[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. VIII. Data for Some Aliphatic Alcohols Using an Improved Flow Calorimeter Requiring only 25 Ml. of Sample[1]

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A flow calorimeter requiring only 25 ml. of liquid sample was used to measure the heat capacity of the C_1- to C_5-aliphatic alcohols from their respective boiling points to 160° at one atmosphere pressure with excellent precision and accuracy. The results indicate that the alcohols are appreciably associated in the vapor phase in a temperature range near the boiling point. Measurements on alcohol-carbon tetrachloride mixtures were interpreted to obtain the heat capacity of unassociated methyl and ethyl alcohol at one atmosphere pressure.

Among the several methods which are thoroughly discussed by Partington[3] for measuring the heat capacity of vapors and gases, the constant flow method is the most simple and direct and has been widely used. In practice the method is subject to systematic errors, as shown by a study of the design of flow calorimeters made by Montgomery and De Vries.[4] Results of high precision do not ensure high accuracy. Recent measurements on benzene by several different investigators are in good agreement, however, and measurements on this substance were used to check the accuracy of the present work, with particular reference to the careful work of Scott, *et al.*[5]

A flow calorimeter requiring only 25 ml. of liquid has been described.[6] That calorimeter was redesigned in this research to give results of greater precision, and a new treatment of the data for heat loss was devised with a resulting appreciable saving in the time required for a determination. The heat capacity of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *s*-butyl, *t*-butyl and *n*-amyl alcohols were determined at one atmosphere pressure from slightly above their boiling points to 160°.

Experimental

Five calorimeters were built and tested. Although differing in design, each consisted essentially of a Pyrex glass tube, about 3-5 mm. i.d. and 0.2-0.3 mm. wall thickness, which contained an electrical heater and some type of temperature measuring element. This tube was surrounded by a glass jacket, silvered and evacuated. The thin-walled tube ensured a small heat capacity and resulting rapid attainment of thermal equilibrium and the jacket provided efficient insulation. Experiments with four of the calorimeters which gave precise but not accurate results showed that these were unsatisfactory because at equilibrium the temperature measuring elements were not actually at the temperature of the flowing vapor. This might result from either (1) a sharp temperature gradient along the lead-out wires so that the elements gained or lost heat along the leads faster than they exchanged heat with the vapor, or (2) excessive heating of the elements by either direct radiation or conduction from a heater which was considerably hotter than the vapor because it had too small an area for good heat transfer.

The importance of the first factor was shown when thermistors were used as temperature measuring elements. The use of thermistors for this purpose has been described in the literature.[7] Curvature in the plot of heat capacity *versus* the reciprocal flow rate could be explained by assuming that the thermistors, Western Electric Type 14B, were cooler than the vapor at the lower rates of vapor flow. Since the element is a small 1 mm. bead covered by a glass envelope, heat transfer from the vapor to the element was probably slower than the leakage of heat along the leads. An empirical equation found to fit the resistance-temperature characteristics to ±0.002° was

$$T = \frac{A - B \log (R - C)}{D + \log (R - C)}$$

in which T is degrees Kelvin, R is the resistance, and the other quantities are empirical constants.

The successful calorimeter was modeled after that of Coleman and De Vries,[8] but was about half its size. The temperature measuring element, T_2, was a four junction copper-constantan thermel. The thermel wires were brought out through a long (at least 20 cm.) and narrow (3 mm. i.d.) thin walled (0.3 mm.) glass tube. The junctions placed in the vapor stream were bare to ensure a very small thermal lag and were insulated from each other with Nylon thread. The reference junction T_1, was placed in a separate vacuum-jacketed tube to smooth out thermostat fluctuations. A separate thermocouple was placed alongside the reference junctions to measure the temperature of the incoming vapor All thermel wires were brought out at the top through a seal of litharge-glycerol cement.

The heater in the other arm (6 mm. i.d.) of the U-shaped calorimeter, consisted of two concentric spirals, 5 cm. long, of No. 28 B and S gage chromel wire separated by a thin glass tube and had a total resistance of 15 ohms. Experiments showed that a heater of this size did not become hotter than the vapor at the flow rates used. Long spiralled copper leads were separated by a thin strip of Teflon. The leads were brought out through short sections of 1 mm. o.d. platinum tubing, sealed through the end of a 5 mm. glass tube and closed with soft solder. The glass tube was sealed in with litharge-glycerol cement.

