Thermodynamic Properties of *n*-Hexane

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Thermodynamic properties of *n*-hexane have been calculated over a temperature range of 32° to 540°F. and up to a pressure of 600 lb./sq. in. abs. These properties were determined from vapor pressure, volumetric, heat capacity, and latent heat of vaporization data through the application of rigorous thermodynamic relationships. The calculated data have been found to be internally consistent. The enthalpy values are believed to be accurate to within ±0.5 B.t.u./lb. and the entropy values to ±0.0005 B.t.u./(lb.)(°R.).

Thermodynamic data are available for six straight-chain saturated hydrocarbons, including methane (*16*), ethane (*7*), propane (*10, 19*), *n*-butane (*17, 18*), *n*-pentane (*9*), and *n*-heptane (*21*) but not for *n*-hexane. Consequently, it is the purpose of this paper to present the derived properties, calculated from rigorous thermodynamic relationships, for *n*-hexane. Sufficient thermal, volumetric, and vapor-pressure-temperature data are reported in the literature to permit the accurate evaluation of these properties over the temperature range of 32° to 540°F. and up to pressures of 600 lb./sq. in abs.

A number of investigators have reported on the volumetric behavior of *n*-hexane. Thomas and Young (*22*) reported saturated liquid and vapor volumes over the temperature range of 158° to 454.6°F., the critical temperature, and superheated-vapor volumetric data from 338° to 536.8°F. from a pressure of 136.7 to 547 lb./sq. in. abs.

Kelso and Felsing (*14*) investigated the behavior of *n*-hexane in the superheated-vapor region from a temperature of 482° to 527°F. and from pressures of 375.6 to over 1,400 lb./sq. in. abs. and confirmed, at least in part, the experimental results of Thomas and Young (*22*). The Benedict-Webb-Rubin equation of state (*8*),

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha' d^6 + cd^3/T^2[(1 + \gamma d^2)e^{-\gamma d^2}] \quad (1)$$

has been fitted to these data of Kelso and Felsing. When the equation of state is used to calculate the pressure at these highly nonideal conditions, the average error is 0.74%. Therefore this equation of state was used to predict the volumetric behavior of *n*-hexane at these high temperatures and pressures. Kelso and Felsing (*15*) later reported the results of an investigation over the temperature range of 212° to 527°F. and from pressures of 35.6 to over 4,300 lb./sq. in. abs. The data reported included those for the saturated liquid and vapor and for the superheated vapor.

Waddington and Douslin (*23*) presented an equation of state,

$$P_{(atm.)}V_{(cc./g.\ mole)} = RT_{(°K.)} - (2{,}270 - 6.25 \times 10^5 T^{-1} + 1.306 \times 10^{13}T^{-4})P \quad (2)$$

for saturated *n*-hexane vapor over a temperature range of 77° to 155.7°F., the normal boiling point. Also they report that if the Berthelot equation of state is used for the calculation of the saturated-vapor volume at the normal boiling point and this value, in turn, is used in the Clapeyron equation, an error of 0.75% will result in the calculated value of the latent heat of vaporization. In view of the magnitude of this error, it was assumed that the Berthelot equation was valid at very low pressures, 0.876 lb./sq. in., for example, and at atmospheric pressure at temperatures above 160°F.

Stewart, Sage, and Lacey (*20*) made an extensive investigation of the volumetric behavior of *n*-hexane in the liquid phase, including the liquid at its bubble point, over a temperature range of 100° to 400°F. More volumetric data in the liquid phase from 30° to 160°F. are reported in A.P.I. Rept. 44 (*1*).

Thermal data, while not sufficient to provide an independent check of the results presented in this work, are reported by a number of investigators. Heat-capacity data for liquid *n*-hexane are reported by Huffman, Parks, and Barmore (*13*) over a temperature range of −119.9° to 68.6°F. and by Douslin and Huffman (*12*) over a temperature range of 8.3° to 80.3°F. Connelly, Sage, and Lacey (*11*) reported the heat capacity of the liquid at its bubble point over a temperature range of 80° to 200°F. The data of the last mentioned authors and those of Huffman et al. were used almost exclusively in the calculations.

