

Figure 1. Drag reduction index vs. viscosity-average molecular weight for commercial Polyox (open circles) and polyacrylamide compounds.

(5). Thus, the effect of changes in molecular structure and molecular weight distribution on the observed drag reduction are clearly indicated here.

For purposes of comparison the ratio of the weight-average to the number-average molecular weight M_w/M_n was determined by Abdel-Alim and Hamielec (7) for a commercial PAM sample (Polyball 402, Stein-Hall, Ltd.) and found to be 2.43 again indicating the narrower molecular weight distribution of commercial PEO samples. Unfortunately, the equation of Collison et al., i.e., $[\eta] = 6.8 \times 10^{-4} M_n^{0.66}$ was used in the molecular weight computations by these authors. The Mark Houwink exponent of 0.66 appears rather low and is thought to be the result of the original experiments by Collison et al. having been made in solutions approximately 0.1 M in perchloric acid and 0.05 M in ferric

and/or ferrous ion. Such high ionic concentrations can easily reduce the value of the exponent. For example, Suen et al. (7) obtained the relation $[\eta] = 3.37 \times 10^{-4} M_w^{0.66}$ for PAM polymers in 1 M NaNO₃. Sholton (8), on the other hand developed the relation $[\eta] = 6.31 \times 10^{-5} M_w^{0.80}$ for PAM polymers in pure water.

While the literature contains an abundance of drag reduction measurements for a large variety of materials in a decade and a half of active research by many groups the characterization of the individual materials used has been neglected. A minimum characterization of drag reducing agents in terms of their molecular weight averages would ensure the quality of future reports published in this area and also promote the possibility of reproducing the experimental results.

Glossary

M_v	viscosity-average molecular weight
M_n	number-average molecular weight
$[\eta]$	intrinsic viscosity
π	osmotic pressure
c	concentration
$(\pi/c)_0$	reduced osmotic pressure extrapolated to zero concentration
A_2	second virial coefficient in equation $\pi/c = RT(1/M_n) + A_2C$
DR_M	maximum drag reduction in equation $DR/DR_M = c/(c + [c])$
$[c]$	intrinsic concentration
$DR_M/[c]$	drag reduction index

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Thermodynamic Properties of Liquid Sulfur Hexafluoride from 0 to 50 °C to 200 Bars

Bahram Keramati* and Carl H. Wolgemuth

Mechanical Engineering Department, Pennsylvania State University, University Park, Pennsylvania 16802

The density of SF₆ was measured from 0 to 50 °C at 5 °C intervals with pressures ranging from saturation to 170 bars. Rational functions representing the experimental isotherms and isobars were developed from which entropy, enthalpy, and isothermal compressibility were calculated.

The purpose of this paper is the presentation of the thermodynamic properties (density, isothermal compressibility, entropy, and enthalpy) of SF₆ in the compressed liquid region. Although some data on the density of liquid SF₆ are available in the liter-

ature (3), the amount of the available data does not allow the accurate calculation of the derived properties. In the present work, the density of liquid SF₆ was measured along isotherms from 0 to 50 °C at 5 °C intervals; the pressure ranged from saturation to 170 bars.

Experimental Section

A detailed discussion of the method used for the measurement of the density is given in ref 1 and 2. The method employed a device which operates on the principle of buoyancy. The device which is supported by a pivot is housed in a pressure vessel and is completely immersed by the fluid under study. The angular orientation of the device is uniquely related to the density of the

* To whom correspondence should be addressed at Corporate Research and Development, General Electric Company, Schenectady, N.Y. 12301.

