Thermodynamic Properties of Acetylene

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The derived thermodynamic properties of acetylene have been determined over a temperature range of 32 to 500°F. and up to pressures of 2,000 lb./sq. in. abs. The data were calculated from vapor pressure, volumetric, and heat-capacity data by the use of rigorous thermodynamic relationships. The calculated data were found to be internally consistent. The enthalpy values are believed to be accurate within ±1.0 B.t.u./lb. and the entropy values to ±0.001 B.t.u./(lb.)(°R.).

In view of the increasing use of acetylene as a raw material in various chemical industries, a study was initiated to determine its derived thermodynamic properties. Sufficient thermal, volumetric, and vapor pressure-temperature data are available in the literature to permit the determination of these properties over the temperature range of 32° to 500°F. and up to pressures of 2,000 lb./sq. in. abs.

The determination of the volumetric data for acetylene has been the subject of a number of investigations. Sameshima (*9*) investigated the volumetric behavior over the temperature range of 32° to 77°F. and up to a pressure of 176 lb./sq. in. abs.; Rimarski and Konshak (*8*) up to 303 lb./sq. in. abs. at 32°F.; Kiyama, Ikegami, and Inous (*6*) over the temperature range of 18° to 482°F. and the pressure range of 294 to 1,760 lb./sq. in. abs.; and Hölemann and Hasselmann (*5*) over the temperature range of 32° to 122°F. and up to pressures of 353 lb./sq. in. abs.; the last investigators correlated their data by the equation

$$PV = RT - aP - bP^2 \qquad (1)$$

where

$$a = 4.89 \times 10^{-1} - 1.08 \times 10^{-3}T$$

$$b = 6.99 \times 10^{-3} - 2.1 \times 10^{-5}T$$

and the pressure is expressed in atmospheres, the temperature in degrees Kelvin, and R in consistent units.

Teranishi (*11*) rechecked the data of Kiyama et al. (*6*) and reported volumetric data for acetylene over the temperature range of 32° to 482°F. and from a pressure of 147 to 1,907 lb./sq. in. abs. The volumetric behavior of the saturated liquid and vapor phases as well as vapor pressure-temperature data are reported in Lange's handbook (*7*).

The most recent heat-capacity data for acetylene are those reported in (*1*). These data were calculated from the spectroscopic data of Wagman, Kilpatrick, Pitzer, and Rossini (*12*). Teranishi (*11*) calculated heat-capacity data by the

TABLE 1. THERMODYNAMIC PROPERTIES OF SATURATED ACETYLENE

Temperature, °F.	Pressure, lb./sq. in. abs.	Fugacity pressure f/p	Volume, cu. ft./lb. Liquid	Vapor	Enthalpy, B.t.u./lb. Liquid	Vaporization	Vapor	Entropy, B.t.u./(lb.)(°R.) Liquid	Vaporization	Vapor
32	386.6	0.771	0.03457	0.357	−63.9	164.2	100.3	1.153	0.334	1.487
40	433.5	0.763	0.03558	0.316	−59.2	158.9	99.7	1.154	0.318	1.472
60	570.1	0.737	0.03844	0.226	−38.2	135.0	96.8	1.187	0.260	1.447
80	739.0	0.704	0.04399	0.152	−5.6	97.4	91.8	1.256	0.180	1.436
97.4	905.0	—	0.0695	0.0695	0	0	—	—	0	

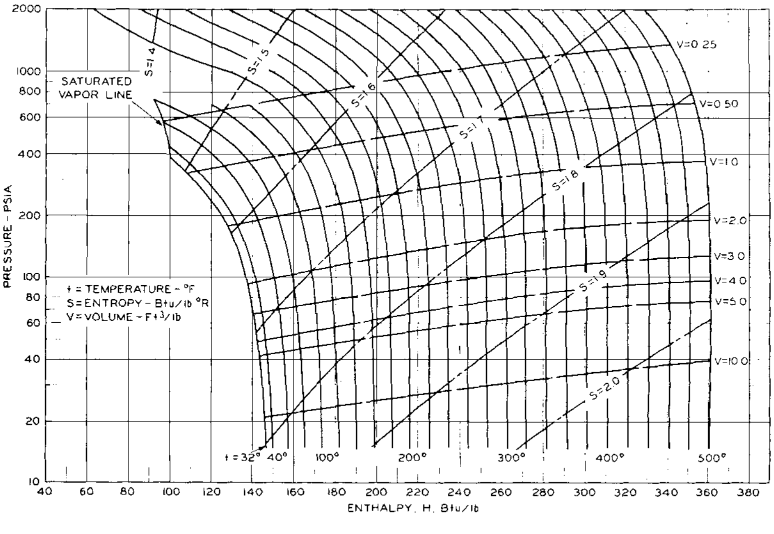

Fig. 1. Pressure-enthalpy diagram for acetylene.

