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Thermodynamic Properties of n-Propyl Alcohol

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VARIOUS USES of n-propyl alcohol as a solvent and chemical intermediate prompted a study of its derived thermodynamic properties. Sufficient volumetric, thermal, and vapor pressure data are available in the literature to evaluate these properties from 77° to 540° F. and pressures up to 700 p.s.i.a.

Extensive measurements of the volumetric behavior of n-propyl alcohol were made by Ramsey and Young (6) over the range from 30° to 263.6° C. and pressures from 800 to 53,480 mm. of mercury. Foz Gazulla, Morcillo, and Mendes (2) measured vapor densities in the low pressure range from 100 to 760 mm. of mercury and the temperature range from 75° to 130° C. Saturated vapor and liquid densities were reported by Young (11).

The vapor pressure–temperature data for n-propyl alcohol have been summarized by Stull (9).

The heat capacity data at zero pressure, calculated from spectroscopic measurements and reported by Kobe, Harrison, and Pennington (4), compare favorably with the calorimetric data of Sinke and De Vries (8).

Calorimetric measurements of the heat of vaporization of n-propyl alcohol were reported by Bennewitz and Rossner (1). The normal boiling point data and the heat of vaporization at the normal boiling point were summarized in International Critical Tables (3).

The critical constants $T_c = 537.3°$ K., $P_c = 50.2$ atm., and $V_c = 220$ cc./gram mole are reported by Lyderson, Greenkorn, and Hougen (5) and these values were used in this work. The molecular weight of n-propyl alcohol used in all the calculation in this work was 60.09. The calculations were based on 1 pound of n-propyl alcohol, and the enthalpy and entropy were set equal to zero at 77° F. for the saturated liquid at its vapor pressure.

VAPOR PRESSURE AND HEATS OF VAPORIZATION

The vapor pressure data reported by Stull (9) were fitted to the following empirical equation:

$$\log P_v = (B/T - 43) + C + D(T - 43) + E(T - 43)^2 \qquad (1)$$

To improve the fit, Equation 1 was applied over a low and a high temperature range. The constants obtained were:

Constant	Temperature Range, ° K.	
	273–373	373–537
B	−1645.194	−2173.147
C	6.66707	11.16614
D	0.590031×10^{-2}	-0.620663×10^{-2}
E	-6.46252×10^{-6}	3.58429×10^{-6}

The latent heats of vaporization were calculated with the thermodynamically rigorous Clapeyron equation

$$\frac{dP_v}{dT} = \frac{\Delta H_v}{T(V_v - V_L)} \qquad (2)$$

The necessary temperature derivatives of the vapor pressure were obtained from Equation 1. The saturated vapor (V_v) and liquid (V_L) volumes of Young allowed evaluation

of ΔH_v. The heats of vaporization used in preparing Table I are smoothed values calculated from Equation 2. At atmospheric pressure the value given in Table I is 295.0 B.t.u. per pound and compares favorably with 295.9 B.t.u. per pound reported in International Critical Tables (3), less favorably with 299.0 B.t.u. per pound reported by Bennewitz and Rossner (1).

VAPOR PHASE THERMODYNAMIC PROPERTIES

Residual volumes were calculated from the volumetric data of Ramsey and Young (6). Low pressure data on the high temperature isotherms were not reported. An extrapolating equation was developed for this low pressure vapor region based on dimerization of the n-propyl alcohol in the vapor phase. The data of Foz Gazulla, Morcillo, and Mendes (2) were used to confirm the extrapolated results. These two sources of volumetric data had so few common values that no direct comparison was possible.

The curves of residual volume vs. pressure were prepared and used to calculate the fugacity coefficients. The relationship used was

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

Equation 3 was evaluated graphically.

The enthalpies of the superheated vapor were calculated as differences between the enthalpy of the gas at pressure P and the value in the zero pressure or ideal state for each isotherm, The thermodynamic relationship used was

$$(H - H°)_T = \int_0^P \left[T \left(\frac{\partial \alpha}{\partial T} \right)_P - \alpha \right] dP \qquad (4)$$

To integrate Equation 4, a curve of α vs. temperature was prepared by cross-plotting the α-pressure diagram. The derivatives, $T \left(\frac{\partial \alpha}{\partial T} \right)_P$, were evaluated numerically using the Gregory-Newton backward and forward interpolation formulas (10) at the ends of the curves and Stirling's formula (7) in the central position. A plot of $T \left(\frac{\partial \alpha}{\partial T} \right)_P$ was prepared and Equation 4 evaluated graphically.