The vapor was brought to thermostat temperature by a preheater of six feet of spiralled 6 mm. glass tubing. The temperature of the thermostat liquid[9] was controlled to 0.01° by a mercury-in-glass regulator. A space above the thermostat was heated to prevent condensation of the vapor.

A flask boiler, previously described,[6] was used to evaporate the sample. Liquid was fed into the boiler at a constant rate from a thermostated 30-ml. hypodermic syringe. Since the sample was injected through a capillary and instantly vaporized, no fractionation of mixtures occurred. The rate of sample injection could be varied from 0.9 to 2.5 ml. per minute by a screw drive, a system of belts and pulleys, and a constant speed electric motor. A revolution counter was geared to the screw drive to measure the volumes delivered. These could be measured with a precision of 0.1%. The rate of flow was timed with a hand operated stop watch, which was checked against the time signals from the National Bureau of Standards.

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(1) Abstracted from the Ph.D. thesis of G. C. Sinke. Presented in part at the 121st Meeting of the American Chemical Society, Buffalo, N. Y., 1952.

(2) Atomic Energy Commission Predoctoral Fellow, 1950-1952.

(3) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. I, Longmans, Green and Co., London, 1949, p. 792.

(4) J. B. Montgomery and T. De Vries, THIS JOURNAL, **64**, 2372 (1942).

(5) D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

(6) A. E. Reynolds and T. De Vries, THIS JOURNAL, **72**, 5443 (1950).

(7) J. A. Becker, C. B. Green and G. L. Pearson, *Elec. Eng.*, **65**, 711 (1946).

(8) C. F. Coleman and T. De Vries, THIS JOURNAL, **71**, 2839 (1949).

(9) General Electric Silicone Oil No. 9981-LTNV-40, J. R. Hartwell, *Anal. Chem.*, **20**, 374 (1948).

Potential measurements were made with a Rubicon Type B potentiometer.

Benzene, carbon tetrachloride and the alcohols were carefully dried and rectified to 0.1° boiling range.

Procedure.—After the thermostat was brought to the desired temperature and the enclosed space above it heated to a temperature above the boiling point of the compound in use, the entire 20–30 ml. sample was run through at least once to bring the interior of the calorimeter to bath temperature. The sample could be returned to the syringe without exposure to the air. The sample was passed through the calorimeter a second time, and by the time the last half of the sample was passing through, equilibrium conditions were established and a measurement could be made with the four-junction thermel of any temperature difference which might exist, even though the heater was off. Usually a small but steady difference was observed, due to heat leak along the wires, Joule–Thomson effect, and possibly other factors. The sample was again returned to the syringe and evaporation started. The heater was turned on as soon as vapor started flowing. By the time half the sample had evaporated, which was from 3 to 10 minutes, depending on flow rate, equilibrium conditions had been reached. The potential of the differential thermal was followed for the next 3 to 10 minutes. This potential was corrected for the small potential observed with no heat added. During this time measurements were also made of the potential drop across the heater and a standard resistance in series with it. The flow rate was determined from the revolution counter readings. Flow rates varied from about 0.01 to 0.04 mole per minute, and the temperature rise was about 4°.

All measurements were made in international units, and the calorie was taken as 4.1833 joules. When a volt box was sometimes used for measuring the potential drop across the heater, a correction was made for the small current flowing through the box.

Calculation and Results

Benzene.—In the flow calorimeter, practically all the heat loss, W, takes place by radiation, hence $W = k_1(T_i^m - T_0^m)$, in which the radiation constant, k_1, depends on the nature of the surface and its dimensions, and the constant m is 4 for black-body radiation but varies from 4 to 5.5 for other surfaces.[10] The temperature difference, $\Delta T' = T_i - T_0$, between the inner and outer walls of the calorimeter will be slightly larger than the measured temperature rise, ΔT, of the heated vapor. The above equation can be expressed very closely by $mk_1T_0^{(m-1)}\Delta T'$, which is the first term of a Taylor's expansion.[11] With $\alpha = 1/2\partial C_p/\partial T$, let $(C_p + \alpha\Delta T)$ be the average heat capacity of the vapor over the temperature interval ΔT near temperature T_0. A heat balance equation can be written, $Q = (C_p + \alpha\Delta T)F\Delta T + mk_1T_0^{(m-1)}\Delta T' + \Delta q$, in which Q is the rate of heat input to the vapor, C_p the heat capacity of the vapor at thermostat temperature T_0, F the flow rate of the vapor, and Δq any heat loss other than that by radiation. The equation can be rewritten as