TABLE 2—THERMODYNAMIC PROPERTIES OF SUPERHEATED ACETYLENE

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. (−119.0°F.)*				
32	13.60	147.1	1.807	0.991
60	14.47	157.8	1.828	0.994
100	15.62	174.0	1.858	0.996
140	16.77	190.8	1.887	0.998
180	17.91	208.1	1.915	0.999
220	19.04	226.0	1.943	0.999
260	20.16	244.4	1.969	1.000
300	21.29	262.8	1.994	1.000
340	22.41	281.9	2.019	1.000
380	25.53	301.3	2.043	1.000
420	24.65	321.1	2.065	1.000
460	25.76	341.1	2.088	1.000
500	26.92	361.0	2.110	1.000
50 lb./sq. in. abs. (−76.9°F.)				
32	3.914	142.6	1.707	0.971
60	4.183	154.2	1.729	0.978
100	4.548	171.3	1.761	0.987
140	4.905	188.8	1.792	0.993
180	5.250	206.7	1.820	0.997
220	5.585	224.9	1.848	0.998
260	5.923	243.4	1.874	0.998
300	6.253	262.3	1.900	0.999
340	6.583	281.5	1.925	0.999
380	6.913	301.0	1.949	0.999
420	7.240	320.8	1.972	0.999
460	7.574	340.9	1.994	0.999
500	7.904	360.9	2.016	0.999
100 lb./sq. in. abs. (−45.8°F.)				
32	1.894	137.2	1.645	0.942
60	2.043	150.3	1.671	0.957
100	2.240	168.8	1.704	0.973
140	2.434	187.2	1.736	0.986
180	2.615	205.3	1.766	0.993
220	2.785	224.3	1.794	0.995
260	2.953	243.2	1.821	0.997
300	3.119	262.1	1.847	0.997
340	3.286	281.5	1.872	0.998
380	3.452	301.0	1.896	0.998
420	3.617	320.7	1.919	0.998
460	3.783	340.9	1.941	0.999
500	3.945	360.8	1.963	0.999
150 lb./sq. in abs. (−25.2°F.)				
32	1.216	130.3	1.604	0.913
60	1.324	145.7	1.633	0.935
100	1.465	165.7	1.669	0.959
140	1.605	185.0	1.703	0.978
180	1.732	204.0	1.733	0.989
220	1.847	223.6	1.762	0.992
260	1.961	242.6	1.789	0.994
300	2.073	261.8	1.815	0.995
340	2.185	281.3	1.840	0.996
380	2.296	300.9	1.864	0.997
420	2.407	320.7	1.887	0.997
460	2.517	340.9	1.910	0.998
500	2.629	360.8	1.931	0.998
200 lb./sq. in. abs. (−9.4°F.)				
32	0.870	125.6	1.573	0.883
60	0.959	141.8	1.605	0.912
100	1.074	163.4	1.644	0.943
140	1.185	183.8	1.679	0.969
180	1.285	203.4	1.711	0.984
220	1.375	222.7	1.740	0.988
260	1.462	242.0	1.768	0.991
300	1.546	261.3	1.794	0.993
340	1.632	280.8	1.820	0.994
380	1.716	300.5	1.842	0.995
420	1.800	320.5	1.867	0.996
460	1.883	340.7	1.890	0.996
500	1.968	360.8	1.911	0.997
500 lb./sq. in. abs. (50.1°F.)				
(At satn.)	0.268	98.3	1.457	0.751
60	0.288	107.2	1.478	0.774
100	0.359	140.2	1.540	0.837
140	0.416	167.2	1.587	0.894
180	0.464	190.9	1.625	0.930
220	0.507	213.0	1.659	0.946
260	0.546	234.1	1.689	0.957
300	0.585	254.7	1.717	0.964
340	0.623	275.0	1.743	0.970
380	0.659	295.3	1.768	0.974
420	0.694	315.6	1.792	0.978
460	0.730	336.0	1.814	0.981
500	0.766	356.8	1.837	0.983
1,000 lb./sq. in. abs.				
140	0.141	129.2	1.485	0.694
180	0.183	165.1	1.543	0.781
220	0.212	193.6	1.587	0.829
260	0.239	218.6	1.622	0.873
300	0.263	241.8	1.653	0.892
340	0.285	263.8	1.682	0.908
380	0.305	285.2	1.708	0.920
420	0.324	306.4	1.733	0.930
460	0.343	327.6	1.756	0.938
500	0.362	348.9	1.779	0.944
1,500 lb./sq. in. abs.				
140	0.0529	83.8	1.392	0.588
180	0.0912	133.7	1.473	0.689
220	0.120	170.3	1.528	0.749
260	0.143	200.2	1.571	0.794
300	0.163	226.6	1.607	0.827
340	0.179	250.8	1.638	0.852
380	0.194	273.7	1.666	0.870
420	0.208	295.8	1.691	0.886
460	0.222	317.7	1.716	0.898
500	0.236	339.8	1.739	0.909
2,000 lb./sq. in. abs.				
140	0.0433	62.0	1.349	0.485
180	0.0557	105.9	1.420	0.591
220	0.0760	146.4	1.481	0.666
260	0.0962	181.1	1.530	0.725
300	0.112	210.6	1.570	0.770
340	0.126	236.8	1.604	0.803
380	0.138	261.2	1.633	0.827
420	0.150	284.6	1.660	0.848
460	0.162	307.4	1.686	0.865
500	0.173	330.0	1.710	0.880

