Part I

Thermodynamic Properties of Isopentane

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The thermodynamic properties, entropy, enthalpy, and specific volume, were calculated for isopentane using experiemntal data from the literature. The calculations were based on rigorous thermodynamic equations using the Benedict-Webb-Rubin (*B-W-R*) equation of state to give analytical expressions for the entropy, enthalpy, and volume. The results are presented in the form of tables and graphs from 1 to 60 atm. and 50° to 600° F. for the superheated vapor, and from 0° F. to the critical point for the saturated liquid and vapor.

EXPERIMENTAL thermodynamic data for isopentane have been published in the literature. However, the derived thermodynamic functions, enthalpy and entropy, have not been published previously. The present paper gives the calculated values of the enthalpy, entropy, and specific volume for the superheated vapor from 1 to 60 atm. and from 50° to 600° F., and for the saturated liquid and vapor from 0° F. to the critical point.

The calculations were based upon rigorous thermodynamic relations using the Benedict-Webb-Rubin (*B-W-R*) equation of state,

$$P = \frac{RT}{V} + \frac{B_0RT - A_0 - C_0/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{T^2V^3}\left[\left(1 + \frac{\gamma}{V^2}\right)e^{-\gamma/V^2}\right]$$

A new set of constants for the *B-W-R* equation of state were calculated using selected experimental data from the literature.

DATA AND METHODS OF CORRELATION

The literature was thoroughly reviewed to find the best data on which to base the calculations. The following sections show the sources of all data used.

P-V-T Data. The *P-V-T* behavior of isopentane has been studied by Young (*15*), Silberberg, McKetta, and Kobe (*11*), Vohra and Kobe (*12*), and Isaac, Li, and Canjar (*4*). The findings of Silberberg, McKetta, and Kobe and of Vohra and Kobe agree very well, within 0.2% maximum difference, even though completely different types of experimental apparatus and techniques were used in the two investigations. However, the results of Isaac, Li, and Canjar, and of Young deviated widely from the other two and did not agree with each other. Therefore, the data of Silberberg, McKetta, and Kobe (*11*) and Vohra and Kobe (*12*) were used in the present work.

Constants for the *B-W-R* equation have been determined by Benedict, Webb, and Rubin (2) based on the data of Young. Since Young's data were thought to be inferior to the data used in this work, new constants were calculated using a least squares method described by Brough (*3*). The constants calculated in this manner are shown in Table I.

The data on which the constants are based include pressures up to 60 atm. There are only five useful data points between 60 and 200 atm. Checks of the *B-W-R*

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Table I. Constants for the *B-W-R* Equation of State for Isopentane

(Units correspond to pressure in atm., temperature in ° R., and volume in cu. ft. per pound)

Constant	Values
$B_0 \times 10^3$	−8.83680
$A_0 \times 10^1$	1.76210
$C_0 \times 10^{-5}$	3.36705
$b \times 10^3$	−1.12055
$a \times 10^2$	−2.86318
$c \times 10^{-3}$	3.32652
$\alpha \times 10^6$	1.29180
$\gamma \times 10^3$	7.00339
$R \times 10^2$	1.01216

Table II. Critical Constants of Isopentane

Source	t_c, ° C.	P_c, Atm.	ρ_c, G./Cc.
Vohra (*12*)	187.8 ± 0.05	33.66 ± 0.05	0.236 ± 0.005
Young (*16*)	187.8	32.9	0.2343
Pawlewski (*5*)	194.8		
Altschul (*1*)	187.1	33.3	

Table III. Constants for the Modified Antoine Equation

(Units: ° F., atm.)

	Temperature Range	
Constant	0° to 120° F.	130° to 370.1° F.
A	3.7978	4.4466
$B \times 10^{-3}$	1.6707	2.4654
$C \times 10^{-4}$	−20.962	3.3614
$D \times 10^{-2}$	4.5969	4.5969

equation using the new set of constants showed that deviations become as large as 20% as pressure increases over this range. The constants fitted in this manner probably make the *B-W-R* equation unsuitable for extrapolation beyond 60 atm. Using the new set of constants, the standard deviation of the compressibility factor, z, is 2.3×10^{-3} based on the 138 available data points below 60 atm., and the maximum deviation is 3.4% at 59.46 atm. and 392° F. The standard deviation of z using the same data and the constants determined by Benedict, Webb, and Rubin (*2*) is 5.6×10^{-3}.