$$C_p' = Q/F\Delta T = (C_p + \alpha\Delta T) + 1/F(k_2T_0^{(m-1)} + \Delta q/\Delta T)$$

writing k_2 for $mk_1\Delta T'/\Delta T$ and realizing that variations in $\Delta T'/\Delta T$ are of second-order importance. At any given thermostat temperature, $k_2T_0^{(m-1)}$ has a constant value that can be experimentally determined. When a series of measurements is made at *constant heat input* and variable flow rate, and $(C'_p - \alpha\Delta T)$ is plotted against the reciprocal flow rate, $1/F$, a linear plot indicates that $(k_2T_0^{(m-1)} + \Delta q/\Delta T)$ is a constant. This leads to the conclusion that Δq is zero or negligibly small since it is highly improbable that $\Delta q/\Delta T$ is a constant quantity for all values of ΔT in view of the fact that ΔT approaches zero as $1/F$ approaches zero for constant heat input. Extrapolation of the linear plot to infinite flow rate gives the heat capacity of the vapor at zero temperature rise, *i.e.*, at thermostat temperature.

The data for a series of measurements of the apparent heat capacity of benzene with a constant heat input are given in Table I. The precision is typical of the results obtained with the calorimeter. Evidence of linearity between apparent heat capacity and reciprocal flow rate is also shown. The extrapolated value of C_p agrees exactly with a value interpolated from the data of Scott, *et al.*[5] It was thus shown that Δq was zero and the accuracy of the calorimeter was verified.

TABLE I

HEAT CAPACITY OF BENZENE AT 370.9°K., HEAT INPUT CONSTANT

ΔT, °C.	$1/F$, sec. mole^{-1}	H, cal. sec.$^{-1}$	C_p', cal. mole^{-1} deg.$^{-1}$
2.429	1740	0.036219	25.95
2.428	1738	.036220	25.92
2.430	1738	.036231	25.91
4.624	3362	.036142	26.27
4.636	3359	.036134	26.18
4.633	3361	.036150	26.22
6.924	5046	.036368	26.50
7.027	5045	.037106	26.64
7.065	5045	.037198	26.56

By extrapn. of medium values of each set, $C_p = 25.58$

By interpolation of the data of Scott, *et al.*,[5] $C_p = 25.58$

Evidence of linearity:

$1/F$	1738	3361	5045
C_p' (calcd.)	25.93	26.22	26.56
C_p' (exptl.)	25.92	26.22	26.56

If a series of measurements of apparent heat capacity at different flow rates is made with the temperature rise held constant, extrapolation to infinite flow rate gives C_p at the average vapor temperature, and the slope, s, of the extrapolated line is equal to $k_2T_0^{(m-1)}$. The latter quantity was determined by runs on benzene at four temperatures between 100 and 160°. A plot of log s against log T_0 gave $(m - 1)$ equal to 4.4, but for convenience the value 4 was used which did not materially affect the results in the temperature range used. The equation which best represented the relation between s and T^4 was $s \times 10^4 = 0.7729T^4 \times 10^{-10} - 0.226$. This equation was used to correct measurements on benzene at a single flow rate at four intermediate temperatures. The heat capacities agree with those of Scott, *et al.*,[5] with a maximum deviation of 0.16 and an average deviation of 0.09 cal. mole^{-1} deg.$^{-1}$. The constant s was of the order of 2×10^{-4} cal. deg.$^{-1}$ sec.$^{-1}$ and the actual C_p correction of the order of 0.4 cal. mole^{-1} deg.$^{-1}$.

Alcohols.—To demonstrate that the heat loss equation was independent of the vapor used, the apparent heat capacity of methyl alcohol was measured at a single flow rate at two temperatures, 364 and 406°K. The true heat capacities found by the use of the heat loss equation were 13.90 and 13.01, respectively. These values agree within 0.05 cal. mole^{-1} deg.$^{-1}$ with recent work on this compound.[12,13]

The procedure used for methyl alcohol was extended to other alcohols, measurements being made from their respec-

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(10) J. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1938, p. 509.

(11) The first term is 0.978 of the total value when T = 400°K., ΔT = 4° and m = 5.4, which are typical values in this research.