Table I. Experimental Data for the Density of Sulfur Hexafluoride

Temp, °C	Pressure, bar	Density, kg m ⁻³	Temp, °C	Pressure, bar	Density, kg m ⁻³
-0.06	169.28	1705.4	15.01	20.89	1444.0
-0.08	144.95	1690.1	15.01	18.55	1437.2
-0.07	132.37	1681.0	20.00	175.48	1618.5
-0.08	118.65	1672.3	20.00	165.55	1611.2
-0.06	117.37	1669.6	20.00	150.11	1598.7
-0.09	99.26	1656.7	19.99	138.26	1587.9
-0.09	78.64	1638.1	20.00	125.23	1574.9
-0.10	65.67	1625.8	20.00	112.53	1560.9
0.02	52.38	1611.2	20.00	99.53	1546.2
0.02	37.01	1592.7	19.99	86.63	1529.2
0.01	31.34	1586.4	19.96	72.53	1509.3
-0.02	22.14	1572.6	20.04	57.31	1480.0
-0.05	16.63	1566.0	20.01	47.15	1462.6
-0.03	14.23	1562.6	20.03	39.57	1445.3
-0.03	12.95	1560.6	20.01	29.40	1418.5
-0.04	12.54	1559.9	20.00	24.96	1403.4
-0.04	12.52	1559.6	19.91	23.68	1399.0
5.02	171.90	1685.3	20.00	21.11	1390.3
5.04	150.82	1671.2	20.00	21.06	1390.1
5.04	139.23	1663.0	20.00	21.03	1389.8
5.04	125.73	1652.4	25.01	170.53	1590.2
5.04	111.81	1640.9	25.00	157.91	1580.4
4.83	98.16	1629.1	25.00	141.57	1564.8
5.00	95.54	1626.6	25.02	125.72	1548.1
5.04	85.21	1616.8	25.00	112.36	1532.0
5.05	71.36	1602.6	25.03	98.04	1513.6
5.00	57.62	1586.8	25.00	85.48	1494.9
5.04	57.57	1586.5	25.01	70.32	1469.7
5.06	44.11	1569.4	25.00	59.92	1449.5
5.00	36.29	1558.9	25.01	49.86	1427.2
5.00	36.29	1558.8	25.01	41.92	1403.4
5.00	28.93	1548.2	25.02	33.47	1377.7
5.00	24.10	1540.7	25.01	33.39	1379.1
5.00	18.37	1529.5	25.01	29.53	1363.6
5.00	15.54	1525.7	25.01	25.72	1348.0
5.00	14.80	1523.8	25.02	23.82	1340.1
5.00	14.38	1522.7	25.01	23.72	1338.1
4.99	14.31	1522.4	30.01	174.51	1570.4
10.07	172.17	1662.8	29.98	164.60	1562.3
10.01	166.65	1659.9	29.97	152.61	1550.2
10.01	153.14	1650.2	29.96	138.12	1534.9
10.00	139.91	1639.7	30.00	126.54	1521.4
10.01	125.58	1627.8	30.00	113.26	1503.4
9.98	111.59	1615.1	29.99	100.22	1486.0
9.97	98.64	1602.7	29.99	86.30	1462.8
10.05	84.81	1587.5	30.00	72.71	1437.1
10.00	71.01	1571.0	29.99	62.45	1414.4
9.97	57.63	1555.1	29.99	54.00	1392.7
9.96	43.13	1534.5	29.98	44.99	1365.1
10.08	36.35	1522.4	30.00	44.24	1361.3
10.04	29.02	1509.5	29.98	36.52	1334.6
9.98	24.96	1499.9	30.02	30.86	1304.9
10.00	17.43	1484.8	29.99	26.57	1276.6
9.96	16.69	1482.5	34.99	176.61	1548.0
9.98	16.37	1480.7	34.99	171.09	1543.5
10.02	16.36	1480.4	34.99	169.48	1542.7
15.01	171.27	1637.4	34.99	160.24	1532.8
15.00	161.19	1631.4	34.97	159.47	1532.3
14.99	152.73	1624.6	34.98	149.66	1521.0
14.99	139.40	1613.8	35.01	141.30	1510.0
14.96	125.44	1601.5	35.01	139.86	1509.1
14.96	111.47	1585.1	35.00	134.47	1500.8
14.96	111.47	1585.9	35.02	127.10	1493.0
14.96	111.44	1586.0	34.99	127.03	1492.7
14.98	97.90	1572.7	34.99	115.36	1476.1
14.98	84.41	1557.2	35.01	113.33	1473.2
14.96	70.37	1539.1	35.00	107.25	1463.7
15.03	57.64	1520.0	34.99	100.50	1452.6
15.04	43.51	1496.3	34.99	98.84	1449.6
15.07	35.98	1481.6	35.00	98.74	1449.1
14.99	28.71	1464.2	35.00	91.73	1437.0
15.01	25.51	1456.5	34.99	86.12	1426.2

