Literature Cited

(1) Bonner, O. D., Flora, H. B., Aitken, H W., *J. Phys. Chem.*, **75**, 2492 (1971).
(2) Ciapetta, F. G., Kilpatrick, M., *J. Am. Chem. Soc.*, **70**, 639 (1948).
(3) Cookson, R. F., *Chem. Rev.*, **74**, 5 (1974).
(4) Covington, A. K., Freeman, J. G., Lilley, T. H., *J. Phys. Chem.*, **74**, 3773 (1970).
(5) Davies, C. W., "Ion Association", Butterworth, London, 1962, p 41.
(6) Diamond, R. M., Tuck, D. G., *Prog. Inorg. Chem.*, **2**, 109 (1960).
(7) Durig, J. R., Bonner, O. D., Breazeale, W. H., *J. Phys. Chem.*, **69**, 3886 (1965).
(8) Fuoss, R. M., *J. Am. Chem. Soc.*, **80**, 5059 (1958).
(9) v. Halban, H., Brüll, J., *Helv. Chim. Acta*, **27**, 1719 (1944).
(10) Harned, H. S., Hawkins, J. E., *J. Am. Chem. Soc.*, **50**, 85 (1928).
(11) Kendall, J., *Medd. Vetenskapsakad., Nobelinst.*, **2** [38] (1913) (*Chem. Zentralbl.*, **35**/1, 841 (1914)).
(12) King, E. J., "Acid-Base Equilibria", The International Encyclopedia of Physical Chemistry and Chemical Physics, Vol. 15/4, Pergamon, Oxford, 1965, Chapter 6.2.
(13) Kortüm, G., Vogel, W., Andtrussow, K., "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworth, London, 1961, pp 294, 295. (reprinted from: *Pure Appl. Chem.*, **1**, 187 (1961)).
(14) Ostwald, W., *Z. Phys. Chem.*, **3**, 170 (1889).
(15) Perlmutter-Hayman, B., Tapuhi, E., *J. Coord. Chem.*, accepted for publication.
(16) Randall, M., Failey, C. F., *Chem. Rev.*, **4**, 291 (1927).
(17) Schreiner, E., *Z. Anorg. Allg. Chem.*, **122**, 201 (1922).
(18) Sillén, L. G., Martell, A. E., *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

Received for review March 22, 1976. Accepted July 23, 1976.

Derived Thermodynamic Properties of Ethylene

Roland H. Harrison* and Donald R. Douslin
Bartlesville Energy Research Center, Energy Research and Development Administration, Bartlesville, Oklahoma 74003

The real fluid values for enthalpy, entropy, and Gibbs energy in the ranges −35 to +175 °C, 0 to 16 mol dm^{-3}, and 0 to 400 bar were derived for ethylene from experimental P–V–T measurements given in a companion paper (*4*) and published values of the ideal gas properties and a derived value of the enthalpy of sublimation at 0 K.

Although the U.S. production of ethylene ranks fifth in all chemicals and first in petrochemicals, its thermodynamic properties have not been known with high accuracy. A recent comprehensive correlation of the available data for ethylene was undertaken by Angus et al. (*1*), from which they prepared tables of thermodynamic properties, but they concluded that a considerable amount of new experimental measurement was needed. When this study was later presented to a group drawn from government, industry, and universities engaged in a critical assessment (*9*) of the published information on the P–V–T surface of ethylene, there was general agreement with the need for more experiment. Thus, an independent comprehensive set of new data on the P–V–T surface of ethylene was measured with the highest accuracy reasonably accessible to modern P–V–T methods and was presented in a companion paper (*4*). The present work is based on those unsmoothed experimental compressibility values given at even temperatures and densities. The real fluid values for enthalpy, entropy, and Gibbs energy presented here cover a wide range of conditions including the region of the critical point. Since the present values of the thermodynamic properties were calculated from a single set of accurate P–V–T data, they are not subject to the large errors in $(\partial P/\partial T)_\rho$ that result when different sets of compressibility data are combined and averaged. Also, the calculative methods used in the investigation reported in this paper were developed especially for isometric data, and inaccuracies that otherwise would have originated from crossplotting, interpolating, or smoothing of original data were not introduced.

The thermodynamic properties of ethylene have been calculated with a reference to the crystal at 0 K from the data on the compressibility of the real fluid and the heats of vaporization given in the companion paper (*4*) and from published values of the ideal gas properties and a derived value of the enthalpy of sublimation at 0 K. The values are presented in graphical and tabular form and are also compared with published experimental and correlated values.

Calculation Methods

The difference between the real fluid and ideal gas thermodynamic properties of enthalpy, entropy, and Gibbs energy were evaluated from isometric and isothermal data by the following relations, in which T appears on the thermodynamic temperature scale:

$$H - H^\circ = {}_T\int_0^\rho \frac{[P - T(\partial P/\partial T)_\rho]\mathrm{d}\rho}{\rho^2} + P/\rho - RT \quad (1)$$

$$S - S^\circ = {}_T\int_0^\rho \frac{[R\rho - (\partial P/\partial T)_\rho]\mathrm{d}\rho}{\rho^2} - R\ln RT\rho \quad (2)$$

$$G - G^\circ = {}_T\int_0^\rho \frac{(P - RT\rho)\mathrm{d}\rho}{\rho^2} + P/\rho - RT + RT\ln RT\rho \quad (3)$$

The superscript degree mark as in H°, S°, and G° indicates the ideal gas state at 1 atm of pressure. Experimental values of P, ρ, and T were taken only from Tables 1–4 and 7 of ref 4. The slopes, $(\partial P/\partial T)_\rho$, of the isometric lines were derived from the original data (Table 9 of ref 4) by combined analytical and graphical residual correlating techniques that reflect all of the inherent accuracy of the original measurements. Details of the method used and an analysis of the uncertainties involved in the calculation of the thermodynamic functions from P–V–T data have been fully described (*7*, *8*). Gibbs energies were calculated at every point of original P–ρ–T data. Enthalpies and entropies were calculated at all points where the slopes, $(\partial P/\partial T)_\rho$, were available. The values of the integrals at zero density were obtained as exact functions of the second virial coefficients and/or their temperature derivatives which were derived from the values given in Table 12 of ref 4. At temperatures below the critical, the path of integration for the enthalpy function (eq 1) passes through the two-phase region and yields the enthalpy of vaporization which is the same as that given by the exact Clapeyron equation in Table 10 of ref 4.

The values for the difference between the thermodynamic properties of the real fluid and the ideal gas were combined with other published data so as to base the final values for ethylene on the perfect crystal at 0 K. The value of the enthalpy of the ideal gas at the normal boiling point, 24 746.8 J mol^{-1} at 169.43 K, was determined by Angus et al. (*1*) for the International Union of Pure and Applied Chemistry. They integrated the low-temperature calorimetric measurements of Egan and Kemp (*5*) for the solid and the liquid and added the enthalpy of fusion and vaporization and a small correction for the gas imperfection. We have combined these data with the ideal gas spectroscopic values of Chao, Wilhoit, and Zwolinski (*2*). Angus et al. (*1*) noted that the calculations based on Egan and Kemp (*5*) were consistent with those of Chao et al. (*2*), and therefore the combination of them in the present paper will not cause any inconsistency. Thus, the enthalpy of sublimation of ethylene at 0 K was found to be 19 097.4 J mol^{-1}. Since the ideal gas spectroscopic values of Chao, Wilhoit, and Zwolinski were tabulated on the Kelvin scale, the values were recalculated at the necessary Celsius temperatures by use of the same spectroscopic and molecular constants to avoid the need for interpolating the data.