Vapor Pressure Data. The vapor pressure data of Willingham, Taylor, Pignocoo, and Rossini (*14*) and of Schumann, Aston, and Sagenkahan (*10*), as interpolated and tabulated in the API Research Project 44 (*9*), were used in the temperature range 0° to 120° F. The data of Silberberg (*11*) were used for the temperature interval 122° to 347° F. The critical constants of isopentane have been measured by Vohra and Kobe (*12*), Young (*16*), Pawlewski (*5*), and Altschul (*1*). A comparison of their results is shown in Table II.

The critical constants of Vohra and Kobe were used in the present work. The reasons are that the data of Vohra and Kobe are the most recent and their extensive *P-V-T* data near the critical point were used in the evaluation of the constants of the *B-W-R* equation of state. Also, the critical constants of Vohra and Kobe agree well with the older determinations by Young and Altschul.

A modified Antoine equation,

$$\log P = A - \frac{B}{t + D} + \frac{C}{(t + D)^2}$$

was used both to interpolate the vapor pressure data of Silberberg and to calculate latent heats via the Clapeyron equation. To refine further this correlation, the best constants, based on the least squares method, were calculated for each temperature range covered by the two sources of data (Table III). The consistency between these two sets of constants, and the data they represent, at the junction of the two temperature ranges was checked both by plotting log P *vs.* $1/(t + D)$ and by comparing the values of the first derivative of P with respect to t calculated with each set of constants at 120° and 130° F. Both methods

