-65.64	-76.61	1626.37	1615.40
2,3,3-Trimethylheptane	11.21	-62.01	-73.22	1630.00	1618.79
2,3,4-Trimethylheptane	11.32	-61.11	-72.43	1630.90	1619.58
2,3,5-Trimethylheptane	11.26	-62.27	-73.53	1629.74	1618.48
2,3,6-Trimethylheptane	11.26	-62.96	-74.22	1629.05	1617.79
2,4,4-Trimethylheptane	10.88	-62.49	-73.37	1629.52	1618.64
2,4,5-Trimethylheptane	11.22	-62.27	-73.49	1629.74	1618.52
2,4,6-Trimethylheptane	11.06	-64.12	-71.58	1627.89	1620.43
2,5,5-Trimethylheptane	11.02	-64.38	-75.40	1627.63	1616.61
3,3,4-Trimethylheptane	11.24	-61.32	-72.56	1630.69	1619.45
3,3,5-Trimethylheptane	11.01	-61.80	-72.81	1630.21	1619.20
3,4,4-Trimethylheptane	11.20	-61.32	-72.52	1630.69	1619.49
3,4,5-Trimethylheptane	11.38	-60.43	-71.81	1631.58	1620.20
2-Methyl-3-isopropylhexane	11.18	-61.11	-72.29	1630.90	1619.72
3,3-Diethylhexane	11.45	-60.15	-71.60	1631.86	1620.41
3,4-Diethylhexane	11.50	-59.19	-70.67	1632.82	1621.32
2,2-Dimethyl-3-ethylhexane	11.04	-61.89	-72.93	1630.12	1619.08
2,2-Dimethyl-4-ethylhexane	10.85	-62.37	-73.22	1629.64	1618.79
2,3-Dimethyl-3-ethylhexane	11.26	-60.75	-72.01	1631.26	1620.00
2,3-Dimethyl-4-ethylhexane	11.31	-60.43	-71.74	1631.58	1620.27
2,4-Dimethyl-3-ethylhexane	11.28	-60.43	-71.71	1631.58	1620.30
2,4-Dimethyl-4-ethylhexane	11.20	-61.23	-72.43	1630.78	1619.58
2,5-Dimethyl-3-ethylhexane	11.12	-62.27	-73.39	1629.74	1618.62
3,3-Dimethyl-4-ethylhexane	11.23	-60.63	-71.86	1631.38	1620.15
3,4-Dimethyl-3-ethylhexane	11.20	-60.06	-71.26	1631.95	1620.75
2,2,3,3-Tetramethylhexane	10.94	-61.63	-72.57	1630.38	1619.44
2,2,3,4-Tetramethylhexane	10.95	-60.55	-71.50	1631.46	1620.51
2,2,3,5-Tetramethylhexane	10.79	-64.29	-75.08	1627.72	1616.93
2,2,4,4-Tetramethylhexane	10.42	-61.50	-71.92	1630.51	1620.09
2,2,4,5-Tetramethylhexane	10.66	-63.61	-74.27	1628.40	1617.74
2,2,5,5-Tetramethylhexane	10.36	-68.18	-78.54	1623.83	1613.47
2,3,3,4-Tetramethylhexane	11.17	-60.66	-71.83	1631.35	1620.18
2,3,3,5-Tetramethylhexane	10.85	-61.83	-72.68	1630.18	1619.33
2,3,4,4-Tetramethylhexane	11.04	-59.98	-71.02	1632.03	1620.99
2,3,4,5-Tetramethylhexane	11.12	-61.67	-72.79	1630.34	1619.22
3,3,4,4-Tetramethylhexane	11.13	-60.37	-71.50	1631.64	1620.51

Table II. Continued

Compound	ΔHv°	ΔHf°		$-\Delta Hc^\circ$	
2,3-Dimethyl-3-isopropylpentane	10.99	-61.67	-72.66	1630.34	1619.35
2-Methyl-3,3-diethylpentane	11.42	-59.49	-70.91	1632.52	1621.10
2,2,3-Trimethyl-3-ethylpentane	11.09	-60.37	-71.46	1631.64	1620.55
2,2,4-Trimethyl-3-ethylpentane	10.85	-60.55	-71.40	1631.46	1620.61
2,3,4-Trimethyl-3-ethylpentane	11.24	-60.09	-71.33	1631.92	1620.68
2,2,3,3,4-Pentamethylpentane	10.91	-59.08	-69.99	1632.93	1622.02
2,2,3,4,4-Pentamethylpentane	10.52	-59.04	-69.56	1632.97	1622.45

[a] Of the given compound in the given state, from solid carbon (graphite) and gaseous hydrogen, with each substance in its thermodynamic standard reference state (*4*).

[b] Of the given compound in the given state, in oxygen, to form gaseous carbon dioxide and liquid water, with each substance in its thermodynamic standard reference state (*4*).

vaporization, all at 25° C., and the boiling point at pressures of 760 and 10 mm. of mercury.

In this investigation, the appropriate foregoing relations have been utilized with auxiliary data to calculate values of the standard (*3*) heat of formation, combustion, and vaporization at 25° C. for each of the 35 nonanes and 75 decanes. The auxiliary values required included the standard heats of formation of water and of carbon dioxide and were taken from the tables of the API Research Project 44 (*4*). The values for the heats of combustion of the five most highly branched nonanes in the liquid state are taken from experimental work (*2*).

Tables I and II present the resulting calculated values of the standard heat of formation, combustion, and vaporization, for the nonanes and decanes, respectively.

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Liquid Viscosity above the Normal Boiling Point

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INTEREST IN THE accurate determination of viscosity coefficients of liquids in the region between the boiling point and the critical temperature has been stimulated by a growing need for these data, notably in the design of fuel systems for liquid propellant missiles. Moreover, the present lack of viscosity data in this temperature region precludes the development of a liquid viscosity correlation of complete generality for the whole liquid region. This article describes a capillary viscometer which has been designed specially to obtain viscosity data for liquids above their boiling points, particularly to establish calibration data for other viscometric instruments (*5*).

The capillary viscometer was selected over other types of viscometric devices on the basis of the simplicity of the theory and the inherent potential accuracy of the capillary method. Capillary viscometers are widely used to obtain accurate, absolute viscosity data for the normal liquid region not only because of the relative ease of experimental manipulation, but also because the raw data may be converted into viscosity coefficients without undue emphasis on unknown end effects and allowance for experimental divergence from restrictions imposed by the derived theoretical equations.

To realize these advantages of the capillary viscometer in the region above the boiling point, apparatus modifications are required for maintaining the Reynolds number below 2300 while dealing with fluids of very small kinematic viscosities, for making accurate low pressure drop and flow rate measurements under conditions of moderate environmental pressures and temperatures, and for minimizing the effect of end-effect correction terms on the accuracy of the determinations.

THEORY

The basic equation applicable to a capillary viscometer operated under the condition of a continuously varying flow rate or pressure drop is

$$\eta = \frac{\pi r^4 \Delta P}{8L\, dQ/dt} - \frac{m\rho dQ/dt}{8\pi L} \tag{1}$$

where η is the viscosity coefficient in poises, ρ is the density

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