The basic gas densities were measured on the International Practical Scale of 1968 which is assumed to be the thermodynamic scale within experimental error limits, so no adjustments were necessary for temperature scale differences. The molecular weight of the sample was calculated by use of the 1969 atomic weights C = 12.011 and H = 1.008; the sample was assumed to be 100%. The value of R used was 83.1433 cm^3 bar K^{-1} mol^{-1}.

Results

The thermodynamic properties of enthalpy, entropy, and Gibbs energy, based on the perfect crystal at 0 K or −273.15 °C, are presented in Table I and Figures 1, 2, and 3. The values of enthalpy can be referred to other bases such as the ideal gas at 0 K by subtracting from the absolute values the enthalpy of sublimation at 0 K, 19 097.4 J mol^{-1}, or to the ideal gas at 25 °C and 1 atm by subtracting 29 610 J mol^{-1}. Values of the properties, $(H - H^o)/T$, $(S_p - S_{p,ideal})$, $(S_v - S_{v,ideal})$, $(G_p - G_{p,ideal})$, $(G_v - G_{v,ideal})$, $(G - G^o)/T$, and activity coefficient, γ, are derivable by direct arithmetic computation. (They are available upon request.)

The values for the enthalpies of the orthobaric liquid and vapor phases, enthalpies of the vapor–liquid equilibrium system along the critical-density locus, and enthalpies in the single-phase regions are shown in Figure 1. As the saturated liquid and vapor branches of the enthalpy envelope approach the critical point, they become increasingly symmetrical and horizontal and are intersected by the critical isometric line with finite angles above and below the critical temperature. These relationships were used to explain the behavior of the heat capacity at the critical volume in the companion paper (*4*). The lines in the single-phase region were drawn smoothly through the data points at intervals of 25° above 50 °C and at intervals of 5° below 30 °C. The data are shown here at the integer values of density from 1 to 15 mol dm^{-3}. Values at each of the half integer values were not plotted to avoid confusion. The isometric lines have a slight S shape with increasing curvature as they approach the two-phase envelope.

The relationship of temperature and entropy is similar to that of temperature and enthalpy as shown in Figure 2. The values of entropy were referred to the crystal at 0 K by use of the same literature sources as were used for the enthalpy. As the saturated liquid and vapor branches of the entropy envelope approach the critical point, they also appear to become increasingly symmetrical and horizontal and are intersected by the critical isometric line with finite angles above and below the critical temperature. The isometric lines pass smoothly through the data points at all densities. A portion of the ideal gas curve is in the lower right-hand region of the figure.

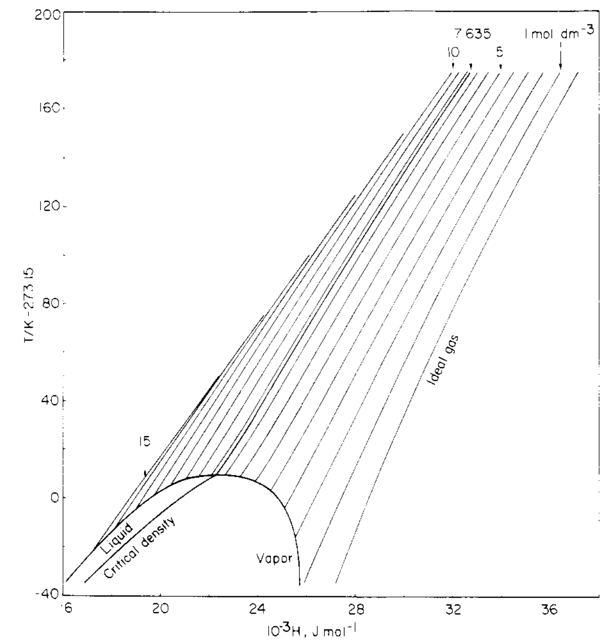

Figure 1. Enthalpy in the single- and two-phase regions.

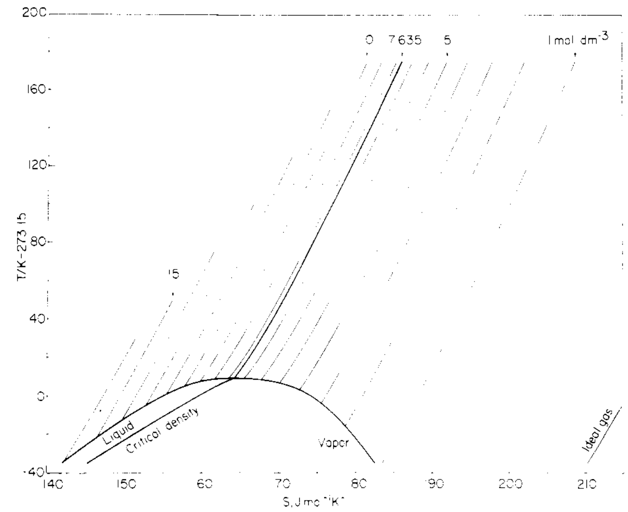

Figure 2. Entropy in the single- and two-phase regions.

The Gibbs energies of coexisting phases in equilibrium are equal so there is no envelope but only a single curve below the critical temperature, 9.2 °C, as shown in Figure 3. The critical density curve at 7.635 mol dm^{-3} merges smoothly and is continuous with the equilibrium curve at the critical point. Only a few selected isometric lines have been drawn because of the close spacing of the lines in the region below the critical point. All isometric lines intersect the equilibrium curve.

The present results are compared in Figure 4 to two other well-recognized data sources. The enthalpy data were all determined on different bases but have been reduced to the same base of the enthalpy of the real gas minus that of the ideal gas at the same temperature, $H - H^o$, by five-point Lagrangian and graphical interpolation. The ordinate in the figure is given by the relation

Table I. Gram-Molar Thermodynamic Properties of Ethylene

-35°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	27199.2	22863.9	210.217
0.8	13.1156	26149.3	18105.8	185.829
0.9	14.3837	-------	17956.4	-------
1.0	15.5722	25885.4	17831.1	183.567
1.05	16.1358	-------	17776.1	-------
1.1	16.6794	-------	17725.5	-------
1.1130	16.8220	25736.2	17712.6	182.443
16.0360	16.8220	16100.9	17712.6	141.984
16.0593	18.5632	-------	17701.7	-------
16.1048	22.1355	-------	17679.5	-------
16.1526	25.7735	-------	17657.0	-------
16.2004	29.5424	-------	17633.7	-------

-30°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	27388.8	23917.0	211.005
0.8	13.5107	26363.2	18987.4	186.513
0.9	14.8369	-------	18831.1	-------
1.0	16.0888	26107.1	18699.1	184.274
1.1	17.2600	-------	18587.4	-------
1.2	18.3601	-------	18491.6	-------
1.2986	19.3702	25724.7	18410.7	181.515
15.6340	19.3702	16522.4	18410.7	143.669
15.6605	21.0558	-------	18399.9	-------
15.7075	24.3768	-------	18378.8	-------
15.7553	27.5623	-------	18358.5	-------
15.8039	30.8036	-------	18388.0	-------