equation

$$C_P = C_p{}^0 - \int_{P_0}^{P} T\left(\frac{\partial^2 V}{\partial T^2}\right)_P dP \quad (2)$$

He used the values of the heat capacity in the ideal-gas state and unit fugacity as calculated by Spencer (*10*), who had used the experimental results of Wagman et al. (*12*) in his calculations.

The critical constants t_c = 97.4°F., P_c = 905 lb./sq. in. abs., and V_c = 0.0695 ft./lb. reported in (*2*) were used in this work. Additional constants used were the molecular weight of acetylene, 26.036; gas-law constant, R, 10.7335 (lb./sq. in.)(cu. ft.)/(lb.-mole)(°R.); ice point, 491.69°R. One pound of acetylene was used as the basis of calculation, and the enthalpy and entropy values of acetylene in the ideal-gas state, unit fugacity, and 0°R. were set equal to zero. This is the reference state used in (*3, 4*).

Residual volumes were calculated from the volumetric data of Sameshima (*9*), Hölemann and Hasselmann (*5*), and Teranishi (*11*) and for the saturated vapor. A plot of α vs. pressure with temperature parameters was made and the data were smoothed. The data of Sameshima, and Hölemann, and Hasselmann were compared at 32° and 77°F. up to pressures of 176 lb./sq. in. abs. Agreement between the two sets of data was good, usually within 0.5%.

A number of comparisons between the data of Hölemann and Hasselmann (*5*) and of Teranishi (*11*) were made. In some instances the agreement between the two sets of data was not so good as might have been expected. For example, over the temperature range of 32° to 122°F. and at a pressure of 147 lb./sq. in. abs. the reported molal volumes differed from 0.05 to 2.11%, with the values reported by Teranishi being consistently the larger of the two at the six temperatures investigated. At the same temperatures but at 247 lb./sq. in. abs. the reported molal volumes differed from −3.20 to +1.99%, with the values of Hölemann and Hasselmann being the greater at the lower temperatures and the lesser at the higher temperatures. To calculate these percentages, the differences in the reported molal volumes were multiplied by one hundred and the products then divided by the molal volumes reported by Teranishi.

The data of Teranishi however appeared to be consistent with the data for the saturated vapor. Hence at conditions of high pressure the data of Teranishi were used to calculate the thermodynamic properties, while under conditions of low or moderate pressures, up to about 176 lb./sq. in. abs., the data of Hölemann and Hasselmann (*5*) were used.