Waddington and Douslin (*23*) reported latent-heat-of-vaporization data over a temperature range of 77° to 155.7°F. and vapor-phase heat-capacity data from 197.6° to 384.3°F. at atmospheric pressure. The heat capacity, enthalpy, and

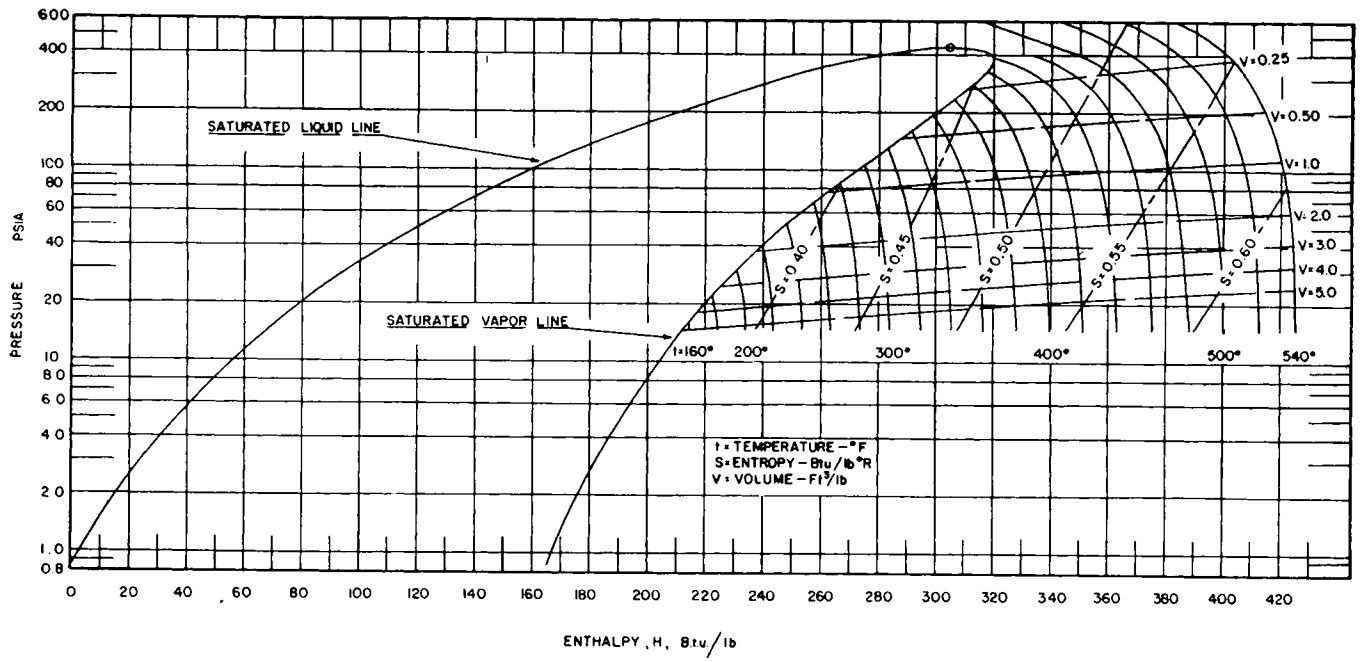

Fig. 1. Pressure-enthalpy diagram for *n*-hexane.

entropy of the gas in the ideal-gas state and unit fucacity are reported in A.P.I. Rept. 44 (*2, 3, 4*).

The vapor-pressure–temperature relationship from the normal boiling to the critical point is reported by Thomas and Young (*22*). Also vapor-pressure data are available from −45° to 200°F. in A.P.I. Rept. 44 (*5*).

The critical constants, T_c = 454.5°F., P_c = 439.7 lb./sq. in. abs., and V_c = 0.685 cu. ft./lb., reported in A.P.I. Rept. 44 (*6*) were used in the calculations. Additional constants used were molecular weight of *n*-hexane, 86.17; gas-law constant, R, 10.7335 (lb./sq. in.)(cu. ft.)/(lb. mole)(°R.); ice point, 491.69°R. One pound of *n*-hexane was used as the basis of calculation and the enthalpy and entropy values of the saturated liquid at 32°F. (pressure equal to 0.876 lb./sq. in. abs.) were set equal to zero.

Prior to the determination of the thermodynamic data, residual volumes, α's, were calculated and the volumetric data smoothed by plotting the residual volume at constant temperature against pressure on a large-scale graph. When volumetric data were lacking, either the Berthelot or the Benedict-Webb-Rubin equation of state was used to predict the necessary information. From this plot it was possible to determine the f/P ratio through the relationship

$$\ln \frac{f}{P} = -\frac{1}{RT}\int_0^P \alpha \, dP \qquad (3)$$

The value of the integral was determined graphically. Some of the f/P ratios calculated for this work can be compared with values presented by Kelso and Felsing (*15*). The agreement between the two sets of values is good, with those presented in this work tending to be from 2½ to ¼% lower than the previously reported data. Kelso and Felsing did not state the assumptions used in the calculations of their f/P ratios.