Table I. Continued

Temp, °C	Pressure, bar	Density, kg m ⁻³	Temp, °C	Pressure, bar	Density, kg m ⁻³
34.99	85.55	1425.1	44.98	87.12	1350.6
35.00	72.79	1397.5	44.98	75.60	1317.8
35.00	71.37	1391.6	44.98	66.86	1286.5
34.96	61.04	1366.2	44.98	62.30	1267.3
35.00	59.98	1363.7	44.96	55.04	1229.7
34.98	51.56	1335.4	44.99	50.98	1204.7
35.00	48.58	1324.4	45.01	47.69	1178.3
35.00	43.33	1301.2	45.01	45.57	1158.1
34.99	41.00	1288.9	45.00	43.31	1130.6
34.99	36.31	1261.8	45.01	42.77	1121.2
34.99	33.13	1238.5	45.00	42.12	1115.2
34.99	32.56	1234.6	45.00	41.07	1096.1
35.00	30.63	1216.3	45.00	40.42	1084.2
34.99	29.80	1207.4	45.00	39.38	1056.6
34.99	29.79	1204.7	44.98	38.92	1045.5
34.99	29.79	1204.1	44.99	38.29	1019.7
34.99	29.73	1205.5	45.00	37.86	990.8
34.99	29.73	1205.3	45.00	37.72	979.7
39.94	173.75	1518.6	44.99	37.28	915.8
39.99	165.33	1510.2	44.99	37.24	906.9
39.98	153.88	1497.5	45.01	37.24	905.1
40.00	140.88	1482.2	49.99	174.02	1467.0
39.97	129.03	1463.9	50.01	166.25	1459.6
40.01	115.11	1443.4	50.00	154.33	1444.0
39.99	101.60	1419.5	50.01	140.54	1423.1
39.99	86.68	1389.7	50.00	127.19	1398.3
40.00	79.27	1369.4	49.99	114.00	1375.4
40.00	72.56	1353.1	50.00	98.01	1336.6
39.99	62.24	1320.6	49.97	91.25	1321.5
40.00	53.08	1283.8	49.99	85.09	1302.8
39.99	44.64	1237.9	50.00	84.23	1299.1
39.99	39.81	1201.6	50.00	76.32	1272.2
39.99	35.86	1157.2	50.00	70.75	1249.8
39.99	33.94	1123.7	49.99	65.67	1225.6
40.00	33.31	1107.2	50.00	61.40	1201.9
39.99	33.29	1108.2	50.00	56.09	1165.0
39.99	33.29	1108.0	50.01	50.14	1106.3
40.00	33.29	1107.9	49.97	47.08	1061.0
45.01	173.86	1493.1	50.00	44.08	983.7
45.01	167.89	1487.1	49.99	43.50	959.6
44.97	155.57	1472.8	49.98	42.17	870.1
45.00	141.93	1454.5	49.99	41.12	698.0
45.00	127.92	1433.0	50.00	39.53	509.6
45.01	114.00	1409.1	49.99	38.33	448.5
44.98	104.03	1387.4	50.00	36.55	386.5
44.98	98.15	1377.1			

liquid. Two different devices were employed for the measurement of the SF₆ densities: one for the high densities and the other for low densities. The uncertainty in the measured densities amounts to ±0.1%.

Pressures were measured by a dead weight gauge that had a sensitivity of 0.2 psi (0.014 bar) and an accuracy of ±0.03%, calibrated in psi traceable to N.B.S. A conversion factor of 14.5038 psi bar⁻¹ was applied to the dead weight gauge measurements. A platinum resistance thermometer, calibrated traceable to N.B.S. on the 1968 IPTS scale was used for the measurement of temperature. The uncertainty in the measured temperatures is ±0.02 °C. The SF₆ used in this work was supplied by Matheson Gas Products and had a minimum purity of 99.99%. No further purification was attempted. The details of the experimental apparatus and procedure are given in ref 2.

