

Thermodynamic Properties of *n*-Propanol

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Selected values of the critical constants, vapor pressure, saturated liquid volume, saturated vapor volume, normal boiling point, latent heat of vaporization, and calculated thermodynamic properties for *n*-propanol are presented. Major emphasis is on literature data since 1962, with the resolution of a previous conflict of literature vapor volumes, heats of vaporization, and vapor enthalpies from 140–225°C.

This work was undertaken for the primary purpose of resolving a conflict of experimental literature values for the heat of vaporization of *n*-propanol between 111° and 200°C. The pressure-enthalpy diagram of Eubank and Smith (8) is also corrected to reflect recent values of C_p° with the result that isothermal enthalpy changes in the vapor at 300°F (149.1°C) are reduced to better agree with those calculated from *PVT* data (7, 14).

PHYSICAL CONSTANTS

The physical and conversion constants (2) used in this work are given in Table I. The critical constants given in Table I are those of Ambrose and Townsend (1) since those of Young (21) in Table II appear less accurate because the instruments used were not of modern quality.

VAPOR PRESSURE

The vapor pressure from 65.559–104.576°C was determined by Biddiscombe et al. (4) with a normal boiling point of 97.151°C as compared to 97.08°C by Brown and Smith (5). Ambrose and Townsend determined the vapor pressure from 132.31–263.56°C (critical temperature).

Table I. Physical and Conversion Constants

Constant	Value
Critical temperature, K	536.71 (1)
Critical pressure, atm	51.02 (1)
Critical density, g/cm ³	0.2754 (1)
Critical volume, cm ³ /mol	218.2 (1)
Normal boiling point, °C/760 mm Hg	97.15 (4)
Molecular weight	60.097
Gas constant, <i>R</i>	82.05606 atm-cm ³ /mol-°F

Table II. Critical Constants of *n*-Propanol

Investigator	T_c , K	P_c , atm	ρ_c , g/ml	V_c , ml/mol
Young (21), 1910	536.85	50.16	0.273	219
Ambrose and Townsend (1), 1963	536.71	51.02	0.2754	218.2

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Biddiscombe et al. fitted their vapor pressure data within ± 0.2 mm by the Antoine equation

$$\log_{10} P = 7.72911 - \frac{1428.977}{197.585 + t} \quad (1)$$

where

$$P = \text{pressure, mm Hg}$$

$$t = \text{temperature, } ^\circ\text{C}; 65 < t < 105$$

This equation gives the vapor pressure to 0.1 mm Hg. Ambrose and Townsend represented their vapor pressure data within $\pm 0.4\%$ with the equation

$$\log_{10} P = 4.90882 - \frac{1428.977}{197.585 + t} - 4.19 \times 10^{-4} t + 2.43 \times 10^{-8} (t - 195)^3; t > 120 \quad (2)$$

where

$$P = \text{vapor pressure, atm}$$

$$t = \text{temperature, } ^\circ\text{C}$$

These equations were differentiated to obtain dP/dT for the Clapeyron equation.

A comparison of the vapor pressures determined by Ramsay and Young (17), by Ambrose and Townsend, and by Biddiscombe et al. is shown in Figure 1 where the calculated pressures are from Equation 1 below 120°C and Equation 2 above that temperature. These calculated pressures were also the final selected values and appear in Tables III and IV. The data of

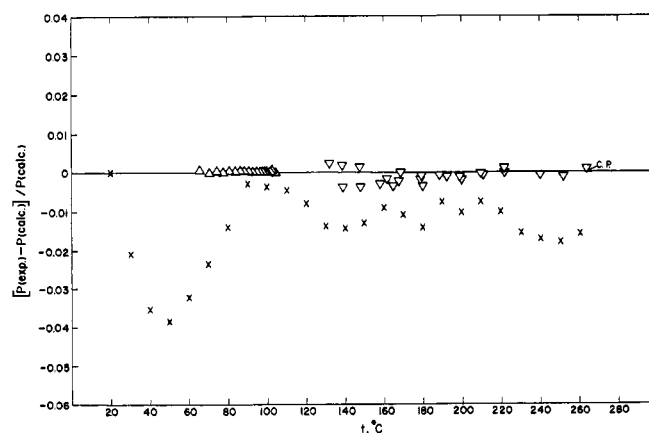


Figure 1. Difference plot of vapor pressure

- X Ramsay and Young (17)
- ▽ Ambrose and Townsend (1)
- △ Biddiscombe et al. (4)