Latent-heat-of-vaporization data were then calculated. Since data were available from 77° to 155.7°F. (*23*), it was necessary

Table 1. Thermodynamic Properties of Saturated *n*-Hexane

t, °F.	Pressure, lb./sq. in. abs.	Fugacity pressure *f/P*	Volume, cu. ft./lb.		Enthalpy, B.t.u./lb.			Entropy, B.t.u./(lb.)(°R.)		
			Liquid	Vapor	Liquid	Vaporization	Vapor	Liquid	Vaporization	Vapor
32	0.876	0.995	0.02366	69.57	0.0	165.1	165.1	0.0000	0.3358	0.3358
40	1.107	0.994	0.02380	55.87	4.2	163.7	167.9	0.0084	0.3276	0.3360
60	1.911	0.991	0.02415	33.55	14.8	160.2	175.0	0.0291	0.3083	0.3374
80	3.143	0.986	0.02452	21.08	25.5	156.9	182.4	0.0494	0.2907	0.3401
100	4.956	0.980	0.02493	13.77	36.5	153.8	190.3	0.0694	0.2748	0.3442
120	7.531	0.972	0.02532	9.306	47.8	150.5	198.3	0.0892	0.2596	0.3488
140	11.075	0.961	0.02578	6.473	59.3	146.9	206.2	0.1087	0.2450	0.3537
160	15.823	0.951	0.02618	4.617	71.1	143.0	214.1	0.1280	0.2308	0.3588
180	22.03	0.937	0.02667	3.371	83.2	139.1	222.3	0.1472	0.2174	0.3646
200	30.00	0.922	0.02722	2.508	96.6	133.9	230.5	0.1678	0.2030	0.3708
220	39.87	0.905	0.02775	1.907	108.9	130.2	239.1	0.1878	0.1916	0.3794
240	52.10	0.886	0.02838	1.469	121.7	126.2	247.9	0.2089	0.1804	0.3893
260	66.94	0.868	0.02903	1.146	136.1	121.3	257.4	0.2295	0.1685	0.3980
280	84.93	0.847	0.02977	0.8992	149.6	116.7	266.3	0.2493	0.1578	0.4070
300	106.1	0.825	0.03060	0.7126	162.8	111.9	274.7	0.2680	0.1473	0.4153
320	131.3	0.803	0.03150	0.5653	176.9	106.0	282.9	0.2868	0.1360	0.4228
340	160.3	0.778	0.03256	0.4533	192.3	98.7	291.0	0.3062	0.1234	0.4296
360	193.6	0.754	0.03377	0.3641	207.8	90.3	298.1	0.3266	0.1102	0.4368
380	231.7	0.729	0.03547	0.2919	223.7	82.4	306.1	0.3455	0.0981	0.4436
400	277.5	0.703	0.03748	0.2284	239.8	72.9	312.7	0.3659	0.0848	0.4507
420	327.5	0.678	0.04052	0.1778	255.2	62.4	317.6	0.3843	0.0709	0.4552
440	386.0	0.653	0.04582	0.1314	274.1	45.9	320.0	0.4058	0.0410	0.4568
454.5	439.7	0.635	0.0685	0.0685	305.0	0.0	305.0	0.4390	0.0	0.4390

to make calculations only over the ranges 32° to 77°F. and 155.7° to 454.5°F. The latent heats were calculated by the Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_v}{T\Delta V} \qquad (4)$$

No assumptions were involved in these calculations, because complete volumetric and vapor-pressure–temperature data were available.

Up to temperatures of 200°F. liquid-phase enthalpy and entropy data could be calculated from the liquid-phase heat capacities (*11, 12, 13*). The relationships used were

$$dH = \int_{T_1}^{T_2} C_p\, dT \qquad (5)$$

and

$$dS = \int_{T_1}^{T_2} \frac{C_p}{T}\, dT \qquad (6)$$

The integrals were evaluated graphically. With these data and previously calculated latent-heat data, the enthalpy and entropy values of the saturated vapor up to 200°F. can be calculated.

Enthalpy values for the superheated vapor were calculated as differences between the real gas and the ideal gas at the same temperature. The relationship used was

$$_M(H_P - H^0)_T = -\int_{P^\circ}^{P}\left[\alpha - T\left(\frac{\partial\alpha}{\partial T}\right)_P\right] dP \qquad (7)$$

and the integral was evaluated graphically. The differences were subtracted from the proper enthalpy values for the ideal gas at unit fugacity obtained from A.P.I. Rept. 44 (*3*). Naturally, the enthalpy data of A.P.I. Rept. 44 had been previously converted to the datum used in this work. By the procedure outlined above it was possible to calculate enthalpy data in the superheated-vapor region as well as for the saturated vapor at temperatures above 200°F.