Results

The raw data appear in Table I. Since a small variation in temperature exists for the data along each isotherm, the measured densities were corrected to integer temperatures (0, 5, 10, . . . , 50 °C). The method used for this correction consisted of fitting rational functions of the form

$$\rho = \frac{b_1 + b_2 p + b_3 p^2 + b_4 p^3}{1.0 + b_5 p + b_6 p^2 + b_7 p^3} \quad (1)$$

to each experimental isotherm. In eq 1, ρ is the density and p is the pressure. The parameters b_j were determined by a non-linear least-squares technique. In all cases, eq 1 was representative of the experimental data to within the latter's absolute accuracy (±0.1%). The rational functions thus obtained were used to estimate the partial derivative $(\partial\rho/\partial T)_p$ for all the experimental points. To correct a measured density, ρ , at temperature T and pressure p to the nearest integer temperature T_i , the following expression was used:

$$\rho(T_i, p) = \rho(T, p) + (\partial\rho/\partial T)_p (T_i - T) \quad (2)$$

where the partial derivative was calculated at T by fitting a second-order polynomial in temperature to the density at T and p , and two other densities at two other temperatures nearest to T for which an isothermal equation was available, all at pressure p . The correction to the density was typically of the order of 0.5 kg m⁻³. Figure 1 shows a pressure vs. density diagram which represents the corrected densities along the 11 isotherms.

The corrected data were then represented by rational func-

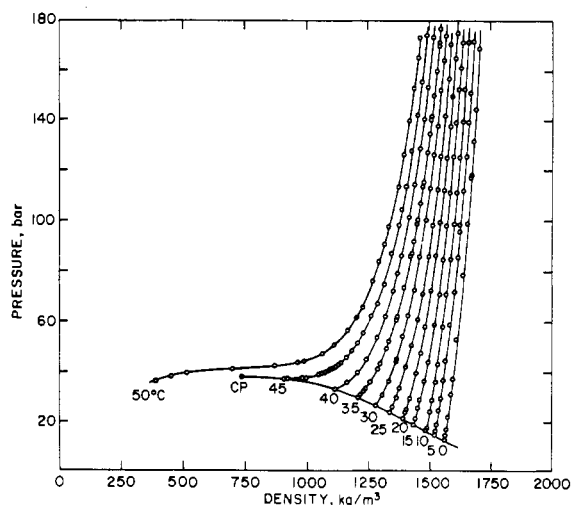


Figure 1. Pressure vs. density diagram for SF₆.

Table II. Parameters b_j for the Isothermal Equation (1) ^a

	0 °C	5 °C	10 °C
b_1	0.15401569D 01	0.14965307D 01	0.14050671D 01
b_2	0.78546060D-02	0.92066194D-02	0.15376794D 00
b_3	0.00000000D 00	0.00000000D 00	0.67722006D-03
b_4	0.00000000D 00	0.00000000D 00	0.00000000D 00
b_5	0.40378422D-02	0.48167536D-02	0.10256864D 00
b_6	0.00000000D 00	0.00000000D 00	0.34294010D-03
b_7	0.00000000D 00	0.00000000D 00	0.00000000D 00
	15 °C	20 °C	25 °C
b_1	0.13537684D 01	0.11378760D 01	0.11125258D 01
b_2	0.55064105D-01	0.30717983D 00	0.10011058D 00
b_3	0.13518330D-03	0.21774561D-02	0.53167608D-03
b_4	0.00000000D 00	0.00000000D 00	0.00000000D 00
b_5	0.35754751D-01	0.22106211D 00	0.70402175D-01
b_6	0.64011900D-04	0.11570838D-02	0.28008617D-03
b_7	0.00000000D 00	0.00000000D 00	0.00000000D 00
	30 °C	35 °C	40 °C
b_1	0.13766330D 01	0.13732130D 01	0.11134607D 01
b_2	-0.10196399D 00	-0.71925063D-01	-0.22432400D-01
b_3	-0.11362639D-02	-0.76124748D-03	-0.69910000D-03
b_4	0.00000000D 00	0.00000000D 00	0.00000000D 00
b_5	-0.84170765D-01	-0.61605202D-01	-0.28019900D-01
b_6	-0.61725281D-03	-0.40930554D-03	-0.39300000D-03
b_7	0.00000000D 00	0.00000000D 00	0.00000000D 00
	45 °C	50 °C	
b_1	0.12332001D 01	0.93971880D 00	
b_2	-0.63796546D-01	-0.25465871D-02	
b_3	0.30950861D-03	-0.57106282D-03	
b_4	0.13978552D-04	0.00000000D 00	
b_5	-0.59069097D-01	-0.14850566D-01	
b_6	0.58555804D-03	-0.32558364D-03	
b_7	0.76895421D-05	0.00000000D 00	