(12) T. De Vries and B. T. Collins, THIS JOURNAL, **63**, 1343 (1941).

(13) W. Weltner, Jr., and K. S. Pitzer, *ibid.*, **73**, 2606 (1951).

TABLE II

HEAT CAPACITY IN CAL. MOLE^{-1} DEG.[1] OF SOME ALIPHATIC ALCOHOLS AT 750 MM.

Alcohol	Temperature, °K. 341	354	359	363	373	375	383	394	405	417	428	437
Methyl	27.00			14.00					13.03			
Ethyl		26.20		22.22	20.72		20.29	20.23	20.33	20.55	20.83	21.03
n-Propyl					30.38		27.61	27.36	27.47	27.73	28.17	28.43
Isopropyl			33.35	29.89	28.54		27.90	27.81	28.07	28.46	28.83	29.11
n-Butyl								37.49	35.38	35.61	35.97	36.40
Isobutyl							37.47	35.34	35.32	35.74	36.15	36.62
s-Butyl						38.33	35.66	35.26	35.50	35.84	36.39	36.76
t-Butyl			41.11	38.29	36.23		35.64	35.68	35.93	36.47	37.04	37.47
n-Amyl										44.72	43.92	44.27

tive boiling points to 437°K. at approximately 10° intervals. The results are given in Table II. Since the heat capacity changes very rapidly with both pressure and temperature near the boiling point, the results in this region are uncertain to ±1 cal. mole^{-1} deg.$^{-1}$. From about 20° above the boiling points to 437°K., the estimated uncertainty, based on the benzene and methyl alcohol results, is ±0.2 cal. mole^{-1} deg.$^{-1}$.

The results for the alcohols are plotted in Figs. 1 and 2, with previous literature values.[6,12-21] The abnormal rise near the boiling point has been ascribed to partial association of the vapor. Values for the heat capacity of liquid methyl and ethyl alcohols are also shown, and it is interesting to note that in a region of 0 to 7° above the boiling point, the heat capacity of methyl alcohol vapor is greater than that of the liquid.

From a comparison of the results for the normal alcohols at 437°K., the average increase in heat capacity per methylene group is 7.65. For the normal hydrocarbon series, excluding methane, equations of Spencer[22] and Pitzer[23] give increases at zero pressure of 7.65 and 7.47, respectively. Values calculated by Stull[24] give 6.71 at one atmosphere. Waddington, Todd and Huffman[25] have measured *n*-heptane, and Waddington and Douslin[26] *n*-hexane, with a difference at 437°K. of 7.61.

The results for the normal hydrocarbons in the ideal state fron Spencer's equations were adjusted for one atmosphere by Berthelot's equation. The results were compared with the corresponding alcohols, and the average increase in heat capacity due to the substitution of –OH for –H in the normal series is 4.20 at 437°K.

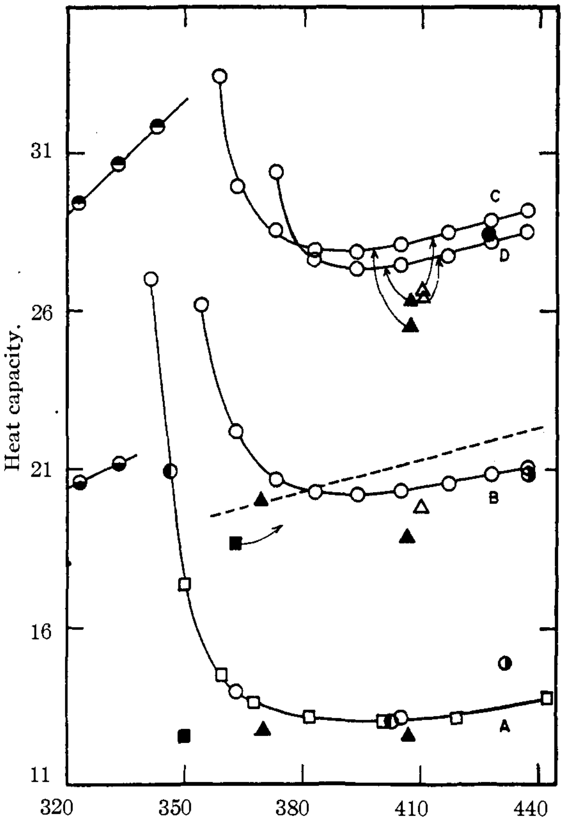

Fig. 1.—Heat capacity of methyl (A), ethyl (B), isopropyl (C) and *n*-propyl (D) alcohols at 750 mm.: ○, this research; ◐, Weltner and Pitzer; □, De Vries and Collins; ▲, Jatkar; ■, Dixon and Greenwood, △ Bennewitz and Rossner; – – –, Brickwedde, Moskow and Aston (C^0_p): ◑, Regnault; ●, Parks and Shomate; ⊖, liquid methyl alcohol; ◓, liquid ethyl alcohol from Fiock, Ginnings and Holton.