At temperatures above 122°F. the temperature parameters on the α vs. pressure plot were extrapolated from 147 to 0 lb./sq. in. abs., as the required volumetric data have not been determined. In most cases these extrapolations were approximately straight lines. This assumption was made after studying the

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*Saturation temperatures are given in parentheses.

*Table 2 is somewhat abbreviated here.

temperature parameter below 122°F. over the same pressure range.

Through the use of the α vs. pressure plot previously mentioned the fugacity to pressure ratios were determined. The basic relationship used was

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

The value of the integral was determined graphically.

Latent heats of vaporization were calculated by the Clapeyron equation

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

since the equation is thermodynamically rigorous, and the necessary vapor-pressure, temperature, and volumetric data were available.

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

$$_M(H_p - H^0)_T = -\int_{P^0}^{P}\left[\alpha - T\left(\frac{\partial\alpha}{\partial T}\right)_p\right]dP \qquad (5)$$

The expression could be evaluated analytically at low pressures, where the volumetric data of Hölemann and Hasselmann (*5*) could be represented by Equation (1). The expression for the residual volume at constant temperature developed from this equation of state is

$$\alpha = a + bP \qquad (6)$$

Once $(H_p - H^\circ)_T$ was calculated, the enthalpy could be determined after the value of the enthalpy in the ideal-gas state had been obtained from (*3*).

At elevated pressures where the volumetric data of Teranishi (*11*) were used, the enthalpy could be calculated from the expression

$$dH = \int_{T_1}^{T_2} C_p\, dT \qquad (7)$$

because Teranishi had previously determined the effect of pressure on the heat capacity of the superheated vapor by Equation (2). The value of the integral was determined graphically.

Entropy differences between the real gas and the ideal gas at the same temperature in the superheated vapor region were determined by the expression

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

The entropy difference $(S_p - S^\circ)_T$ could be evaluated entirely analytically under conditions of low pressure, where the data of Hölemann and Hasselmann were used. Once the entropy differences were calculated, the entropy could be determined with the aid of entropy values of the ideal gas obtained from (*4*).

At elevated pressures the heat-capacity data calculated by Teranishi (*11*) were employed, and entropy values were calculated by the expression

$$dS = \int_{T_1}^{T_2}\frac{C}{T}p\, dT \qquad (9)$$

The integral was evaluated graphically.

The enthalpy values for the saturated vapor were determined by plotting H vs. T and extrapolating the isobars to the saturation temperature. The entropy data for the saturated vapor were determined by plotting S vs. T and again extrapolating the isobars to the saturation temperature.

Enthalpy and entropy data for the saturated liquid phase were obtained by subtracting the enthalpy or entropy of vaporization from their respective values in the saturated vapor phase. Finally all the data were plotted and smoothed on large scale H vs. S, S vs. T, and H vs. S plots. The smoothed data are reported in tabular form in Tables 1 and 2* and the data for the saturated and superheated vapors are shown graphically in the form of a log P vs. H plot (Figure 1).

The final results were checked for internal consistency through the relationship

$$dH = T\, dS + V\, dP \qquad (10)$$

which is a statement of the first and second laws of thermodynamics. Setting the value of the entropy at a constant reduces the equation to

$$dH = V\, dP \qquad (11)$$

If the right-hand side of Equation (*11*) is multiplied by P/P and integrated, the result is

$$H_2 - H_1 = \frac{144}{778.3}\int_{P_1}^{P_1} PV\, d\ln P \qquad (12)$$

The right-hand side of the equation can be evaluated graphically and compared with the enthalpy differences obtained from the calculated data. A number of consistency checks of this type were made and showed that the results presented are internally consistent. Data however are not available to check the accuracy of the final results, but the enthalpy values are probably accurate to ±1.0 B.t.u./lb. and the entropy values accurate to 0.001 B.t.u./(lb.)(°F.).

In summation f/P ratios, enthalpy, and entropy data, determined by rigorous thermodynamic methods, are presented for acetylene over the temperature range of 32° to 500°F. and up to pressures of 2,000 lb./sq. in. abs. The results are internally consistent.

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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.
a and b = empirical constants of Equation (1)
f = fugacity, same units as pressure
t = temperature, °F.
α = residual volume, cu. ft./lb.-mole, $RT/P-V_M$

Subscripts

c = critical property
M = molal quantity
v = vaporization

Superscripts

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

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