Table III. Calculated Saturation Properties of *n*-Propanol

<i>t</i> , °C	<i>P</i> , atm	<i>dP/dt</i> , atm/°C	<i>v_l</i> , ml/g	<i>v_v</i> , ml/g	<i>λ</i> , cal/g
25	0.02682	0.001781	1.250	14646 ^a	188.2 (8)
70.75	0.3334	0.01524	1.315	1377 ^a	174.5 (9)
86.85	0.6674	0.02714	1.341	714 ^a	168.4
97.15	0.9999	0.03787	1.360	484 ^a	163.9
104.95	1.3334	0.04793	1.375	367 ^a	160.4
111.35	1.6703	0.05758	1.387	296 ^a	157.7
141.65	4.300	0.1227	1.455	110 (2)	133.7 ^a
154.18	6.029	0.1601	1.493	74.1	120.2 ^a
165.85	8.070	0.2007	1.531	57.8	120.0 ^a
176.93	10.447	0.2447	1.575	45.4	116.8 ^a
186.29	12.830	0.2861	1.612	37.0	112.6 ^a
192.77	14.700	0.3170	1.646	31.8	107.8 ^a
201.01	17.360	0.3592	1.688	26.0	102.2 ^a
206.40	19.282	0.3884	1.719	24.2	101.3 ^a
225.12	27.201	0.5004	1.860	16.18	86.4 ^a
232.54	30.934	0.5499	1.936	13.48	77.7 ^a
240.11	35.130	0.6031	2.036	11.30	69.4 ^a
245.33	38.267	0.6416	2.117	9.671	60.8 ^a
250.22	41.400	0.6791	2.223	8.425	53.3 ^a
254.61	44.381	0.7140	2.344	7.369	45.8 ^a
256.69	45.851	0.7310	2.423	6.784	40.9 ^a
263.56	51.023	0.7894	3.631	3.631	0

^a Calculated by Clapeyron equation.

Table IV. Selected Saturation Properties of *n*-Propanol

<i>t</i> , °C	<i>P</i> , atm	<i>dP/dt</i> , atm/°C	<i>v_l</i> , ml/g	<i>v_v</i> , ml/g	<i>λ</i> , cal/g
25	0.02683	0.001781	1.250	14646	188.2
30	0.03711	0.002357	1.256	10815	187.0
40	0.06816	0.003972	1.270	6120	184.2
50	0.1193	0.006407	1.285	3618	181.2
60	0.1999	0.009912	1.299	2230	178.1
70	0.3221	0.01480	1.314	1423	174.7
80	0.5017	0.02142	1.330	935.4	171.0
90	0.7575	0.03013	1.347	632.0	167.0
100	1.113	0.04134	1.365	437.4	162.8
110	1.594	0.05543	1.385	309.6	158.4
120	2.232	0.07280	1.406	222.7	153.3
130	3.059	0.09368	1.430	163.2	147.9
140	4.104	0.1183	1.455	121.8	142.3
150	5.403	0.1468	1.482	92.3	136.6
160	6.991	0.1795	1.514	71.0	130.8
170	8.907	0.2165	1.549	55.3	124.8
180	11.189	0.2578	1.586	43.4	118.3
190	13.878	0.3036	1.629	34.4	111.4
200	17.017	0.3538	1.686	27.3	103.9
210	20.651	0.4086	1.748	21.8	96.0
220	24.832	0.4682	1.820	17.5	87.8
230	29.616	0.5327	1.911	14.0	78.4
240	35.065	0.6022	2.04	11.0	67.2
250	41.255	0.6774	2.21	8.35	52.6
260	48.271	0.7584	2.62	5.69	30.3
263.56	51.023	0.7894	3.63	3.63	0

Ramsay and Young are lower by about 1% of the pressure throughout much of the temperature range.

SATURATED LIQUID VOLUME

The saturated liquid volume was determined by Ramsay and Young from 0°C to the critical point, 25°C by Chu and Thompson (6), and from 141.65°C to the critical point by Ambrose and Townsend. Figure 2 shows the data of Ramsay and Young to be in excellent agreement with those of Ambrose and Townsend with differences generally less than 0.5%. The 240.11°C point of Ambrose and Townsend is not in line with the rest of their data or that of Ramsay and Young. The selected liquid volumes of Table IV are identical to those of Ramsay and Young from 0–140°C. From 140–260°C, the selected values are read from Figure 2 to place equal weight on the two data sets.