^a Pressures are in bars and densities in g cm⁻³. Experimental data from saturation pressure to 170 bars were used for the determination of the parameters.

tions of the form of eq 1. The parameters b_j for the corrected data are given in Table II. The use of the entries in Table II in eq 1 will yield densities in g cm⁻³ if the pressure is expressed in bars. The rational function representing the supercritical isotherm at 50 °C should not be used for pressures below 43.5 bars. Figure 2 shows the deviation between eq 1 and the corrected data for the 35 °C isotherm for which both density measuring devices were used. The scatter depicted in Figure 2 is indicative of all the other isothermal representations.

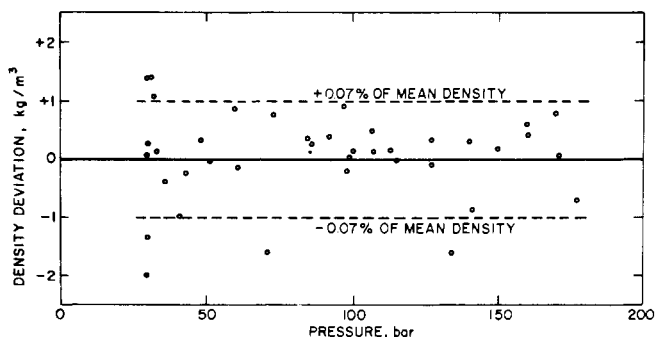


Figure 2. Deviation between eq 1 and the corrected data for the 35 °C isotherm.

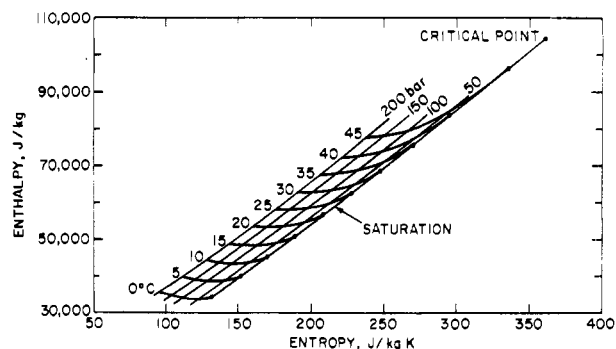


Figure 3. Enthalpy vs. entropy diagram for SF₆.

Derived Properties

For the calculation of entropy and enthalpy, the following expressions were employed:

$$S(p, T) = \left[\int_{p_T}^p \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial T} \right)_p dp \right]_T + S_T \quad (3)$$

$$H(p, T) = T[S(p, T) - S_T] + \left[\int_{p_T}^p \frac{1}{\rho} dp \right]_T + H_T \quad (4)$$

where the subscript T refers to the saturated liquid at temperature T , S is entropy, and H is enthalpy. The saturated liquid entropies and enthalpies are available from the "Table of Thermodynamic Properties of Sulfur Hexafluoride" obtained from Allied Chemical Corporation (4). In the Allied tables, the saturated liquid entropies and enthalpies are taken to be zero at -40 °C.

In order to evaluate the integral in eq 3, analytic expressions for isobars must be developed so that the partial derivative $(\partial \rho / \partial T)_p$ can be calculated. The evaluation of the integral in eq 4 was performed analytically since analytic isothermal representations are already available from eq 1.