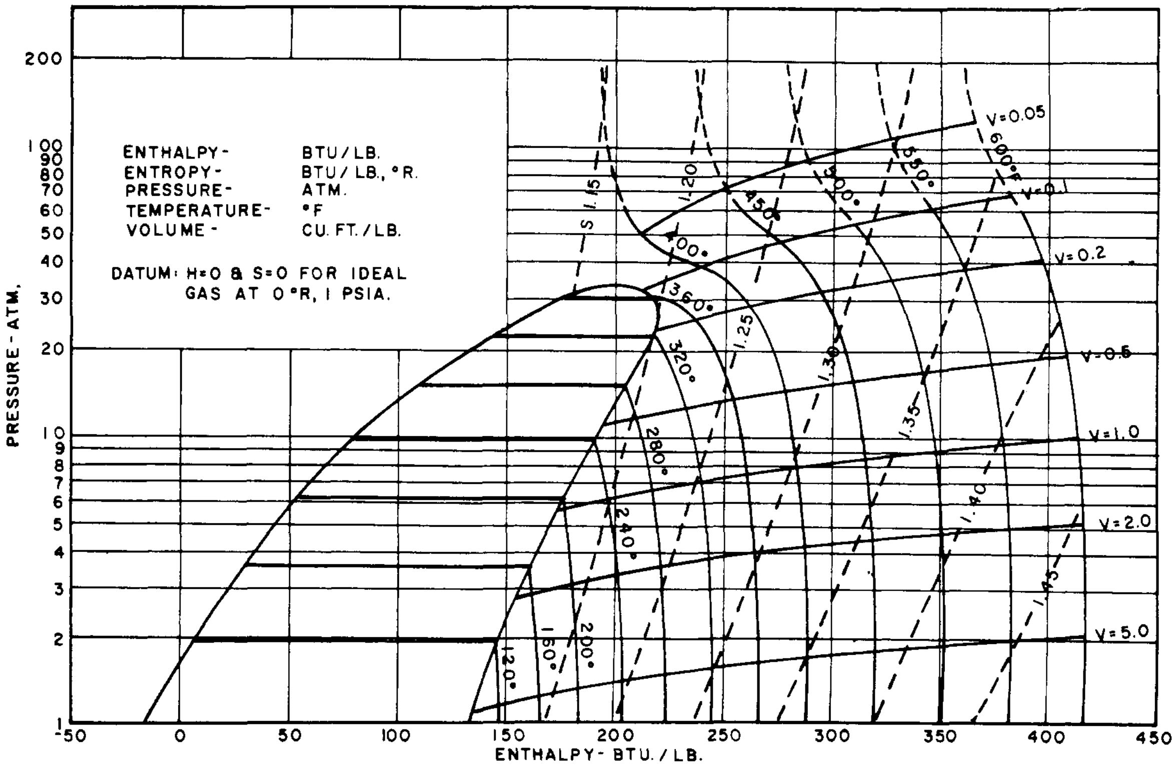

Figure 1. Pressure-enthalpy diagram for isopentane

Table IV. Thermodynamic Properties of Saturated Isopentane

(Datum: H and $S = 0$ for ideal gas at 0° R. and 1 p.s.i.a.)

Temp., °F.	Pressure		Volume, Cu. Ft./Lb.		Enthalpy, B.T.U./Lb.		Entropy, B.T.U./Lb., °R.	
	P.s.i.a.	Atm.	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
0	2.18	0.15	0.02440	31.00	−58.8	102.9	0.7807	1.1325
10	2.87	0.20	0.02461	23.99	−53.8	106.2	0.7918	1.1325
20	3.73	0.25	0.02480	18.79	−48.7	109.6	0.8023	1.1323
30	4.78	0.33	0.02501	14.92	−43.5	113.0	0.8131	1.1327
40	6.05	0.41	0.02522	11.98	−38.3	116.5	0.8236	1.1334
50	7.59	0.52	0.02544	9.69	−33.0	120.0	0.8340	1.1342
60	9.42	0.64	0.02567	7.92	−27.6	123.5	0.8445	1.1353
70	11.57	0.79	0.02590	6.53	−22.1	127.1	0.8549	1.1366
80	14.12	0.96	0.02614	5.43	−16.6	130.7	0.8651	1.1380
90	17.06	1.16	0.02639	4.54	−11.1	134.3	0.8751	1.1396
100	20.46	1.39	0.02664	3.83	−5.5	137.9	0.8852	1.1414
110	24.35	1.66	0.02691	3.25	0.2	141.5	0.8954	1.1434
120	28.79	1.96	0.02718	2.77	5.9	145.1	0.9051	1.1454
130	33.86	2.30	0.02747	2.40	11.6	148.8	0.9151	1.1478
140	39.46	2.69	0.02776	2.06	17.4	152.5	0.9247	1.1500
150	45.77	3.11	0.02807	1.78	23.2	156.1	0.9344	1.1524
160	52.84	3.60	0.02838	1.55	29.0	159.8	0.9437	1.1548
170	60.72	4.13	0.02870	1.35	34.9	163.5	0.9531	1.1573
180	69.49	4.73	0.02905	1.19	40.9	167.2	0.9626	1.1600
190	79.20	5.39	0.02942	1.04	46.9	170.9	0.9717	1.1626
200	89.92	6.12	0.02984	0.917	53.0	174.7	0.9809	1.1654
210	101.70	6.92	0.03025	0.810	59.1	178.4	0.9900	1.1681
220	114.70	7.80	0.03070	0.720	65.3	182.1	0.9992	1.1710
230	128.80	8.76	0.03115	0.636	71.7	185.7	1.0083	1.1736
240	144.2	9.81	0.03165	0.565	78.6	189.3	1.0182	1.1764
250	160.9	10.95	0.03221	0.500	85.9	192.8	1.0285	1.1791
260	179.1	12.19	0.03281	0.442	93.3	196.2	1.0387	1.1817
270	198.7	13.52	0.03350	0.390	101.7	199.5	1.0488	1.1842
280	219.9	14.96	0.03421	0.346	108.2	202.8	1.0589	1.1868
290	242.7	16.51	0.03498	0.307	115.7	206.1	1.0688	1.1894
300	267.2	18.18	0.03584	0.276	123.5	209.5	1.0792	1.1924
310	293.4	19.96	0.03684	0.249	131.6	212.9	1.0898	1.1954
320	321.4	21.87	0.03806	0.222	140.0	216.1	1.1003	1.1979
330	351.4	23.91	0.03960	0.195	148.8	218.5	1.1114	1.1997
340	383.2	26.08	0.04129	0.168	158.3	220.1	1.1232	1.2005
350	417.1	28.38	0.04375	0.138	169.0	219.7	1.1362	1.1988
360	453.0	30.82	0.04762	0.1055	181.7	216.1	1.1512	1.1932
370.1	494.7	33.66	0.06790	0.0679	202.9	202.9	1.1763	1.1763