-25°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	27580.2	24974.0	211.784
0.8	13.9026	26578.2	19872.5	187.188
1.0	16.5983	26329.6	19571.2	184.972
1.2	18.9975	-------	19352.0	-------
1.4	21.1085	-------	19189.0	-------
1.5	22.0542	25710.7	19123.8	180.675
1.5141	22.1869	25693.6	19115.0	180.570
15.1960	22.1869	16969.5	19115.0	145.414
15.2332	24.0129	-------	19103.0	-------
15.2678	26.2136	-------	19088.5	-------
15.3161	28.9918	-------	19070.4	-------
15.3656	31.6838	-------	19052.8	-------
15.5	39.0023	16911.7	19005.4	144.739
16.0	74.7177	16856.4	18778.8	143.604

-20°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	27773.6	26034.8	212.555
0.8	14.2915	26791.3	20761.5	187.844
1.0	17.1034	26548.3	20447.1	185.643
1.2	19.6270	-------	20216.7	-------
1.4	21.8710	-------	20043.5	-------
1.5	22.8884	25944.8	19973.3	181.387
1.6	23.8414	-------	19911.7	-------
1.7	24.7293	-------	19857.9	-------
1.7672	25.2886	25624.9	19825.6	179.540
14.7230	25.2886	17427.5	19825.6	147.158
14.7302	25.7845	-------	19822.2	-------
14.7545	26.6461	-------	19816.4	-------
14.7914	28.2279	-------	19805.7	-------
14.8390	30.3274	-------	19791.5	-------
14.8878	32.5340	-------	19776.7	-------

-15°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	27969.0	27099.5	213.320
0.8	14.6781	27006.3	21654.1	188.497
1.0	17.6040	26769.0	21327.1	186.311
1.5	23.7131	26181.8	20827.1	182.099
1.8	26.5969	-------	20651.3	-------
1.9	27.4287	-------	20606.3	-------
2.0	28.2049	25602.7	20566.5	178.847
2.0677	28.6960	25525.0	20542.3	178.452
14.2070	28.6960	17914.6	20542.3	148.971
14.2355	29.6058	-------	20536.0	-------
14.2586	30.4388	-------	20530.1	-------
14.2827	31.2563	-------	20524.4	-------
14.3187	32.4493	-------	20516.0	-------
14.3540	33.6622	-------	20507.6	-------

-10°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28166.4	28168.0	214.077
0.8	15.0623	27221.2	22550.1	189.137
1.0	18.1014	26988.7	22210.5	186.962
1.5	24.5231	26414.2	21685.2	182.783
2.0	29.3844	25850.1	21403.5	179.569
2.3	31.6058	-------	21299.7	-------
2.4	32.2392	-------	21272.7	-------
2.4321	32.4312	25370.8	21264.8	177.220
13.6300	32.4312	18424.8	21264.8	150.825
13.6694	33.3822	-------	21257.8	-------
13.6918	33.9656	-------	21253.5	-------
13.7160	34.5386	-------	21249.4	-------
13.7508	35.3832	-------	21243.2	-------
13.7849	36.2609	-------	21236.8	-------

-5°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28366.0	29240.3	214.828
0.8	15.4449	27438.1	23449.5	189.773
1.0	18.5959	27210.5	23097.3	187.611
1.5	25.3255	26649.7	22547.3	183.468
2.0	30.5385	26101.3	22245.3	180.297
2.5	34.3824	25565.8	22072.7	177.656
2.6	34.9940	-------	22048.7	-------
2.7	35.5668	-------	22027.1	-------
2.8	36.0871	-------	22008.2	-------
2.8905	36.5196	25156.4	21993.0	175.832
12.9660	36.5196	18992.1	21993.0	152.844
12.9739	36.6760	-------	21991.8	-------
12.9742	36.6575	-------	21991.9	-------
12.9843	36.8142	-------	21990.7	-------
13.0063	37.1651	-------	21988.0	-------
13.0282	37.4975	-------	21985.5	-------
13.0494	37.8923	-------	21982.4	-------
13.0718	38.2622	-------	21979.6	-------

0°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28567.7	30316.3	215.574
0.8	15.8256	27656.5	24352.4	190.404
1.0	19.0865	27433.6	23988.0	188.254
1.5	26.1197	26885.8	23413.4	184.145
2.0	31.6752	26351.9	23091.8	181.013
2.5	35.9055	25832.9	22901.9	178.418
3.0	38.9602	25329.0	22789.9	176.163
3.3	40.2893	-------	22747.6	-------
3.4	40.6540	-------	22736.7	-------
3.5	40.9844	24840.3	22727.1	174.144
3.5025	40.9931	24837.9	22726.9	174.134
12.1460	40.9931	19643.8	22726.9	155.119
12.1569	41.0677	-------	22726.2	-------
12.1666	41.1830	-------	22725.3	-------
12.1772	41.2848	-------	22724.5	-------
12.1970	41.4422	-------	22723.2	-------
12.2166	41.6255	-------	22721.7	-------
12.2363	41.8147	-------	22720.1	-------
12.5	44.7429	19501.5	22696.4	154.486
13.0	52.5969	19311.1	22634.9	153.564
13.5	64.4270	19139.0	22545.7	152.607
14.0	81.0745	18989.0	22424.7	151.615
14.5	103.794	18867.9	22265.4	150.589
15.0	133.574	18780.0	22063.7	149.528
15.5	172.313	18735.5	21809.8	148.436
16.0	220.913	18737.0	21501.4	147.312

5°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28771.6	31396.0	216.313
0.8	16.2045	27875.8	25258.8	191.029
1.0	19.5719	27656.9	24882.5	188.889
1.5	26.9022	27120.0	24284.0	184.806
2.0	32.7916	26597.5	23943.2	181.703
2.5	37.3922	26090.2	23736.9	179.137
3.0	40.8575	25598.3	23609.9	176.913
3.5	43.3411	25122.2	23533.0	174.925
4.0	44.9972	24662.2	23488.5	173.111
4.4	45.8260	-------	23468.7	-------
4.4471	45.8980	24264.3	23467.1	171.603
10.9950	45.8980	20433.2	23467.1	157.830
10.9980	45.9113	-------	23467.0	-------
11.0061	45.9358	-------	23466.7	-------
11.0145	45.9597	-------	23466.5	-------
11.0388	46.0326	-------	23465.9	-------
11.0558	46.1014	-------	23465.3	-------
11.0885	46.2152	-------	23464.2	-------
11.1053	46.2671	-------	23463.8	-------
11.4101	47.7085	-------	23451.0	-------
11.5	48.2459	20217.5	23446.3	156.979
12.0	52.3668	20010.2	23411.2	156.108
12.5	58.8819	19813.3	23358.1	155.209

6°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28812.6	31612.4	216.461
4.0	45.5551	24721.1	23646.6	173.268
4.5	46.6321	24280.7	23621.1	171.599
4.7	46.9080	-------	23615.1	-------
4.7246	46.9367	24088.3	23614.5	170.886
10.6740	46.9367	20632.8	23614.5	158.507
10.6880	46.9708	-------	23614.2	-------
10.6960	46.9905	-------	23614.0	-------
10.7193	47.0421	-------	23613.5	-------
10.7585	47.1427	-------	23612.5	-------
10.7975	47.2466	-------	23611.6	-------
11.0	47.9137	20491.7	23605.5	157.969
11.5	50.5144	20278.1	23582.4	157.122
12.0	54.9167	20071.3	23545.0	156.247
12.5	61.7567	19875.3	23489.2	155.345