In order to develop isobaric equations, the rational function representations for the isotherms were used to generate densities at constant pressure. The densities at each pressure were then represented by a rational function of the form

$$\rho = \frac{a_1 + a_2 T + a_3 T^2 + a_4 T^3}{1.0 + a_5 T} \quad (5)$$

where T is in °C and ρ is in g cm⁻³. The parameters a_j were determined by a least-square criterion. The pressures for which these equations were developed range from the saturation pressure at 0 °C to 200 bars at 5 bars intervals, and all the saturation pressures at the temperatures investigated were included also. Since data at lower than 0 °C were not collected, the equations for the four lowest pressures (12.52, 14.31, 15.0, and 16.36 bars) reflected the extrapolation of the isothermal equations for at most three higher temperatures in the two-phase

Table III. Parameters a_j for the Isobaric Equation (5)^a

PRESSURE bar	a_1	a_2	a_3	a_4	a_5
12.52	0.156019D 01	-0.278849D-01	0.000000D 00	0.000000D 00	-0.128984D-01
14.31	0.156265D 01	-0.274975D-01	0.000000D 00	0.000000D 00	-0.127644D-01
15.00	0.156360D 01	-0.273163D-01	0.000000D 00	0.000000D 00	-0.126863D-01
16.36	0.156547D 01	-0.269193D-01	0.000000D 00	0.000000D 00	-0.124991D-01
18.55	0.156848D 01	-0.261985D-01	0.000000D 00	0.000000D 00	-0.121282D-01
20.00	0.157047D 01	-0.256846D-01	0.000000D 00	0.000000D 00	-0.118502D-01
21.03	0.157191D 01	-0.250024D-01	0.000000D 00	0.000000D 00	-0.114319D-01
23.72	0.157555D 01	-0.298149D-02	-0.787187D-04	-0.183435D-05	0.251091D-02
25.00	0.157729D 01	0.330886D-01	-0.210490D-03	-0.473339D-05	0.253988D-01
26.57	0.157926D 01	-0.521328D-01	0.101160D-03	0.244604D-05	-0.288329D-01
29.73	0.158347D 01	-0.441090D-01	0.800689D-04	0.155196D-05	-0.237281D-01
30.00	0.158381D 01	-0.441579D-01	0.796559D-04	0.157087D-05	-0.237655D-01
33.29	0.158818D 01	-0.410322D-01	0.769239D-04	0.115248D-05	-0.217570D-01
35.00	0.159033D 01	-0.399075D-01	0.734836D-04	0.107081D-05	-0.210589D-01
37.24	0.159292D 01	-0.397775D-01	0.662944D-04	0.121260D-05	-0.210523D-01
40.00	0.159658D 01	-0.366146D-01	0.662131D-04	0.801707D-06	-0.189939D-01
43.50	0.160096D 01	-0.340539D-01	0.642951D-04	0.544072D-06	-0.173547D-01
45.00	0.160276D 01	-0.328595D-01	0.621171D-04	0.453012D-06	-0.166041D-01
50.00	0.160851D 01	-0.286224D-01	0.504363D-04	0.232036D-06	-0.139851D-01
55.00	0.161402D 01	-0.247480D-01	0.375817D-04	0.112581D-06	-0.116241D-01
60.00	0.161938D 01	-0.214498D-01	0.267729D-04	0.406679D-07	-0.962884D-02
65.00	0.162378D 01	-0.155424D-01	0.000000D 00	0.000000D 00	-0.615113D-02
70.00	0.162909D 01	-0.146709D-01	0.000000D 00	0.000000D 00	-0.562821D-02
75.00	0.163414D 01	-0.139298D-01	0.000000D 00	0.000000D 00	-0.519592D-02
80.00	0.163898D 01	-0.132825D-01	0.000000D 00	0.000000D 00	-0.482695D-02
85.00	0.164365D 01	-0.127066D-01	0.000000D 00	0.000000D 00	-0.450494D-02
90.00	0.164816D 01	-0.121876D-01	0.000000D 00	0.000000D 00	-0.421954D-02
95.00	0.165252D 01	-0.117157D-01	0.000000D 00	0.000000D 00	-0.396389D-02
100.00	0.165676D 01	-0.112841D-01	0.000000D 00	0.000000D 00	-0.373327D-02
105.00	0.166087D 01	-0.108879D-01	0.000000D 00	0.000000D 00	-0.352433D-02
110.00	0.166486D 01	-0.105233D-01	0.000000D 00	0.000000D 00	-0.333459D-02
115.00	0.166874D 01	-0.101876D-01	0.000000D 00	0.000000D 00	-0.316216D-02
120.00	0.167252D 01	-0.987837D-02	0.000000D 00	0.000000D 00	-0.300556D-02
125.00	0.167619D 01	-0.959393D-02	0.000000D 00	0.000000D 00	-0.286358D-02
130.00	0.167977D 01	-0.933267D-02	0.000000D 00	0.000000D 00	-0.273525D-02
135.00	0.168326D 01	-0.909327D-02	0.000000D 00	0.000000D 00	-0.261968D-02
140.00	0.168665D 01	-0.887457D-02	0.000000D 00	0.000000D 00	-0.251614D-02
145.00	0.168996D 01	-0.867550D-02	0.000000D 00	0.000000D 00	-0.242395D-02
150.00	0.169319D 01	-0.849510D-02	0.000000D 00	0.000000D 00	-0.234248D-02
155.00	0.169634D 01	-0.833245D-02	0.000000D 00	0.000000D 00	-0.227118D-02
160.00	0.169942D 01	-0.818672D-02	0.000000D 00	0.000000D 00	-0.220949D-02
165.00	0.170242D 01	-0.805708D-02	0.000000D 00	0.000000D 00	-0.215692D-02
170.00	0.170535D 01	-0.794276D-02	0.000000D 00	0.000000D 00	-0.211296D-02
175.00	0.170821D 01	-0.784301D-02	0.000000D 00	0.000000D 00	-0.207716D-02
180.00	0.171101D 01	-0.775710D-02	0.000000D 00	0.000000D 00	-0.204907D-02
185.00	0.171375D 01	-0.768434D-02	0.000000D 00	0.000000D 00	-0.202825D-02
190.00	0.171642D 01	-0.762404D-02	0.000000D 00	0.000000D 00	-0.201427D-02
195.00	0.171904D 01	-0.757554D-02	0.000000D 00	0.000000D 00	-0.200675D-02
200.00	0.172160D 01	-0.753820D-02	0.000000D 00	0.000000D 00	-0.200528D-02