demonstrated good consistency of the vapor pressure data from the two sources.

Saturation Volumes. The saturated liquid volumes were taken from the International Critical Tables (*13*) and covered the range from 86° F. to the critical point. From 0° to 80° F., the liquid volumes at 1 atm. were taken from API Research Project 44 (*8*). Changing the pressure from 1 atm. to the saturation pressure would have a negligible effect on the liquid volume in this range.

The saturated vapor volumes were taken from the work of Silberberg (*11*) for the temperature range from 130° F. to the critical point. Below 130° F., the *B-W-R* equation was employed using the vapor pressure data calculated from the modified Antoine equation.

Ideal Gas State Properties. The ideal gas state properties for isopentane were taken from API Research Project 44 (*6, 7*). Graphical interpolation of the enthalpy, H°, and the entropy, S°, was carried out to find the values at the proper intervals for the present work. The datum state was chosen to be identical to that used in the API Research Project 44—namely, the ideal gas state at absolute zero temperature and 1 p.s.i.a.

METHODS OF CALCULATION

The equations used to calculate the enthalpy and the entropy of isopentane in the superheated region and for the saturated vapor were formulated by substituting the *B-W-R* equation of state into rigorous thermodynamic relations between the properties in the real state and in the ideal gas state at the same temperature. The integrated expressions which were used are:

$$H = H^\circ + PV - RT - \frac{A_0}{V} - \frac{a}{2V^2} + \frac{a\alpha}{5V^2} - \frac{3}{T^2}\left[\frac{C_0}{V} - \frac{c}{\gamma} + \left(\frac{c}{\gamma} + \frac{c}{2V^2}\right)e^{-\gamma/V^2}\right]$$

$$S = S^\circ_{1\text{ p.s.i.a.}} + R\left[\ln\frac{V}{RT} - \frac{B_0}{V} - \frac{b}{2V^2}\right] - \frac{2}{T^3}\left[\frac{C_0}{V} - \frac{c}{\gamma} + \left(\frac{c}{\gamma} + \frac{c}{2V^2}\right)e^{-\gamma/V^2}\right]$$

In the latter equation, the R in the term, $\ln(V/RT)$, must be used in units of (cu. ft.-p.s.i.a.)/(pound$_m$, °R.) rather than (cu. ft.-atm.)/(pound$_m$, °R.), since this term arises from the $\ln V/V^\circ_{1\text{p.s.i.a.}}$ term of the integration, by replacing $V^\circ_{1\text{p.s.i.a.}}$ with (RT/P) where $P = 1$ p.s.i.a.

The latent heats of vaporization were determined by differentiating the modified Antoine equation and substituting it into the Clapeyron equation to give:

$$\Delta H_v = \frac{6.265\,PT}{(t + D)^2}\left(B - \frac{2C}{t + D}\right)(V_g - V_l)$$

From the smoothed latent heats and saturated vapor properties, the enthalpy and entropy of the saturated liquid were readily calculated. All of the computations were performed on a digital computer.

Table V. Thermodynamic Properties of Superheated Isopentane

(Datum: H and $S = 0$ for ideal gas at 0° R. and 1 p.s.i.a.)
(Units: H, B.t.u./lb.; S, B.t.u./lb. ° R.; V, cu. ft./lb.)