Mixtures.—A study was made of the change in heat capacity with composition of various mixtures with the object of eliminating the association effect. Measurements on a series of benzene–carbon tetrachloride mixtures at 373°K. showed that the heat capacity changed linearly with composition in mole per cent., as given in Table III. However, methyl alcohol–carbon tetrachloride mixtures gave results at 352°K. which were far from linear. Determinations were also made for ethyl alcohol–carbon tetrachloride mixtures at 355 and 437°K. From the data for the mixtures (see Table IV) the heat capacity of unassociated methyl alcohol was calculated by extrapolation of the apparent molal heat capacity, ϕ, defined by the equation $\phi = (C_p - 22.02n_1)/n_2$, where n_1 and n_2 are the mole fractions of carbon tetrachloride and methyl alcohol, respectively.[27] The result, 12.50 cal.

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(14) S. K. K. Jatkar, *J. Indian Inst. Sci.*, **22A**, 39 (1939).

(15) S. K. K. Jatkar and D. Lakshminarayan, *ibid.*, **28A**, 1 (1946).

(16) V. Regnault, *Mem. l'Acad. Sci. Paris*, **26**, 1 (1862).

(17) H. B. Dixon and G. Greenwood, *Proc. Roy. Soc.* (*London*), **105A**, 199 (1924).

(18) K. Bennewitz and W. Rossner, *Z. physik. Chem.*, **B39**, 126 (1938).

(19) G. S. Parks and C. H. Shomate, *J. Chem. Phys.*, **8**, 429 (1940).

(20) E. F. Fiock, D. C. Ginnings and W. B. Holton, *Bur. Standards J. Research*, **6**, 881 (1931).

(21) F. Brickwedde, M. Moskow and J. G. Aston, *ibid.*, **37**, 263 (1946).

(22) H. M. Spencer, *Ind. Eng. Chem.*, **40**, 2152 (1948).

(23) K. S. Pitzer, THIS JOURNAL, **63**, 2413 (1941).

(24) D. R. Stull, *Ind. Eng. Chem.*, **35**, 1303 (1943).

(25) G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947).

(26) G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

(27) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 35.

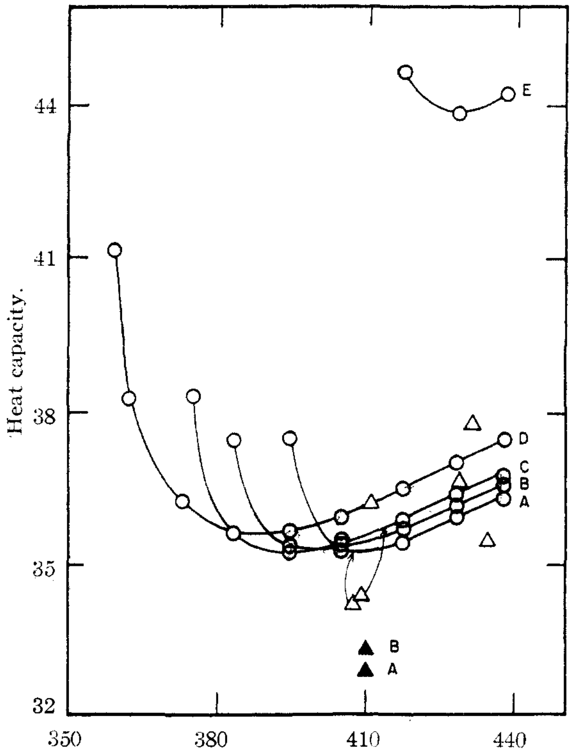

Fig. 2.—Heat capacity of *n*-butyl (A), isobutyl (B), *s*-butyl (C), *t*-butyl (D) and *n*-amyl (E) alcohols at 750 mm.: O, this research; △, Reynolds and De Vries; ▲, Bennewitz and Rossner.

mole^{-1} deg.$^{-1}$, can be compared with data given by Weltner and Pitzer[13] for methyl alcohol. By using their expression for the second virial coefficient, β, the difference between C_p of the unassociated vapor at one atmosphere and C^0_p was calculated to be 1.06 by the relationship $(\partial C_p/\partial p)_T = -T(d^2\beta/dT^2)$. Adding this to Weltner and Pitzer's value for C^0_p (11.57) gives 12.6 to be compared with the value 12.5 of this research.