Entropy data in the superheated-vapor region and for the saturated vapor above 200°F. were determined through a similar procedure by use of the appropriate relationship,

$$_M(S_p - S^0)_T = -\int_{P^\circ}^{P}\frac{R}{P}\, dP + \int_{P^\circ}^{P}\left(\frac{\partial\alpha}{\partial T}\right)_P dP \qquad (8)$$

As in the previous case, the entropy values for the ideal gas at unit fugacity given in A.P.I. Rept. 44 (*4*) were used after they had been converted to the datum selected for this work.

TABLE 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED *n*-HEXANE

Temperature, °F.	Volume, cu. ft./lb.	Enthalpy, B.t.u./lb.	Entropy, B.t.u./(lb.)(°R.)	Fugacity/pressure f/P
		14.696 lb./sq. in. abs. (155.7)*		
(At satn.)	4.96	212.5	0.3578	0.953
160	5.00	214.5	0.3623	0.954
200	5.37	233.6	0.3954	0.961
240	5.73	253.2	0.4247	0.968
280	6.09	273.4	0.4540	0.972
320	6.45	294.7	0.4839	0.976
360	6.80	316.5	0.5130	0.979
400	7.15	339.6	0.5418	0.982
440	7.51	363.0	0.5702	0.985
480	7.86	388.5	0.5989	0.987
520	8.21	412.6	0.6273	0.989
		25 lb./sq. in. abs. (188.8)*		
(At satn.)	2.99	225.8	0.3670	0.932
200	3.06	232.1	0.3795	0.935
240	3.29	252.1	0.4114	0.946
280	3.51	272.4	0.4409	0.953
320	3.72	293.7	0.4708	0.959
360	3.94	315.6	0.5000	0.965
400	4.15	338.7	0.5288	0.970
440	4.36	362.1	0.5573	0.974
480	4.58	386.7	0.5860	0.978
520	4.79	412.0	0.6146	0.981
		50 lb./sq. in. abs. (236.8)*		
(At satn.)	1.53	246.6	0.3872	0.890
240	1.54	248.8	0.3924	0.893
280	1.66	269.9	0.4226	0.908
320	1.78	291.2	0.4526	0.920
360	1.90	313.2	0.4820	0.931
400	2.01	336.4	0.5109	0.941
440	2.12	360.0	0.5396	0.949
480	2.24	384.8	0.5684	0.957
520	2.35	410.3	0.5973	0.963
		75 lb./sq. in. abs. (269.6)*		
(At satn.)	1.02	261.5	0.4016	0.858
280	1.05	267.3	0.4109	0.865
320	1.13	288.8	0.4411	0.882
360	1.21	310.9	0.4707	0.899
400	1.30	334.2	0.5011	0.913
440	1.38	357.9	0.5286	0.925
480	1.46	382.8	0.5575	0.936
520	1.54	408.6	0.5867	0.946
		100 lb./sq. in. abs. (294.4)*		
(At satn.)	0.758	272.5	0.4125	0.831
320	0.805	286.2	0.4322	0.846
360	0.874	308.5	0.4620	0.867
400	0.940	331.9	0.4926	0.885
440	1.00	355.8	0.5203	0.901
480	1.08	380.8	0.5493	0.916
520	1.13	407.0	0.5788	0.929
		150 lb./sq. in. abs. (333.4)*		
(At satn.)	0.489	288.4	0.4274	0.786
360	0.529	303.4	0.4482	0.806
400	0.581	327.4	0.4794	0.833
440	0.630	351.6	0.5075	0.855
480	0.677	377.4	0.5375	0.877
520	0.723	403.7	0.5670	0.894
		200 lb./sq. in. abs. (363.6)*		
(At satn.)	0.350	299.8	0.4378	0.750
400	0.398	322.4	0.4684	0.782
440	0.442	347.3	0.4973	0.812
480	0.482	372.8	0.5269	0.839
520	0.519	400.3	0.5578	0.862
		250 lb./sq. in. abs. (388.2)*		
(At satn.)	0.264	308.9	0.4467	0.718
400	0.280	316.4	0.4574	0.732
440	0.326	342.3	0.4879	0.769
480	0.363	368.3	0.5182	0.803
520	0.397	396.8	0.5500	0.830

TABLE 2.—(Continued)