P, Atm.	Property	Temperature, ° F.									
		100	120	140	160	180	200	220	240	260	280
1	H	138.86	147.29	155.60	164.87	174.02	183.46	193.07	202.88	213.07	223.36
	S	1.1518	1.1667	1.1815	1.1961	1.2106	1.2251	1.2394	1.2536	1.2681	1.2825
	V	5.4310	5.6558	5.8772	6.0967	6.3136	6.5288	6.7426	6.9552	7.1667	7.3773
2	H			153.95	163.03	172.35	181.94	191.68	201.60	211.90	222.27
	S			1.1599	1.1748	1.1896	1.2044	1.2189	1.2333	1.2479	1.2624
	V			2.8334	2.9527	3.0696	3.1843	3.2974	3.4094	3.5199	3.6295
3	H				161.06	170.58	180.34	190.23	200.27	210.68	221.15
	S				1.1613	1.1765	1.1914	1.2062	1.2207	1.2355	1.2502
	V				1.9008	1.9851	2.0669	2.1471	2.2256	2.3030	2.3790
5	H						176.86	187.11	197.45	208.11	218.80
	S						1.1735	1.1887	1.2037	1.2189	1.2338
	V						1.1679	1.2227	1.2756	1.3268	1.3768
10	H									200.58	212.08
	S									1.1919	1.2080
	V									0.5844	0.6171

P, Atm.	Property	Temperature, ° F.									
		300	320	340	360	380	400	450	500	550	600
1	H	233.93	244.70	255.66	266.91	278.37	290.01	320.11	351.09	383.35	417.01
	S	1.2968	1.3110	1.3251	1.3389	1.3525	1.3659	1.3992	1.4330	1.4661	1.4984
	V	7.5871	7.7963	8.0048	8.2122	8.4197	8.6269	9.1431	9.6567	10.169	10.681
2	H	232.92	243.76	254.79	266.10	277.60	289.29	319.49	350.55	382.88	416.58
	S	1.2768	1.2911	1.3053	1.3191	1.3328	1.3463	1.3797	1.4136	1.4467	1.4790
	V	3.7382	3.8461	3.9535	4.0599	4.1662	4.2720	4.5350	4.7961	5.0555	5.3138
3	H	231.89	242.80	253.89	265.27	276.82	288.56	318.87	350.00	382.40	416.16
	S	1.2647	1.2790	1.2934	1.3073	1.3210	1.3345	1.3681	1.4020	1.4353	1.4676
	V	2.4542	2.5286	2.6023	2.6754	2.7480	2.8202	2.9988	3.1753	3.3507	3.5247
5	H	229.73	240.81	252.05	263.55	275.22	287.07	317.59	348.90	381.44	415.31
	S	1.2486	1.2632	1.2777	1.2917	1.3056	1.3193	1.3530	1.3872	1.4206	1.4530
	V	1.4255	1.4733	1.5205	1.5669	1.6127	1.6580	1.7693	1.8787	1.9867	2.0933
10	H	223.67	235.31	247.02	258.93	270.95	383.11	314.26	346.05	378.96	413.13
	S	1.2237	1.2389	1.2540	1.2686	1.2829	1.2969	1.3314	1.3661	1.3998	1.4326
	V	0.6479	0.6772	0.7052	0.7323	0.7586	0.7843	0.8461	0.9054	0.9630	1.0193
20	H		219.89	233.87	247.40	260.67	273.83	306.81	339.87	373.70	408.57
	S		1.2044	1.2223	1.2389	1.2547	1.2699	1.3065	1.3425	1.3772	1.4106
	V		0.2594	0.2840	0.3051	0.3242	0.3417	0.3812	0.4169	0.4501	0.4817
30	H				225.79	245.17	261.19	297.88	332.88	367.97	403.73
	S				1.2054	1.2285	1.2472	1.2879	1.3260	1.3620	1.3963
	V				0.1359	0.1655	0.1854	0.2226	0.2522	0.2782	0.3019
40	H					194.23	237.00	286.51	324.88	361.73	398.60
	S					1.1647	1.2147	1.2701	1.3118	1.3496	1.3850
	V					0.0500	0.0898	0.1398	0.1686	0.1917	0.2119
50	H					186.39	209.89	271.94	315.82	355.01	393.24
	S					1.1538	1.1813	1.2508	1.2984	1.3386	1.3752
	V					0.0431	0.0499	0.0891	0.1183	0.1399	0.1580
60	H					182.90	203.76	258.17	306.41	348.11	387.79
	S					1.1483	1.1726	1.2334	1.2857	1.3284	1.3665
	V					0.0401	0.0440	0.0624	0.0868	0.1064	0.1228
80	H					179.08	198.50	246.08	292.19	336.01	377.77
	S					1.1413	1.1639	1.2170	1.2670	1.3118	1.3519
	V					0.0367	0.0389	0.0463	0.0572	0.0699	0.0820
100	H					176.93	195.90	241.70	285.55	328.38	370.40
	S					1.1364	1.1585	1.2096	1.2572	1.3010	1.3413
	V					0.0346	0.0362	0.0409	0.0469	0.0541	0.0620
150	H					174.33	193.00	237.77	280.25	321.66	362.68
	S					1.1280	1.1498	1.1997	1.2458	1.2882	1.3275
	V					0.0314	0.0324	0.0350	0.0377	0.0406	0.0437
200	H					173.49	192.15	236.90	279.29	320.56	361.40
	S					1.1221	1.1439	1.1937	1.2397	1.2820	1.3212
	V					0.0293	0.0301	0.0319	0.0337	0.0355	0.0373