The entropies of the superheated vapor were calculated as differences between the entropy of the gas at pressure P and the ideal gas state at zero pressure by the expression

$$(S - S°)_T = \int_0^P - \left(\frac{\partial V}{\partial T} \right)_P dP \qquad (5)$$

When the residual volume is substituted in Equation 5, the integral becomes indeterminate at the lower limit. Equation 5 can be evaluated from $P = 0$ to $P = P^*$, an ideal gas state at unit fugacity. When this is substracted from Equation 5, the lower limit $P = 0$ is eliminated and the result is

$$(S - S^*)_T = (S - S°)_T = \int_{P*}^P \left(\frac{\partial \alpha}{\partial T} \right)_P dP - \int_{P*}^P \left(\frac{R}{P} \right) dP \qquad (6)$$

Equation 6 was evaluated using the results of Equations

Table I. Thermodynamic Properties of Saturated n-Propyl Alcohol

Temp., °F.	Pressure, P.S.I.A.	Volume, Cu. Ft./Lb.		Enthalpy, B.t.u./Lb.			Entropy, B.t.u./Lb.-° R.			Fugacity Ratio, f/P
		Liquid	Vapor	Liquid	Vapori-zation	Vapor	Liquid	Vapori-zation	Vapor	
77	0.39	0.0200	244.7	0.0	337.5	337.5	0.0	0.629	0.629	0.997
100	0.85	0.0203	116.4	12.60	333.0	345.6	0.103	0.595	0.698	0.994
140	2.83	0.0208	37.26	35.74	324.5	360.0	0.243	0.541	0.784	0.986
180	7.94	0.0214	13.98	60.24	315.6	375.9	0.358	0.493	0.851	0.973
280	14.696	0.0217	7.86	90.02	295.0	385.0	0.455	0.442	0.897	0.959
220	19.17	0.0219	6.21	99.81	291.8	390.0	0.486	0.429	0.915	0.952
260	40.18	0.0231	2.94	139.4	268.4	402.7	0.580	0.373	0.953	0.924
300	76.17	0.0237	1.55	165.4	249.6	415.0	0.659	0.328	0.987	0.886
340	132.9	0.0249	0.880	208.9	218.8	427.7	0.752	0.274	1.026	0.842
380	216.5	0.0265	0.530	243.6	194.1	437.7	0.823	0.231	1.054	0.788
420	333.1	0.0289	0.321	284.0	160.6	445.0	0.905	0.182	1.087	0.747
460	488.2	0.0320	0.186	329.7	116.1	445.8	0.977	0.126	1.103	0.687
500	688.5	0.0410	0.0995	380.6	58.1	440.0	1.053	0.060	1.113	0.652
507	737.9	0.0587	0.0587	414.5	0.0	414.5	1.115	0.0	1.115	...

3 and 4. Dividing Equation 4 by T and substracting from this, R times Equation 3 gives the first integral in Equation 6. Thus:

$$(S - S°)_T = \left(\frac{H - H°}{T}\right) - R \ln\left(\frac{f}{P}\right) - R \ln\left(\frac{P}{P^*}\right) \qquad (7)$$

Equation 7 was used to evaluate the superheated vapor entropy values.

The ideal gas, or zero pressure enthalpies were calculated from the heat capacity data of Kobe, Harrison, and Pennington (4) with the expression

$$dH = C_p° \, dT \qquad (8)$$

The ideal gas entropy values were obtained from the expression

$$dS = C_p°/T \, dT \qquad (9)$$

Saturated enthalpy values were obtained by plotting a temperature-enthalpy diagram and extrapolating the isobars to the saturated temperature. The saturated entropy values were obtained in a similar manner on a temperature-entropy diagram.