SATURATED VAPOR VOLUME

Ramsay and Young determined the saturated vapor volume from 80°C to the critical, while more recently Ambrose and Townsend measured from 141.65°C to the critical.

Figure 3 shows the vapor volumes of Ambrose and Townsend to be significantly lower from those of Ramsay and Young from 140–210°C. The difference is about 8% at 140°C, 14% at 150°C, 11% at 160°C, 7% at 170°C, 5% at 180°C, and then decreases uniformly to less than 0.2% at 210°C. Differences between the two data sets from 210°C to near the critical point are generally less than 0.5% and within the combined uncertainty claimed by the authors. The magnitude of the disagreement near 150°C is surprisingly large although the vapor volumes of Ramsay and Young have proved to be high for compounds for which modern PVT data exist. For example, Lashakov (13) found his superheated methanol vapor volumes 4% lower than Ramsay and Young as did Keyes and Felsing (11) for ethyl ether vapor.

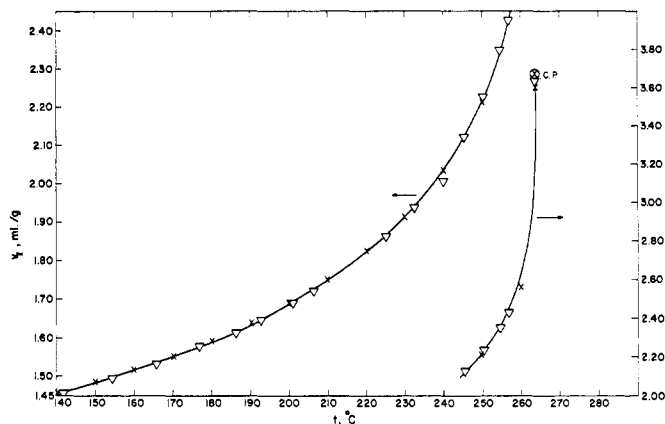


Figure 2. Saturated liquid volumes

- ▽ Ambrose and Townsend (1)
- × Ramsay and Young (17)
- ⊙ Young (21)

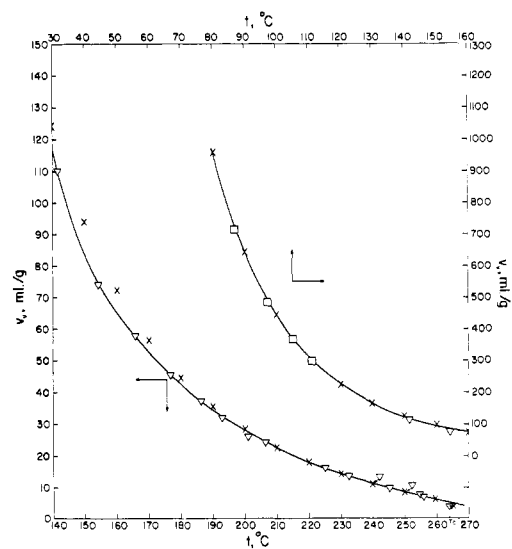


Figure 3. Saturated vapor volumes

- × Ramsay and Young (17)
- ▽ Ambrose and Townsend (1)
- Calcd from Matthews and McKetta (15)

HEAT OF VAPORIZATION

Measurements of the latent heat of vaporization were made at 25°C by Wadso (20), 11.31 ± 0.02 K-cal/mol, and by McCurdy and Laidler (16), 11.13 K-cal/mol. Bennewitz and Rossner (3) measured 9.98 K-cal/mol at 96.6°C near the normal boiling point. Matthews and McKetta (15) measured from 70.8–114°C with claimed accuracies of (1/1000) or better. Eubank and Smith (8) made measurements on a flow calorimeter from 149.1–260.2°C with indicated accuracy of 2 cal/g. These values appear on Figure 4 along with those calculated from the Clapeyron equation.