7°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28853.8	31828.9	216.608
4.0	46.1127	24781.0	23805.8	173.431
4.5	47.2843	24344.7	23778.1	171.775
4.9	47.8423	-------	23766.2	-------
5.0	47.9381	23925.6	23764.2	170.230
5.0710	47.9973	23867.5	23763.0	170.018
10.2900	47.9973	20863.4	23763.0	159.295
10.3070	48.0263	-------	23762.8	-------
10.3291	48.0596	-------	23762.4	-------
10.3654	48.1214	-------	23761.8	-------
10.4018	48.1814	-------	23761.3	-------
10.5	48.3757	20771.9	23759.4	158.955
11.0	49.9379	20554.7	23744.9	158.128
11.5	52.7916	20341.4	23719.6	157.277
12.0	57.4847	20135.6	23679.7	156.400
12.5	64.6192	19940.7	23621.6	155.496

8°C

Density mol dm^{-3}	P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28895.0	32045.6	216.755
4.5	47.9289	24407.3	23936.0	171.948
5.0	48.6833	23992.6	23920.0	170.417
5.3	48.9472	-------	23914.8	-------
5.4	49.0082	-------	23913.7	-------
5.5	49.0601	23596.3	23912.8	168.981
5.5460	49.0813	23560.8	23912.4	168.853
9.7670	49.0813	21158.7	23912.4	160.310
9.7673	49.0837	-------	23912.4	-------
9.7737	49.0885	-------	23912.3	-------
9.7803	49.0938	-------	23912.2	-------
9.7937	49.1022	-------	23912.2	-------
9.8133	49.1168	-------	23912.0	-------
9.8329	49.1325	-------	23911.9	-------
9.8991	49.1885	-------	23911.3	-------
10.0	49.2924	21055.2	23910.2	159.934
10.5	50.1853	20833.9	23901.5	159.116
11.0	51.9783	20615.4	23884.9	158.280
11.5	55.0906	20402.3	23857.3	157.423
12.0	60.0700	20197.3	23815.0	156.544

Table I (*continued*)

Density mol dm^{-3}	9°C P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28936.3	32262.4	216.901
1.0	19.9632	27836.2	25599.9	189.389
1.5	27.5284	27306.7	24982.4	185.324
2.0	33.6827	26792.6	24626.5	182.240
2.5	38.5729	26294.1	24407.3	179.697
3.0	42.3533	25812.2	24268.8	177.498
3.5	45.1803	25347.3	24181.4	175.540
4.0	47.2027	24899.8	24127.1	173.762
4.5	48.5664	24470.4	24094.9	172.126
5.0	49.4195	24060.1	24076.8	170.608
5.5	49.8973	23669.6	24067.7	169.191
5.8	50.0530	-------	24064.9	-------
5.9	50.0892	-------	24064.3	-------
6.0	50.1181	23299.4	24063.8	167.865
6.2	50.1606	-------	24063.1	-------
6.3	50.1741	-------	24062.9	-------
6.4	50.1843	-------	24062.7	-------
6.4890	50.1915	22958.0	24062.6	166.651
8.7800	50.1915	21680.9	24062.6	162.125
8.8	50.1951	-------	24062.6	-------
8.8023	50.1959	-------	24062.6	-------
8.8452	50.1990	-------	24062.5	-------
8.9	50.2061	-------	24062.5	-------
9.0	50.2198	21578.7	24062.3	161.761
9.1	50.2425	-------	24062.0	-------
9.2	50.2694	-------	24061.8	-------
9.5	50.4078	21349.1	24060.3	160.940
10.0	50.9211	21123.2	24055.0	160.121
10.5	52.0165	20900.3	24044.3	159.294
11.0	54.0239	20681.2	24025.7	158.451
11.5	57.3832	20468.0	23995.8	157.589
12.0	62.6192	20263.3	23951.4	156.706

Density mol dm^{-3}	9.1°C P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28940.5	32284.1	216.916
5.5	49.9803	23677.5	24083.1	169.214
6.0	50.2118	23308.0	24079.0	167.890
6.4	50.2842	-------	24077.9	-------
6.5	50.2939	22960.0	24077.7	166.653
6.6	50.2995	-------	24077.6	-------
6.75	50.3035	-------	24077.6	-------
6.7567	50.3046	22790.8	24077.5	166.053
8.5175	50.3046	21814.5	24077.5	162.594
8.6	50.3089	-------	24077.5	-------
8.7	50.3142	-------	24077.4	-------
8.8	50.3238	-------	24077.3	-------
9.0	50.3540	-------	24077.0	-------

Density mol dm^{-3}	9.2°C P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28944.6	32305.8	216.931
0.8	16.5214	28060.7	26022.5	191.547
1.0	19.9807	27845.0	25636.0	189.414
1.5	27.5585	27316.1	25017.4	185.350
2.0	33.7260	26802.5	24660.7	182.267
2.5	38.6330	26304.8	24440.8	179.726
3.0	42.4295	25823.6	24301.8	177.529
3.5	45.2729	25359.4	24213.7	175.574
4.0	47.3096	24912.7	24159.1	173.798
4.5	48.6930	24484.3	24126.4	172.165
5.0	49.5656	24074.9	24108.0	170.650
5.5	50.0613	23685.4	24098.5	169.236
6.0	50.3051	23316.5	24094.2	167.915
6.5	50.3966	22969.5	24092.8	166.681
7.0	50.4178	22648.0	24092.5	165.541
7.25	50.4186	22497.4	24092.5	165.008
7.5	50.4194	22353.3	24092.5	164.497
7.635	50.4197	22278.1	24092.5	164.231
7.75	50.4200	22215.4	24092.5	164.009
8.0	50.4200	22083.4	24092.5	163.541
8.5	50.4295	21834.8	24092.4	162.661
9.0	50.4902	21598.6	24091.7	161.821
9.5	50.7067	21368.3	24089.4	160.997
10.0	51.2506	21141.6	24083.8	160.175
10.5	52.3803	20918.0	24072.8	159.344
11.0	54.4327	20698.3	24053.8	158.499
11.5	57.8675	20485.0	24023.3	157.635
12.0	63.1075	20279.8	23978.7	156.751
12.5	70.9274	20087.0	23915.0	155.842
13.0	82.0584	19909.7	23827.8	154.905
13.5	97.3605	19752.1	23712.4	153.938
14.0	117.738	19618.6	23564.3	152.941
14.5	144.379	19515.1	23377.5	151.913
15.0	178.683	19448.1	23145.1	150.852
15.5	221.743	19422.5	22862.8	149.762
16.0	275.731	19448.9	22520.2	148.642

Density mol dm^{-3}	10°C P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	28977.7	32479.4	217.048
0.8	16.5821	28096.3	26168.1	191.645
1.0	20.0588	27881.2	25779.7	189.514
1.5	27.6842	27353.8	25157.3	185.453
2.0	33.9022	26841.7	24797.7	182.375
2.5	38.8665	26345.6	24575.2	179.837
3.0	42.7251	25866.0	24433.9	177.644
3.5	45.6358	25403.6	24343.8	175.693
4.0	47.7449	24959.1	24287.3	173.923
4.5	49.2011	24533.2	24252.8	172.297
5.0	50.1491	24126.7	24232.8	170.791
5.5	50.7200	23740.4	24221.9	169.388
6.0	51.0345	23375.4	24216.4	168.080
6.5	51.1928	23033.2	24213.8	166.862
6.75	51.2379	-------	24213.1	-------
7.0	51.2707	22714.8	24212.7	165.734
7.25	51.2950	-------	24212.3	-------
7.5	51.3169	22420.8	24212.0	164.693
7.635	51.3277	22345.4	24211.8	164.426
7.75	51.3368	-------	24211.8	-------
8.0	51.3594	22149.1	24211.4	163.731
8.5	51.4271	21895.2	24210.6	162.832
9.0	51.5732	21653.7	24208.9	161.973
9.5	51.8994	21419.9	24205.4	161.135
10.0	52.5792	21190.8	24198.4	160.301
10.5	53.8690	20965.8	24185.9	159.462
11.0	56.1023	20745.7	24165.1	158.611
11.5	59.7049	20532.1	24133.2	157.744
12.0	65.2023	20327.5	24086.4	156.857
12.5	73.2486	20135.0	24020.8	155.945
13.0	84.6100	19958.2	23931.7	155.006
13.5	100.145	19801.3	23814.6	154.038
14.0	120.723	19668.3	23665.0	153.040
14.5	147.719	19566.4	23475.7	152.011
15.0	182.112	19499.3	23242.7	150.951
15.5	225.445	19474.7	22958.7	149.862
16.0	279.730	19502.1	22614.2	148.742