Enthalpy and entropy data for the saturated liquid were obtained by subtracting the enthalpy and entropy of vaporization from their saturated vapor values. The data were smoothed by plotting on enthalpy-entropy, tempera-
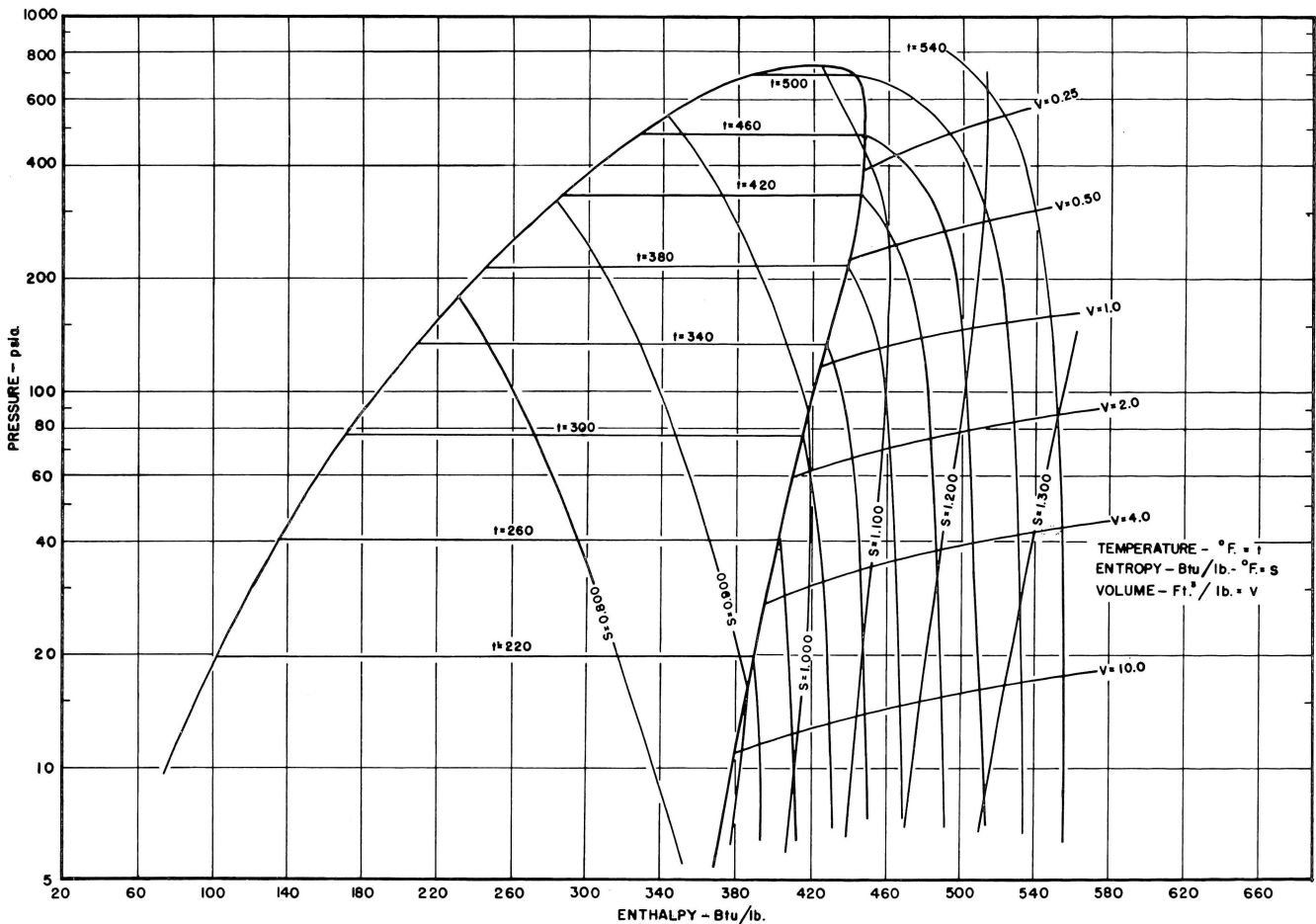

Figure 1. Pressure-enthalpy diagram for n-propyl alcohol

Reference state: $H = 0$, $S = 0$ at 77° F., saturated liquid

Table II. Thermodynamic Properties of Superheated n-Propyl Alcohol

Temp., °F.	Volume, Cu. Ft./Lb.	Enthalpy, B.t.u./Lb.	Entropy, B.t.u. per Lb.-° R.	Fugacity, Ratio, f/P
		0 P.S.I.A.		
77	Undefined	337.7	0.509	1.000
100		346.0	0.604	1.000
140		361.3	0.732	1.000
180		377.4	0.833	1.000
220		394.4	0.918	1.000
260		412.1	0.993	1.000
300		430.6	1.058	1.000
340		450.5	1.119	1.000
380		469.9	1.174	1.000
420		490.6	1.226	1.000
460		512.0	1.275	1.000
500		534.1	1.321	1.000
540		556.5	1.362	1.000
		10 P.S.I.A. (190° F.ᵃ)		
220	11.414	392.5	0.915	0.9708
260	11.803	410.6	0.990	0.9795
300	13.349	429.4	1.056	0.9838
340	14.094	449.2	1.117	0.9870
380	14.837	468.6	1.172	0.9892
420	15.565	489.5	1.225	0.9908
460	16.294	511.2	1.274	0.9920
500	17.011	533.4	1.321	0.9927
540	17.743	556.0	1.361	0.9934
		14.696 P.S.I.A. (208 ° F.ᵃ)		
220	7.932	392.5	0.913	0.9526
260	8.201	409.7	0.988	0.9709
300	9.016	429.1	1.054	0.9770
340	9.532	448.7	1.116	0.9812
380	10.041	468.4	1.171	0.9843
420	10.546	489.2	1.224	0.9867
460	11.047	510.8	1.273	0.9883
500	11.545	533.0	1.319	0.9899
540	12.043	555.7	1.359	0.9913
		25 P.S.I.A. (233 ° F.ᵃ)		
240	4.712	395.6	0.934	0.9451
260	4.883	407.5	0.971	0.9512
300	5.373	428.4	1.037	0.9610
340	5.530	447.5	1.098	0.9681
380	5.837	467.2	1.155	0.9734
420	6.141	488.3	1.217	0.9774
460	6.442	510.0	1.256	0.9804
500	6.739	532.4	1.302	0.9828
540	7.032	554.9	1.346	0.9849
		50 P.S.I.A. (273 ° F.ᵃ)		
280	2.377	410.0	0.973	0.9167
300	2.441	422.1	1.009	0.9244
340	2.677	444.2	1.072	0.9375
380	2.842	464.5	1.129	0.9476
420	3.005	486.2	1.181	0.9555
460	3.160	505.7	1.231	0.9618
460	3.160	505.7	1.231	0.9618
500	3.315	530.8	1.277	0.9667
540	3.464	553.8	1.322	0.9706