^a Temperatures are in °C and densities in g cm⁻³. The parameters for isobars above 170 bars are based on densities which are extrapolated from the isothermal equation (1) with the parameters b_j from Table II.

region. It must also be noted that pressures beyond 170 bars represent the extrapolation of the experimental results. The parameters a_j are given in Table III.

The partial derivative $(\partial\rho/\partial T)_p$ was then calculated by differentiating the isobaric equations. The integral in eq 3 was performed numerically. In addition to entropy and enthalpy, the isothermal compressibility given by

$$\kappa = \frac{1}{\rho} \left(\frac{\partial\rho}{\partial p} \right)_T \quad (6)$$

was also calculated by the direct differentiation of the isothermal equations. The thermodynamic properties of SF₆ consisting of density, isothermal compressibility, entropy, and enthalpy are given in Table IV (deposited with the ACS Microfilm Depository Service; see paragraph at end of paper regarding supplementary material). Table IV is arranged by temperature, ranging from 0 to 50 °C; entropy and enthalpy were not calculated for the supercritical isotherm at 50 °C, and these properties do not appear in Table IV for this temperature. An enthalpy vs. entropy diagram appears in Figure 3.

The absolute accuracy of the calculated derived properties depends primarily on the accuracy of the partial derivatives that were generated through the isobaric and isothermal equations. Although there is no direct statistical method for obtaining a reasonable bound on the possible error in the partial derivatives, a more stringent test of the accuracy of the derived properties would be the examination of the thermodynamic consistency of the calculated properties. For this purpose, the basic thermodynamic relation

$$\left(\frac{\partial \rho}{\partial T}\right)_p = -\rho^2 \left(\frac{\partial S}{\partial \rho}\right)_T \quad (7)$$

was employed. The two sides of eq 7 were found to be well within 2% of each other for several states which were selected at random (1).

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Supplementary Material Available: Table IV, thermodynamic properties of SF₆ (11 pages). Ordering information is given on any current masthead page.