Density mol dm^{-3}	15°C P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	29186.2	33566.5	217.778
0.8	16.9587	28318.3	27081.0	192.259
1.0	20.5413	28106.5	26680.8	190.135
1.5	28.4610	27588.5	26034.7	186.094
2.0	35.0031	27085.8	25656.5	183.038
2.5	40.3243	26599.9	25418.0	180.524
3.0	44.5660	26131.2	25262.8	178.358
3.5	47.8851	25680.5	25160.1	176.438
4.0	50.4221	25248.4	25092.1	174.702
4.5	52.3250	24835.3	25047.2	173.113
5.0	53.7253	24441.9	25017.6	171.645
5.5	54.7454	24069.0	24998.1	170.283
6.0	55.4964	23717.1	24984.9	169.016
6.5	56.0692	23385.7	24975.8	167.834
6.75	56.3106	-------	24972.1	-------
7.0	56.5366	23074.0	24968.8	166.728
7.25	56.7503	-------	24966.0	-------
7.5	56.9652	22780.5	24962.9	165.689
7.635	57.0808	22704.1	24961.3	165.419
8.0	57.4088	22503.5	24957.1	164.708
8.5	57.9342	22240.6	24950.8	163.774
9.0	58.6313	21988.3	24942.8	162.871
9.5	59.6313	21745.3	24932.0	161.990
10.0	61.1098	21509.9	24916.9	161.120
10.5	63.3296	21281.3	24895.2	160.252
11.0	66.6283	21059.6	24864.6	159.376
11.5	71.4474	20846.3	24821.8	158.487
12.0	78.3042	20643.5	24763.5	157.581
12.5	87.8247	20454.0	24685.8	156.654
13.0	100.804	20281.9	24584.1	155.704
13.5	118.088	20131.1	24453.8	154.728
14.0	140.633	20006.1	24289.9	153.726
14.5	169.575	19912.0	24086.9	152.695
15.0	206.367	19856.0	23837.6	151.635
15.5	253.591	19851.9	23528.1	150.547
16.0	309.227	19882.8	23175.1	149.429

Density mol dm^{-3}	20°C P bar	H J	-G J	S J K^{-1}
Ideal Gas	1.01325	29396.9	34657.2	218.503
0.8	17.3337	28542.4	27996.9	192.868
1.0	21.0232	28334.3	27584.8	190.752
1.5	29.2311	27825.4	26915.3	186.733
2.0	36.0949	27332.4	26518.6	183.698
2.5	41.7660	26856.2	26264.6	181.207
3.0	46.3831	26396.9	26095.7	179.064
3.5	50.0990	25955.5	25980.8	177.166
4.0	53.0545	25532.8	25901.6	175.454
4.5	55.3869	25129.1	25846.6	173.889
5.0	57.2242	24744.7	25807.8	172.446
5.5	58.6849	24379.7	25779.9	171.106
6.0	59.8672	24033.9	25759.3	169.856
6.5	60.8774	23706.9	25743.1	168.685
7.0	61.7782	23397.4	25729.7	167.584
7.5	62.6526	23104.5	25717.6	166.543
7.635	62.8886	23027.8	25714.5	166.271
8.0	63.5743	22826.1	25705.7	165.553
8.5	64.6250	22560.0	25693.0	164.602
9.0	65.9227	22304.8	25678.2	163.681
9.5	67.6196	22059.1	25659.8	162.780
10.0	69.9048	21821.7	25636.3	161.890
10.5	73.0284	21592.1	25605.9	161.003
11.0	77.3777	21371.1	25565.5	160.111
11.5	83.3687	21159.9	25512.3	159.209
12.0	91.5927	20961.1	25442.3	158.293
12.5	102.623	20777.1	25352.4	157.358
13.0	117.222	20611.1	25237.9	156.401
13.5	136.175	20466.9	25095.0	155.422
14.0	160.447	20348.6	24918.6	154.417
14.5	191.586	20264.5	24700.2	153.385
15.0	230.570	20218.2	24436.0	152.325
15.5	278.840	20215.9	24119.7	151.239
16.0	338.160	20265.2	23743.2	150.122

Table I (*continued*)