Temperature, °F.	Volume cu. ft./lb.	Enthalpy, B.t.u./lb.	Entropy, B.t.u./(lb.)(°R.)	Fugacity/pressure f/P
		300 lb./sq. in. abs. (409.4)*		
(At satn.)	0.203	315.2	0.4536	0.692
440	0.245	336.1	0.4782	0.728
480	0.283	363.7	0.5100	0.767
520	0.315	393.2	0.5429	0.800
		400 lb./sq. in. abs. (444.4)*		
(At satn.)	0.119	319.3	0.4564	0.648
480	0.176	350.2	0.4930	0.698
520	0.209	384.8	0.5294	0.741
		500 lb./sq. in. abs.		
480	0.0970	330.9	0.4675	0.627
520	0.142	374.2	0.5153	0.684
		600 lb./sq. in. abs.		
480	0.0512	315.3	0.4485	0.555
520	0.102	364.5	0.4989	0.625

*Saturation temperature.

Entropy and enthalpy data for the saturated liquid above 200°F. were obtained by subtracting the entropy or enthalpy of condensation from the respective values for the saturated vapor.

The results were plotted on large-scale temperature-entropy, enthalpy-temperature, and enthalpy-entropy plots and smoothed graphically. The final results are reported in Tables 1 and 2* and in graphical form on a log pressure vs. enthalpy plot, Figure 1.

The results were checked for internal consistency through the relationship

$$dH = T\,dS + V\,dP \qquad (9)$$

Setting the value of the entropy at a constant reduces the equation to

$$dH = V\,dP \qquad (10)$$

Multiplying the right-hand member by P/P and integrating results in the equation

$$H_2 - H_1 = \frac{144}{778.3}\int_{P_1}^{P_2} PV\,d\ln P \qquad (11)$$

The right-hand member can then be evaluated by graphical integration and compared with enthalpy differences obtained from the calculated data. Such consistency checks were made on the thermodynamic data presented in this paper, and good agreement was obtained in each instance.

Only one check can be made of the thermodynamic data presented in this work with data from an independent source. Waddington and Douslin (*23*) report heat-capacity data for the superheated vapor at 14.7 lb./sq. in. abs. over a temperature range of 197.6° to 384.3°F. With the data of these investigators, the enthalpy difference over the temperature range in question is 100.4 B.t.u./lb., and from this work the enthalpy difference is 97.7 B.t.u./lb. This would appear to be a large error, but in reality it is not. From the data of Waddington and Douslin (*23*) the enthalpy difference for the ideal gas over this temperature range is 99.5 B.t.u./lb., and from A.P.I. Rept. 44 (*3*) the difference is 96.2 B.t.u./lb. This would indicate that the heat-capacity data of Waddington and Douslin are too high. There is a good degree of consistency between the two sets of data, however. If the quantity $(\Delta H° - \Delta H_{14.7})$ over the temperature range is considered, the difference by Waddington and Douslin's data is 99.5–100.4, or −0.9 B.t.u./lb., but by A.P.I. Rept. 44 and this work the difference is 96.2–97.7, or −1.5 B.t.u./lb.

With this single minor exception, there are no thermal data available to check the accuracy of the thermodynamic data presented here. However, it is believed that the reported enthalpy values are accurate to ±0.5 B.t.u./lb. and the entropy values accurate to ±0.0005 B.t.u./(lb.)(°R.).

In conclusion, f/P ratios, enthalpy, and entropy data, calculated by rigorous thermodynamic relationships, are presented for *n*-hexane over a temperature range of 32° to 540°F. and up to a pressure of 600 lb./sq. in. abs. The results were found to be internally consistent.

*Tabular material has been deposited as document 5056 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

NOTATION

C_p = heat capacity at constant pressure, B.t.u./(lb.)(°R.)
H = enthalpy, B.t.u./lb.
P = pressure, lb./sq. in. abs., unless otherwise specified
S = entropy, B.t.u./(lb.)(°R.)
T = absolute temperature, °R. unless specified as °K.
V = specific volume, cu. ft./lb.
d = density, lb. moles/cu. ft.
f = fugacity, same units as pressure
t = temperature, °F.
α = residual volume, cu. ft./lb. mole, $RT/P - V_M$

Constants of Benedict-Rubin-Webb Equation of State (8)

A_0 = 54,434
B_0 = 2.84835
C_0 = 40,556.2 × 10^6
a = 429,901
b = 28.0032
c = 296,077
α' = 11,553.9 × 10^{-3}
γ = 1,711.15 × 10^{-2}

Subscripts

c = critical property
M = molal quantity
v = vaporization

Superscripts

° = property in the ideal-gas state at unit fugacity

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