Table III

Heat Capacity of Benzene–Carbon Tetrachloride Mixtures at 750 Mm. and 373 °K.

Mole % CCl_4	C_p(exptl.)	C_p(calcd.)	Deviation
0.00	25.80	...	....
24.48	25.02	24.92	−0.10
50.80	24.02	23.97	− .05
74.80	23.06	23.10	− .04
100.00	22.19	...	....

Table IV

Heat Capacity of Alcohol–Carbon Tetrachloride Mixtures

Mole % alcohol	C_p in cal. mole^{-1} deg.$^{-1}$ CH_3OH (352°K.)	C_2H_5OH (355°K.)	C_2H_5OH (437°K.)
0	22.02	22.10	22.78
10	21.22	21.69	
20	20.38	21.36	
25			22.20
30	19.52	20.89	
40		20.82	
50		20.84	21.66
60	17.64	20.99	
75			21.12
80	16.83	22.26	
100	16.30	25.50	21.00

For ethyl alcohol the values 16.01 and 20.54 were calculated for C_p of the unassociated vapor at one atmosphere at 355 and 437°K., respectively. There are no C^0_p values with which these can be compared.

Lafayette, Indiana

[Contribution No. 33 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

The Thermodynamic Properties of 2-Methyl-2-propanethiol from 0 to 1000°K.[1]

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Various thermodynamic properties of solid, liquid and gaseous 2-methyl-2-propanethiol were measured from 12 to 450 °K. The data that were obtained are: heat capacity of the solid (12–274 °K.); heats of transition, 972.0, 154.9 and 232.0 cal. mole^{-1} at 151.6, 157.0 and 199.4 °K., respectively; heat of fusion, 593.2 cal. mole^{-1} at the triple point, 274.42 °K.; heat capacity of the liquid, $C_{satd} = 28.57 + 4.005 \times 10^{-2}\ T + 1.500 \times 10^{-5}\ T^2$, cal. deg.$^{-1}$ mole^{-1} (274–330 °K.); entropy of the saturated liquid at 298.16 °K., 58.90 cal. deg.$^{-1}$ mole^{-1}; entropy of the ideal gas at 298.16 °K. and unit fugacity, 80.79 cal. deg.$^{-1}$ mole^{-1}; vapor pressure from 22 to 99°, $\log_{10}p$ (mm.) $= 6.78781 - 1115.565/(t + 221.314)$; heat of vaporization, $\Delta H_v = 9699 - 2.224\ T - 0.01891\ T^2$, cal. mole^{-1} (298–337 °K.); heat capacity of the ideal gas, $C^\circ_p = 2.38 + 0.10229\ T - 4.516 \times 10^{-5}\ T^2$, cal. deg.$^{-1}$ mole^{-1} (325–450 °K.); the second virial coefficient, $B = (PV - RT)/P = -592 - 16.6 \exp(1200/T)$, cc. mole^{-1} (298–450 °K.); and the standard heat of formation of the liquid from graphite, hydrogen and rhombic sulfur, $\Delta H_f = -33.78$ kcal. mole^{-1} (298.16 °K.). These thermodynamic data were used with available spectroscopic and molecular-structure information to compute the following chemical thermodynamic properties at selected temperatures from 0 to 1000 °K.: $(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)$, S°, C°_p, ΔH°_f, ΔF°_f and $\log_{10}K_f$.

An integrated experimental and computational program is conducted in this Laboratory to obtain thermodynamic data for organic sulfur compounds important in petroleum production and refining. For structurally simple compounds, experimental thermodynamic data are used with spectroscopic and molecular-structure information to calculate the following thermodynamic properties at selected temperatures from 0 to 1000°K.: $(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)$, S°, C°_p, ΔH_f, ΔF°_f and

(1) This investigation was performed as part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurements of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.