Density	25°C				30°C				50°C				75°C			
	P	H	-G	S	P	H	-G	S	P	H	-G	S	P	H	-G	S
mol dm^{-3}	bar	J	J	JK^{-1}	bar	J	J	JK^{-1}	bar	J	J	JK^{-1}	bar	J	J	JK^{-1}
Ideal Gas	1.01325	29610.0	35751.5	219.223	1.01325	29825.4	36849.4	219.940	1.01325	30711.4	41276.6	222.769	1.01325	31874.5	46889.3	226.235
0.8	17.7069	28768.2	28915.9	193.474	18.0803	28995.8	29838.2	194.076	19.5635	29925.6	33558.2	196.453	21.4007	31136.7	38276.5	199.377
1.0	21.5041	28563.6	28491.8	191.365	21.9823	28794.0	29402.4	191.972	23.8816	29734.8	33076.0	194.370	26.2308	30957.7	37737.3	197.314
1.5	29.9981	28063.3	27799.2	187.364	30.7616	28301.1	28686.7	187.986	33.7818	29269.4	32269.8	190.435	37.5019	30521.5	36820.2	193.427
2.0	37.1789	27579.0	27384.3	184.348	38.2561	27824.3	28253.8	184.985	42.5082	28820.2	31766.2	187.487	47.7171	30100.5	36231.1	190.526
2.5	43.1899	27111.3	27115.2	181.876	44.6105	27364.2	27969.4	182.529	50.1854	28386.8	31422.7	185.083	57.0087	29694.8	35815.7	188.168
3.0	48.1802	26660.7	26932.7	179.753	49.9604	26921.0	27773.8	180.421	56.9573	27969.9	31175.3	183.027	65.5011	29304.4	35505.6	186.155
3.5	52.2896	26227.6	26805.7	177.875	54.4507	26495.5	27635.0	178.560	62.9567	27569.5	30990.1	181.215	73.3229	28929.1	35264.3	184.384
4.0	55.6532	25812.6	26715.7	176.181	58.2199	26088.4	27534.2	176.885	68.2950	27185.2	30847.3	179.584	80.5802	28568.1	35070.3	182.790
4.5	58.4065	25416.3	26650.7	174.634	61.3885	25699.5	27459.4	175.355	73.1042	26817.1	30733.9	178.094	87.4167	28221.8	34909.2	181.333
5.0	60.6783	25038.6	26602.7	173.206	64.0832	25329.1	27402.5	173.945	77.4977	26464.7	30641.3	176.717	93.9317	27889.3	34771.9	179.983
5.5	62.5726	24679.3	26566.6	171.880	66.4164	24976.6	27358.0	172.636	81.5994	26127.8	30563.1	175.432	100.249	27570.2	34651.5	178.721
6.0	64.2028	24338.4	26538.2	170.641	68.4890	24641.1	27321.9	171.410	85.4955	25805.5	30495.3	174.225	106.487	27264.0	34542.9	177.530
6.5	65.6526	24015.1	26515.0	169.479	70.3963	24321.4	27291.4	170.255	89.3100	25497.2	30434.2	173.082	112.772	26970.3	34442.3	176.397
7.0	67.0124	23708.8	26494.9	168.384	72.2319	24016.8	27264.1	169.160	93.1491	25201.8	30377.3	171.992	119.234	26688.5	34346.5	175.313
7.5	68.3652	23417.3	26476.2	167.344	74.0872	23726.3	27238.5	168.117	97.1314	24918.7	30322.3	170.945	126.048	26418.7	34252.5	174.268
7.635	68.7365	23340.8	26471.3	167.071	74.6149	23650.2	27231.6	167.844	98.2615	24844.4	30307.4	170.669	127.958	26347.7	34227.3	173.991
8.0	69.8029	23138.9	26457.7	166.348	76.0625	23448.6	27213.0	167.117	101.401	24647.0	30267.2	169.934	133.332	26160.0	34158.6	173.255
8.5	71.4174	22872.3	26438.1	165.388	78.2674	23182.5	27186.3	166.151	106.103	24386.6	30210.2	168.952	141.297	25912.7	34062.0	172.267
9.0	73.3468	22616.6	26416.0	164.456	80.8490	22927.1	27156.8	165.212	111.413	24136.8	30149.5	167.991	150.188	25677.1	33960.4	171.299
9.5	75.7508	22370.3	26390.1	163.543	83.9804	22681.3	27123.0	164.289	117.578	23897.9	30082.9	167.046	160.285	25453.8	33851.3	170.344
10.0	78.8281	22132.8	26358.5	162.641	87.9026	22444.7	27082.8	163.376	124.865	23670.1	30008.2	166.110	171.865	25243.1	33732.6	169.397
10.5	82.9048	21904.3	26318.8	161.741	92.8873	22217.4	27034.2	162.466	133.600	23453.8	29923.1	165.177	185.335	25046.6	33601.2	168.456
11.0	88.3227	21685.6	26268.4	160.838	99.3213	22000.7	26974.4	161.554	144.191	23250.3	29824.6	164.242	201.116	24865.6	33454.5	167.514
11.5	95.4827	21477.7	26204.8	159.928	107.631	21796.1	26900.5	160.635	157.205	23062.2	29709.0	163.303	219.643	24701.6	33289.8	166.570
12.0	104.964	21282.9	26124.1	159.004	118.374	21605.5	26809.2	159.705	173.107	22890.8	29573.7	162.354	241.973	24560.5	33099.9	165.619
12.5	117.363	21103.4	26023.0	158.063	132.206	21431.4	26696.4	158.759	192.540	22738.7	29415.2	161.392	268.209	24439.8	32885.8	164.658
13.0	133.483	20943.1	25896.6	157.101	149.753	21275.8	26558.8	157.792	216.393	22610.0	29228.2	160.415	299.592	24346.2	32639.7	163.682
13.5	154.209	20805.9	25740.3	156.117	172.408	21147.1	26388.0	156.804	245.612	22509.0	29007.8	159.421	336.939	24282.4	32358.0	162.690
14.0	180.447	20695.9	25549.6	155.108	200.736	21046.3	26182.0	155.792	281.011	22438.6	28750.4	158.406	380.911	24249.7	32038.3	161.677
14.5	213.601	20620.3	25317.0	154.075	235.640	20977.2	25937.3	154.757	323.866	22404.5	28449.8	157.371				
15.0	254.610	20582.4	25039.1	153.015	279.161	20950.9	25642.3	153.697	375.487	22412.0	28100.0	156.311				
15.5	305.451	20591.8	24705.9	151.929	331.678	20966.1	25298.1	152.611								
16.0	366.979	20649.9	24315.4	150.815	395.590	21034.2	24892.4	151.498								

Density	100°C				125°C				150°C				175°C			
	P	H	-G	S	P	H	-G	S	P	H	-G	S	P	H	-G	S
mol dm^{-3}	bar	J	J	JK^{-1}	bar	J	J	JK^{-1}	bar	J	J	JK^{-1}	bar	J	J	JK^{-1}
Ideal Gas	1.01325	33100.4	52587.8	229.635	1.01325	34389.3	58370.5	232.977	1.01325	35740.3	64236.2	236.267	1.01325	37152.2	70183.5	239.508
0.8	23.2237	32403.8	43069.2	202.259	25.0378	33729.1	47934.6	205.108	26.8434	35113.6	52872.0	207.930	28.6419	36558.3	57880.4	210.730
1.0	28.5598	32234.9	42473.5	200.210	30.8725	33568.9	47283.3	203.070	33.1731	34961.4	52165.5	205.901	35.4639	36414.8	57119.0	208.711
1.5	41.1760	31823.5	41447.7	196.359	44.8172	33178.7	46150.0	199.243	48.4335	34591.4	50925.9	202.097	52.0236	36065.9	55774.2	204.932
2.0	52.8540	31426.5	40774.6	193.491	57.9335	32802.0	45394.3	196.399	62.9744	34234.3	50088.3	199.273	67.9698	35729.8	54856.0	202.133
2.5	63.7171	31043.6	40289.1	191.164	70.3502	32439.0	44839.6	194.094	76.9157	33889.8	49465.7	196.988	83.4211	35405.6	54166.0	199.870
3.0	73.8903	30674.8	39917.8	189.180	82.1730	32088.8	44408.3	192.131	90.3829	33558.1	48974.4	195.043	98.5179	35093.5	53615.4	197.945
3.5	83.4924	30319.7	39621.6	187.435	93.5395	31752.0	44057.7	190.405	103.493	33238.7	48570.1	193.333	113.349	34791.9	53158.0	196.251
4.0	92.6497	29978.1	39376.9	185.864	104.569	31428.3	43763.0	188.852	116.365	32931.1	48226.3	191.794	128.080	34501.9	52764.6	194.726
4.5	101.479	29649.8	39168.8	184.426	115.397	31117.7	43507.9	187.431	129.158	32636.1	47924.9	190.384	142.837	34223.1	52417.0	193.328
5.0	110.109	29334.3	38987.0	183.093	126.128	30819.0	43281.8	186.113	142.003	32353.1	47654.2	189.076	157.761	33955.3	52102.5	192.029
5.5	118.661	29031.5	38823.9	181.845	136.927	30532.4	43076.0	184.876	155.035	32081.8	47405.9	187.848	173.027	33699.2	51811.6	190.808
6.0	127.284	28741.1	38673.9	180.665	147.910	30257.4	42884.9	183.705	168.408	31822.1	47173.2	186.684	188.817	33455.0	51536.9	189.651
6.5	136.077	28462.3	38533.2	179.540	159.256	29994.2	42703.3	182.588	182.297	31574.2	46950.9	185.573	205.250	33222.1	51273.8	188.544
7.0	145.230	28195.1	38397.5	178.461	171.151	29743.0	42527.0	181.515	196.895	31338.3	46734.6	184.504	222.597	33001.9	51016.8	187.479
7.5	154.905	27939.5	38264.1	177.418	183.708	29502.9	42353.8	180.476	212.466	31115.5	46519.8	183.470	241.055	32794.5	50762.2	186.448
7.635	157.659	27872.8	38227.7	177.142	187.274	29440.4	42306.7	180.201	216.882	31057.9	46461.5	183.196	246.268	32740.9	50693.3	186.175
8.0	165.322	27695.8	38129.7	176.405	197.289	29276.1	42178.5	179.467	229.163	30905.2	46304.4	182.464	260.844	32600.2	50506.9	185.445
8.5	176.643	27463.7	37992.5	175.415	212.015	29061.5	42000.1	178.479	247.310	30708.8	46084.4	181.480	282.347	32420.9	50246.2	184.463
9.0	189.109	27243.8	37850.1	174.444	228.141	28859.8	41815.8	177.510	267.066	30525.5	45858.7	180.513	306.013	32258.8	49975.8	183.498
9.5	203.150	27038.2	37698.4	173.487	246.225	28674.5	41620.4	176.554	289.073	30359.7	45620.8	179.559	331.984	32112.3	49695.1	182.545
10.0	219.077	26847.4	37535.1	172.538	266.479	28505.0	41412.7	175.606	313.570	30210.8	45369.6	178.614	360.784	31984.1	49399.8	181.600
10.5	237.248	26672.3	37357.8	171.594	289.278	28352.2	41190.3	174.664	341.102	30081.2	45101.1	177.673	392.864	31875.2	49086.9	180.658
11.0	258.125	26514.5	37163.7	170.650	315.130	28217.9	40949.9	173.723	372.144	29972.1	44812.4	176.733				
11.5	282.328	26376.8	36948.6	169.705	344.939	28107.1	40685.0	172.779								
12.0	310.374	26261.0	36710.1	168.755	379.138	28019.6	40394.1	171.829								
12.5	343.550	26174.5	36439.4	167.798												
13.0	382.131	26116.0	36136.9	166.831												