ᵃ Saturated temperature.

Temp., °F.	Volume, Cu. Ft./Lb.	Enthalpy, B.t.u./Lb.	Entropy, B.t.u. per Lb. ° R.	Fugacity Ratio, f/p
		100 P.S.I.A. (319° F.ᵃ)		
340	1.243	436.3	1.042	0.8804
380	1.349	458.8	1.101	0.9008
420	1.439	481.5	1.155	0.9155
460	1.526	504.2	1.210	0.9274
500	1.610	527.5	1.252	0.9368
540	1.690	550.9	1.296	0.9440
		150 P.S.I.A. (345° F.ᵃ)		
360	0.803	438.4	1.051	0.8423
380	0.848	452.2	1.082	0.8561
420	0.928	476.3	1.138	0.8772
460	0.984	499.8	1.189	0.8957
500	1.044	524.0	1.236	0.9098
540	1.104	548.0	1.281	0.9199
		200 P.I.S.A. (374° F.ᵃ)		
380	0.584	442.5	1.062	0.8124
420	0.656	471.3	1.123	0.8431
460	0.711	496.0	1.176	0.8662
500	0.761	520.6	1.224	0.8843
540	0.807	544.9	1.269	0.8979
		250 P.S.I.A. (393° F.ᵃ)		
400	0.452	446.7	1.076	0.7895
420	0.493	463.8	1.109	0.8239
460	0.546	496.5	1.164	0.8376
500	0.590	517.1	1.214	0.8602
540	0.632	542.0	1.260	0.8773
		300 P.S.I.A. (410° F.ᵃ)		
420	0.373	453.4	1.093	0.7725
460	0.433	486.1	1.154	0.8094
500	0.475	513.5	1.205	0.8363
540	0.510	539.2	1.252	0.8564
		400 P.S.I.A. (439° F.ᵃ)		
460	0.284	471.3	1.131	0.7283
480	0.308	489.4	1.161	0.7524
500	0.329	504.8	1.188	0.7898
540	0.363	533.0	1.238	0.8170
		500 P.S.I.A. (459° F.ᵃ)		
480	0.213	471.4	1.142	0.7211
500	0.236	492.8	1.171	0.7441
520	0.254	509.1	1.198	0.7633
540	0.266	525.7	1.224	0.7785
		600 P.S.I.A. (479° F.ᵃ)		
500	0.167	472.9	1.152	0.6966
520	0.190	497.3	1.182	0.7211
540	0.205	515.9	1.209	0.7402
		700 P.S.I.A. (501° F.ᵃ)		
520	0.136	480.5	1.161	0.6774
540	0.152	505.3	1.196	0.7025

ture-enthalpy, and temperature-entropy diagrams. Tabulated data are given in Tables I and II, and the data are plotted on a pressure-enthalpy diagram (Figure 1).

The calculated data were checked for internal consistency with the combined first and second law of thermodynamics

$$dH = TdS + VdP \qquad (10)$$

Equation 10 was integrated graphically at both constant pressure and constant entropy and compared with the enthalpy from the calculated data. These checks showed that the data presented are internally consistent.

The accuracy of the data cannot be checked by direct comparison, because the necessary data are lacking. The vapor phase enthalpy values are probably accurate to ±1.00 B.t.u. per pound and the entropy values to ±0.001 B.t.u. per pound ° R.

NOMENCLATURE

B, C, D, E = constants in Equation 15
C_p = constant pressure heat capacity
f = pure component fugacity

H = enthalpy
P = pressure
R = universal gas constant, 1.9872 B.t.u./lb.-mole ° R.
S = entropy
T = temperature
V = volume
α = residual volume

Superscripts

° = zero pressure, ideal gas state
* = unit fugacity, ideal gas state

Subscripts

c = critical constants
L = liquid phase
v = vapor phase

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