RESULTS

The results are presented in Tables IV and V and in Figure 1. It should be remembered that the *B-W-R* equation gave a poor fit to the *P-V-T* points above 60 atm., so the tabulated and graphed results are probably not accurate much above 60 atm.

The internal consistency of the results was checked by using the relations:

$$\left(\frac{\partial \ln P}{dH}\right)_S = \frac{1}{PV}$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

The slopes measured on the appropriate graphs were compared with the quantities on the right hand side of the above equations. Agreement was within 0.4% at the 10 points that were checked. The error introduced into the entropy and enthalpy owing to the use of the *B-W-R* equation of state is estimated at about 1% in the enthalpy and 0.5% in the entropy. This error was estimated by observing the variation in *H* and *S* as the *B-W-R* equation was made to fit the experimental data more and more closely.

NOMENCLATURE

A,B,C,D = constants in the modified Antoine equation
$A_0,B_0,C_0,$ a,b,c,α,γ = constants in the Benedict-Webb-Rubin equation of state
H = enthalpy of real gas state, B.t.u./lb.
H° = enthalpy of ideal gas state, B.t.u./lb.
ΔH_v = latent heat of vaporization, B.t.u./lb.
P = absolute pressure, atm.
P_c = critical pressure, atm.
R = gas constant for isopentane
S = entropy of real gas state, B.t.u./lb., ° R.
S° = entropy of ideal gas state, B.t.u./lb., ° R.
t = temperature, ° F.
T = absolute temperature, ° R., = t ° F. + 459.688
V = specific vapor volume, cu. ft./lb.
V_g = specific volume of saturated vapor, cu. ft./lb.
V_l = specific volume of saturated liquid, cu. ft./lb.
z = compressibility factor, pV/RT

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Compressibility Factors for Helium-Nitrogen Mixtures

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Experimental compressibility factors for the helium-nitrogen system from −140° to 0° C. up to 500 atm. were determined by the Burnett method. A total of 1186 compressibility factors for the two pure components and six mixtures are reported. Derived thermodynamic properties of this system are compared with recent calorimetric determinations.

THIS PAPER presents compressibility factors for the helium-nitrogen system from 0° to 140° C. at pressures to 500 atm. Compressibility data for this system have been reported by a number of previous investigators, but no data in the present temperature range have been published. Pfefferle, Goff, and Miller (*13*), Kramer and Miller (*6*), and Witonsky and Miller (*17*) have published data on the helium-nitrogen system at temperatures from 30° to 475° C. and at pressures to 100 atm. Other data have been collected by Ku (*7*) at 38.48° and 100° C. up to 295 atm. Miller, Brandt, and Stroud (*10*) report compressibility factors at 70° F. up to 4000 p.s.i.a. Such an abundance of data has been published for pure helium and pure nitrogen that it will be left to the writers of monographs to review these data. The present authors collected data for the pure components

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