$$\frac{(H - H^{\circ})\text{ERDA} - (H - H^{\circ})\text{ other}}{(H - H^{\circ})\text{ERDA}} \times 100$$

The density scale has been broken beyond 4 mol dm^{-3} so as to show the comparisons in better detail at low densities and also to show the comparisons at the higher densities. The values shown for Dawe and Snowdon (*3*) were measured in a Joule-Thomson calorimeter in the range of 1 to 60 bars and 0 to 100 °C and provide an excellent comparison with the present results. The agreement of the present results with the extensive correlated data prepared for the International Union of Pure and Applied Chemistry by Angus et al. (*1*) is also shown.

At the three isotherms shown in Figure 5 of 50, 100, and 150 °C, the present results are also compared to those calculated by Geldermans (*6*) from the original P–V–T data of Michels and his co-workers at the van der Waals laboratory. The values of Geldermans and the calorimetric values of Dawe and Snowdon agree very well with the present results. Note also that our values lie above, below, and in-between the values of Geldermans and Angus at successive isotherms.

These curves show the value of calculating the thermody-

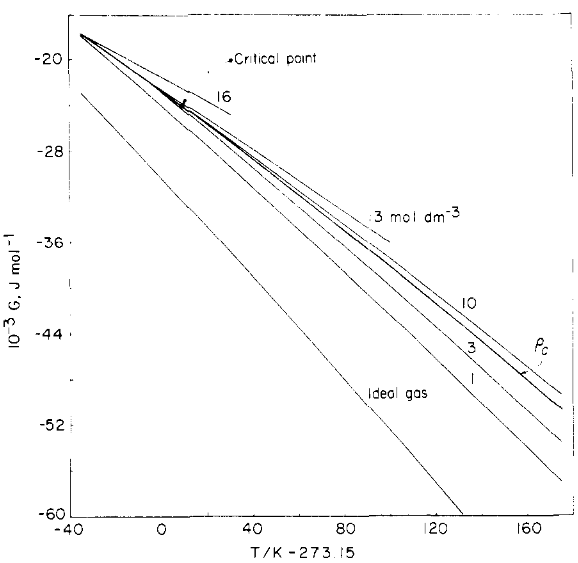

Figure 3. Gibbs energy in the single- and two-phase regions.

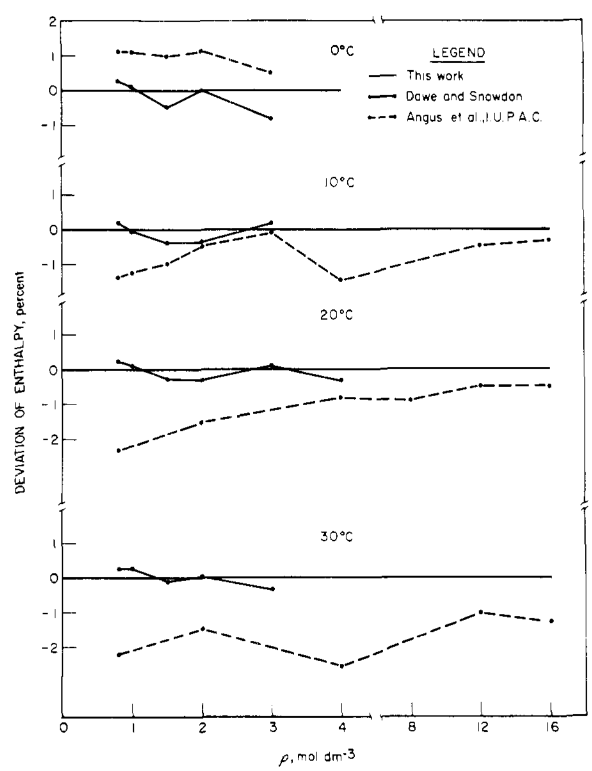

Figure 4. Comparison of enthalpy values: (—) this work, (•—•) Dawe and Snowdon, (• - - •) Angus et al., IUPAC.

namic properties from a single source of P-V-T data rather than from a correlation of several sets of data. Correlations are necessary when no single set of basic data covers the desired ranges of temperature and pressure or when no single set of data is obviously more accurate than another. Previously it was necessary to correlate the P-V-T data, and Angus used the data of Geldermans exclusively at high pressures but included several other data sets at low pressures. Thus, the calculated enthalpy data of Geldermans and Angus approach each other with increasing density.

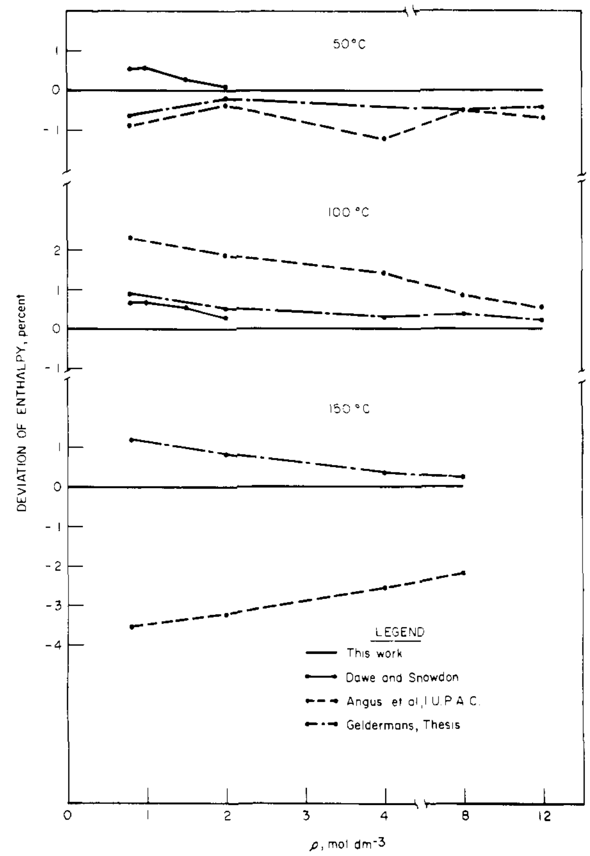

Figure 5. Comparison of enthalpy values: (—) this work, (•—•) Dawe and Snowdon, (• - - •) Angus et al., IUPAC, (•— - —•) Geldermans, thesis.