CALCULATED SATURATED PROPERTIES

The Clapeyron equation,

$$\frac{dP}{dt} = \frac{\lambda}{T(v_v - v_l)} \quad (3)$$

may be used to calculate the heat of vaporization from the vapor volume (or vice versa) once the vapor pressure curve and the liquid volumes are established. From 25–111.35°C, the experimental heats of vaporization of Wadso and of Matthews and McKetta were used to calculate vapor volumes as given in Table III. Figure 3 shows these calculated vapor volumes to be in reasonable agreement with those measured by Ramsay and Young from 80–110°C with the latter values about 1.5% higher.

Next the vapor volumes of Ambrose and Townsend were used to calculate heats of vaporization from 141.65–256.69°C as given in Table III and Figure 4. The values are somewhat

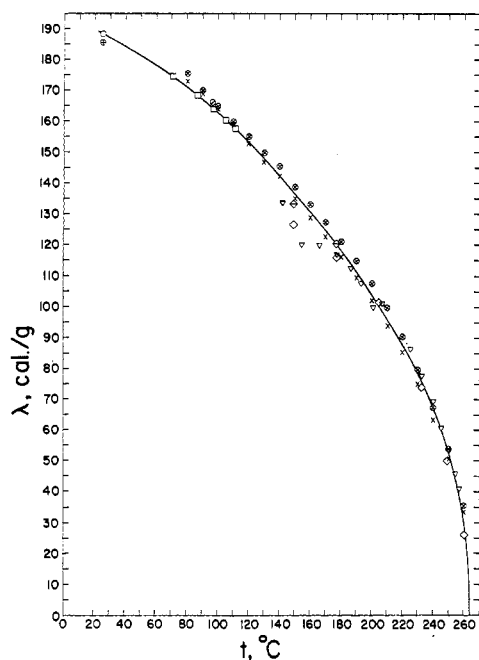


Figure 4. Heats of vaporization

- Bennewitz and Rossner (3)
- ⊕ McCurdy and Laidler (16)
- Wadso (20)
- ◇ Matthews and McKetta (15)
- ▽ Calcd from Ambrose and Townsend (1)
- ◇ Eubank and Smith (8)
- ◇ Eubank and Smith, Corrected
- × Ramsay and Young (17)
- ⊗ Ramsay and Young calcd with (dP/dT) of Ambrose and Townsend
- Selected curve

irregular from 141.65–225.12°C, the region of disagreement for vapor volumes. Figure 4 also contains latent heats calculated by Ramsay and Young with their vapor pressure data and calculated from the orthobaric volumes of Ramsay and Young with the present vapor pressure equations.

From 25–111°C the heats of vaporization of Wadso and of Matthews and McKetta are accepted with the calculated values of Ramsay and Young about 1.5% high from 80–111°C. Above 200°C, Figure 4 shows the data of Eubank and Smith to be in agreement with values calculated from the vapor volumes of both Ambrose and Townsend and Ramsay and Young.

Between 111° and 200°C, the calculated values of Ramsay and Young are considerably higher than the irregular values computed from the vapor volumes of Ambrose and Townsend. Although two experimental points of Eubank and Smith (at 149.1° and 176.9°C) support the lower trend of Ambrose and Townsend, Figure 4 proves that these data are not in line with the agreed curves below 111°C and above 200°C. The curve must lie closer to the values of Ramsay and Young which should, at least, provide an upper bound. The selected curve is shown on Figure 4 corresponding to the values in Table IV.

VAPOR ENTHALPY

Martin et al. (14) noted the low value of the heat of vaporization at 300°F (149.1°C) of Eubank and Smith. The selected value of Table IV is 247 Btu/lb which compares well with Martin's value of 249.5 and 249.6 of Cosner et al. (?); both of the latter reviews are based on the data of Ramsay and Young. Martin stated that the data of Eubank and Smith are good but the method of preparation of their graphs was at fault. Re-examination of that data indicates this analysis to be correct for *n*-propanol. Specifically, a flow calorimeter produces point enthalpy values as shown on Figure 5. These points can be inside the saturation dome as well as outside. The dew point curve is determined by extending an isotherm drawn through the superheated vapor phase data to a horizontal line at the known vapor pressure. Figure 1 of the original article by Eubank and Smith shows two data points of the 300°F isotherm but at about the vapor pressure. It was assumed that these points were in the superheated vapor region, but it is now apparent that they were inside the two-phase region.