The Enthalpies of Combustion and Formation of 2-Methyl-2-oxazoline and 2-Ethyl-2-oxazoline

Walter S. Hamilton,* Patricia Thompson, and Sharon Pustejovsky

Department of Chemistry, Texas Woman's University, Denton, Texas 76204

The enthalpies of combustion of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline were determined by precision oxygen-bomb combustion calorimetry. The following values, based on the mass of sample burned, are reported for the standard enthalpy of combustion ΔH_c° (298.15 K) kcal_{liq} mol⁻¹ of these compounds in the liquid state: 2-methyl-2-oxazoline, -574.79 ± 0.20 kcal mol⁻¹; 2-ethyl-2-oxazoline, -731.51 ± 0.25 kcal mol⁻¹. (Throughout this paper cal_{liq} = 4.184 J, atm = 101.325 kPa.) Enthalpies of formation in the condensed and in the gaseous state are derived.

In continuation of a study of the thermodynamic properties of oxazole, isoxazole, and related compounds, we have measured the enthalpy of combustion of 2-methyl-2-oxazoline and 2-ethyl-2-oxazoline. These values have not been previously reported in the literature.

Experimental Section

Apparatus and Procedures. The apparatus and experimental procedures have been described previously (2). The temperature rise was measured by quartz thermometry. The internal volume of the bomb was 0.342 dm³. For every experiment approximately 1 g of water was added to the bomb, and the bomb was flushed and charged to 30 atm with pure oxygen. Fragile flexible ampoules of borosilicate glass confined the liquid samples. The samples were weighed to an accuracy of 0.01 mg, and corrections for air buoyancy were applied. Ignition was accomplished by fusing a 10 cm length of no. 44 s.w.g. platinum wire in contact with a small piece (≈ 4 mg) of Whatman No. 1 filter paper. The value of $\Delta E_c^\circ/M$ for the filter paper was taken as -4118 ± 10 cal g⁻¹ (7). The extent of combustion was based on the mass of sample. All calculations, including conversion of time and temperature measurements to initial and final temperature, correction for heat exchange between calorimeter and jacket, and reduction to the standard state, were carried out on a digital

computer (8). The computer program followed the procedure of Hubbard et al. (3).

Materials. 2-Methyl-2-oxazoline and 2-ethyl-2-oxazoline were obtained from Aldrich Chemical Co., Inc., and had a claimed purity of 99+%. Both compounds were further purified by distillation through a molecular sieve directly into glass ampoules. Samples of the two compounds purified by the above method were tested on a gas chromatograph, and 2-ethyl-2-oxazoline was additionally tested via ir; no impurities were found.

The calorimeter was calibrated with benzoic acid, NBS sample 39i, which had a heat of combustion of 26.434 ± 0.0003 absolute kJ g⁻¹ under certificate conditions.

The auxiliary oil had empirical formula CH_{1.96}. The value of $\Delta E_c^\circ/M$ for the oil was determined by us and found to be $-11\,018.75 \pm 1.05$ cal g⁻¹ (mean and standard deviation).

Results

Units of Measure and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (1) and the 1963 fundamental constants and definitions of the thermodynamic temperature scale. For reducing weights in air to weights in vacuo and correcting to standard states, the values summarized in Table I, all for 298.15 K, were used for density, ρ , specific heat, C_p , and $(\partial E/\partial P)_T$ for the substances. Values of density were measured in a Weld type pycnometer. Specific heat values were measured with a Perkin-Elmer DSC-1B differential scanning calorimeter (5). Values of $(\partial E/\partial P)_T$ were derived from the ap-

Table I. Physical Properties at 298.15 K

	ρ , g ml ⁻¹	C_p , cal deg ⁻¹ g ⁻¹	$(\partial E/\partial P)_T$, cal atm ⁻¹ g ⁻¹
2-Methyl-2-oxazoline	0.997	0.492	-0.001 06
2-Ethyl-2-oxazoline	0.974	0.417	-0.005 19
Benzoic acid	1.320	0.289	-0.002 78
Auxiliary oil	0.870	0.530	(-0.006)
Fuse	1.50	0.400	(-0.002 8)