In conclusion, the present data cover a very wide range of variables and compare favorably with the few calorimetric data that are available. The results are directly useful for the thermodynamic analysis of processes and will also serve as a good base on which equations of state may be tested and to which future correlations may be compared.

Glossary

G molar Gibbs energy, J mol^{-1}
H molar enthalpy, J mol^{-1}
J joule
P pressure, bar
R gas constant = 83.1433 cm^3 bar mol^{-1} K
S molar entropy, J K^{-1} mol^{-1}
T thermodynamic temperature, K = $t + 273.15$
t International Practical Celsius temperature, 1968
V molar volume, dm^3 mol^{-1}
ρ molar density, mol dm^{-3}
γ activity coefficient = $\exp[(G - G^{\circ})/RT]/P$
atm 101 325 Pa = 1.013 25 bar

Subscripts

ideal ideal gas state
p constant pressure along isotherms
v constant volume along isotherms
ρ constant density
T constant temperature

Superscripts

$^{\circ}$ standard state

Literature Cited

(1) Angus, S., Armstrong, B., de Reuck, K. M., Featherstone, W., Gibson, M. R., "Ethylene, 1972 International Thermodynamic Tables of the Fluid State", International Union of Pure and Applied Chemistry, Butterworths, London, 1972.
(2) Chao, J., Wilhoit, R. C., Zwolinski, B. J., "The Ideal Gas Chemical Thermodynamic Properties of Ethylene", Report of Investigations, Thermodynamics Research Center, Texas A&M University, College Station, Texas, 1972. Note: Present work based on above cited report which was revised slightly and published as Chao, J., Zwolinski, B. J., *J. Phys. Chem. Ref. Data*, **7**, 251 (1975), after present calculations were completed.
(3) Dawe, R. A., Snowdon, P. N., *J. Chem. Thermodyn.*, **6**, 743 (1974); *ibid.*, **7**, 607 (1975).
(4) Douslin, D. R., Harrison, R. H., *J. Chem. Thermodyn.*, **8**, 301 (1976).
(5) Egan, C. J., Kemp, J. D., *J. Am. Chem. Soc.*, **59**, 1265 (1937).
(6) Geldermans, M. A., "Physical Properties of Compressed Ethylene", Thesis, University of Amsterdam, 1954.
(7) Harrison, R. H., Douslin, D. R., *J. Chem. Eng. Data*, **11**, 383 (1966).
(8) Harrison, R. H., Douslin, D. R., "Perfluorocyclobutane: Thermodynamic Properties of the Real Gas", *Bur. Mines (U.S.) Rep. Invest., No.* **6475** (1964).
(9) Symposium, "Industrial Needs for Critically Evaluated PVT Data of Ethylene and Related Substances", Rept. of Panel Discussions, June 13–16, 1972, Airlie House, Warrenton, Pa., Numerical Data Advisory Board, NRC, and Office of Standard Reference Data, NBS.

Received for review May 24, 1976. Accepted August 27, 1976. The work reported in this manuscript was carried out at the Bartlesville Energy Research Center, Energy Research and Development Administration, as part of the Joint Industry–Government Project on the "Thermophysical Properties of Ethylene" administered by the Office of Standard Reference Data, National Bureau of Standards. Contribution No. 220 from the thermodynamics research group at the Bartlesville Energy Research Center.

Vapor Pressure of Azulene between 114 and 261 °C

Edwin F. Meyer* and Timothy H. Gens
Chemistry Department, DePaul University, Chicago, Illinois 60614

The vapor pressure of a sample of azulene (99.8% purity by gas–liquid chromatography) has been measured between 114 and 160 °C using an oil manometer, and between 169 and 261 °C using comparative ebulliometry with water as reference. Cox and Frost–Kalkwarf equations fit the latter data with an average $\Delta p/p$ of 9.2×10^{-5}; the Antoine equation, 1.1×10^{-4}. When the oil manometer data are included, $\Delta p/p$ for the first two equations rises to 2.5×10^{-4}. Calculated vaporization properties (liquid → vapor) at 25 °C, $\Delta H^\circ = 14.14$ kcal mol^{-1}, $\Delta S^\circ = 28.64$ eu, do not agree with values in the literature.

There is serious disagreement among authors (*1, 4, 5, 8*) concerning the vaporization properties of azulene. Because of its interest as an aromatic, polar isomer of naphthalene, its standard thermodynamic properties ought to be at least as well known. Toward this end we have measured the vapor pressure of azulene from a temperature close to its triple point to about 10° above its normal boiling point, and have fitted the data to Antoine, Cox, and Frost–Kalkwarf equations.

Experimental Section

Azulene was purchased from Aldrich Chemical Co., and was 99.8% pure by gas–liquid chromatography, the only impurity found being naphthalene. It was used as received.

Measurements were made using the same apparatus as previously described (*7*). The sample was repeatedly rinsed with helium in an attempt to remove all traces of oxygen before any heating was done. Measurements started at 144 °C using an oil manometer. Pressure was decreased in intervals until a temperature of 108 °C was reached, when temperature instability was encountered. The pressure was then raised until the highest pressure compatible with the oil manometer was attained, corresponding to a temperature of 160 °C. The first stable comparative ebulliometric point was at 169 °C, and these data extend to 261 °C at intervals of about 8 °C. Once the azulene was heated, measurements were made continuously for 72 h, to avoid the unnecessary heating associated with shut-down and warm-up times.

Immediately after completion of the last data point, the pressure in the system was reduced to a value corresponding to the neighborhood of our fourth comparative ebulliometric point. (Lower pressures have sometimes led to uneven boiling, and a reliable check was desired.) The observed pressure was 0.018 cmHg above the originally measured one, a discrepancy ten times experimental error.

After removing the azulene from the boiler, another GLC analysis was run which indicated a slight increase in naphthalene content (to about 0.3%), consistent with the increase in vapor pressure during the experiment, but no other impurities were apparent. The presence of traces of another decomposition product, a brown residue, however, remained on the glass in the top part of the boiler. Attempts to evaluate its effect on the data are made in the discussion section.

The values for R_0 for both platinum resistance thermometers were checked using the triple point of water before and after the measurements.

Results

Table I presents the equilibrium temperatures and pressures for azulene, and includes the temperature of the water equilibrium for those points obtained using comparative ebulliometry. Table II presents constants for Antoine, Cox, and Frost–Kalkwarf (*3*) equations fitted to the comparative data only, and the last two equations fitted to both sets of data. The table includes average values of $\Delta p/p$ for each equation, where Δp is the absolute value of the difference between the observed and calculated values. Though the Frost–Kalkwarf is less convenient to work with, it has a basis in theory and was included to provide a check on the ability of the Cox equation to extrapolate to lower temperatures. All data fitting was accomplished using the rigorous, iterative least-squares method described by Wentworth (*10*), with weighting as previously discussed (*7*).

Discussion

There have been three studies of the vapor pressure of azulene published: Heilbronner and Wieland (*4*) (HW) used a static method, sealing their sample into one arm of a mercury manometer. They measured the vapor pressure of the solid from