Figure 5 is the corrected diagram which differs from the original figure only in the placement of the dew point curve below 400°F and the superheated vapor isotherms below 300 psia which is discussed below. The corrected heats of vaporization are 240 Btu/lb (133.3 cal/g) and 217 Btu/lb (120.7

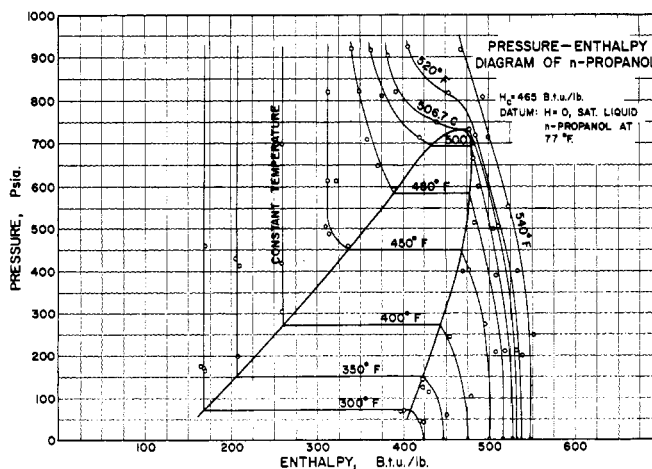


Figure 5. Corrected enthalpy diagram

cal/g) at 300°F (149.1°C) and 350°F (176.9°C), respectively. The value at 350°F is then in exact agreement with the selected curve but that at 300°F is 2.8% low. It should be noted that the dew point curve at the lowest isotherm is particularly difficult to fix as (1) there are few superheated vapor data due to a lower pressure bound of about 40 psia of the calorimeter and (2) there is no information on the location of the dew point from a lower, adjacent isotherm.

A second correction appears on Figure 5 to the vapor enthalpy isotherms of Eubank and Smith which were anchored to the ideal gas state enthalpy H° at zero pressure. Values of H° were calculated from the ideal gas state heat capacities C_p° of Kobe et al. (12) and the equation of Jones and Bowden (10) for the heat of vaporization at 77°F:

$$H^\circ(t) = \lambda \Big|_{77^\circ\text{F}} + \int_{77^\circ\text{F}}^t C_p^\circ dT \quad (4)$$

where $H = 0$ for saturated liquid at 77°F (25°C). The isothermal enthalpy change at 77°F for the vapor is neglected in Equation 4, as the vapor pressure is but 0.02683 atm. The value calculated at 300°F was 442 Btu/lb which is higher than that of Martin of 435 and Cosner of 431. At 540°F the calculated value was 573 compared to 557 and 556.

Martin has calculated changes of H° with temperature with an equation for C_p° which agrees with the measurements of Matthews and McKetta, Sinke and DeVires (19), and Jatkar (9) but yields values 3–4% lower than Kobe which accounts for the higher ideal gas state enthalpies of Eubank and Smith. With the heat of vaporization of Wadso at 77°F and the equation of Martin for C_p° , the following values of H° were calculated: 428.0 (300°F), 451.4 (350°F), 475.9 (400°F), 501.5 (450°F), 517.3 (480°F), 528.1 (500°F), 531.7 (506.7°F), 539.0 (520°F), and 550.1 (540°F). These results differ less than 2 Btu/lb from those of the TRC tables (18) but are somewhat lower than Martin who gave 345.9 Btu/lb as the latent heat at 77°F which is about 7 Btu/lb higher than the later experimental value of Wadso.

The shift of H° produces significantly lower values for the isothermal change of enthalpy from zero to the saturation pressure. In particular, Martin found the value at 300°F of 45 Btu/lb of Eubank and Smith to be much higher than their calculated value of about 12. Figure 5 provides a corrected value of 17 Btu/lb which is in excellent agreement with 15.6 Btu/lb obtained by Cosner. Both Martin and Cosner integrated the PVT data of Ramsay and Young—the former using an analytical equation of state and the latter numerical integration. Since the vapor volumes of Ramsay and Young are about 1% high at saturation, calculated enthalpy changes should be low

by 5–15%. Calculations also show an underestimation of the enthalpy change from measured second virial coefficients with a truncated Berlin equation of state. This equation provides linear isotherms, while Figure 5 shows considerable curvature indicating the importance of the higher virial coefficients at pressures approaching saturation.

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