magnitude difference in the sulfur contents of the slags for the atmospheres pure SO_2 and $SO_2/CO = 20.7$, the results of Table VI indicate that there is no major effect on the relation between j and the calcium content when S atoms replace oxygen atoms in the slag up to at least two atomic per cent. sulfur. Also the results eliminate the possibility of appreciable amounts of polymeric forms of SO being present under the experimental conditions because their presence would have prevented the agreement reported in Table VI.

The average of ΔH_0° for the first four atmospheres listed in Table VI is -18.7 kcal./mole. Referring to Table III it can be seen that a clear choice for the heats of formation of SO and S_2 from the atoms is indicated. The combination of the high heat of formation of SO with the intermediate heat of formation of S_2 results in a heat of formation of SO from S_2 and O_2 of -18.2 kcal./mole. These selected data lead to the recommended values of ΔH_0°, $\Delta F_{298.16}^\circ$ and ΔF_{1823}° for the reactions involved in the thermal dissociation of sulfur dioxide presented in Table VII.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION NO. 41 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Nitromethane: The Vapor Heat Capacity, Heat of Vaporization, Vapor Pressure and Gas Imperfection; the Chemical Thermodynamic Properties from 0 to 1500°K.

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Because nitromethane is important both as an industrial chemical and, from a theoretical standpoint, as the simplest member of the family of nitroparaffins, measurements were made of several of its thermodynamic properties. The properties studied were: (1) the vapor pressure at 15 temperatures from 55 to 136° [$\log_{10} p(\text{mm.}) = 7.28050 - 1446.186/(t + 227.515)$; t in °C.]; (2) the heat of vaporization at 4 temperatures from 318 to 374°K. [$\Delta H_v = 11{,}730 - 4.9977\,T - 1.2400 \times 10^{-2}T^2$ cal. mole^{-1}]; and (3) the vapor heat capacity at 2 to 4 pressures at each of 6 temperatures from 363 to 523°K. [$C_p^\circ = 2.352 + 4.2882 \times 10^{-2}\,T - 1.694 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1}]. The observed effects of gas imperfection on the thermodynamic properties were correlated with the equation of state, $PV = RT(1 + B/V)$, where $B = -300 - 12.97 \exp(1700/T)$ cc. mole^{-1}. The results of these studies and the entropy and heat of formation data reported by other investigators provide relatively complete and highly accurate experimental thermodynamic data for nitromethane. These data form a sound basis for computing the chemical thermodynamic properties by appropriate methods of statistical mechanics and thermodynamics. Values of the following properties were computed at selected temperatures from 0 to 1500°K.: $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S°, C_p°, ΔH_f°, ΔF_f° and $\log_{10} K_f$.

Because of the importance of nitromethane as an industrial chemical, and because of its importance in theoretical considerations as the simplest member of the nitroparaffin family, many investigations have been made of its physical and chemical properties. Measurements of properties related to the subject matter of this paper include determinations of the vapor heat capacity,[1,2] the heat of vaporization,[1,3–5] the vapor pressure,[5–8] the vapor density,[1,9,10] the entropy at 298.16°K.,[5] and the heat of formation at 298.16°K.[8,11] The present investigation was made to provide more accurate and extensive values of the chemical thermodynamic properties of nitromethane. The experimental studies consisted of determinations of: (1) the vapor pressure at 15 temperatures from 55 to 136°; (2) the heat of vaporization at 4 temperatures from 318 to 374°K.; and (3) the vapor heat capacity at 2 to 4 pressures at each of 6 temperatures from 363 to 523°K. The heat capacity in the ideal gaseous state and an equation of state for the real vapor were obtained from the experimental results. These thermodynamic data, the value of the entropy reported by Jones and Giauque,[5] and the value of the standard heat of formation reported by Prosen[11] were used with available spectroscopic and molecular structure information in calculations of the chemical thermodynamic properties of nitromethane at selected temperatures from 0 to 1500°K.

Experimental

Physical Constants.—All data reported in this paper are based on a molecular weight of 61.042 for nitromethane and the following definitions: 0°C. = 273.16°K.; 1 cal. = 4.1840 abs. j. = 4.1833 int. j. The 1951 International Atomic Weights[12] and the 1951 values of the fundamental physical constants[13] were used for all computations.

The Material.—The sample of nitromethane used in these experiments was obtained by chemical and physical purification of a sample donated by the Commercial Solvents Corporation, Terre Haute, Indiana. The method of purification employed and some physical properties of the purified sample were described elsewhere.[14] Before use in the experimental studies, the sample was dried by passing the vapors through $Mg(ClO_4)_2$. The purity of the sample, as determined by the time-temperature freezing-point method,[15] was 99.9 mole %. That impurities of different volatility were not present in significant quantities was verified in the vapor pressure study by the observation that the difference in the boiling and condensation temperatures of the sample was only 0.006° at 760 mm. pressure. However, it was necessary to reflux the sample in the ebulliometer for about 2 hours before the difference was reduced to

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[1] K. S. Pitzer and W. D. Gwinn, THIS JOURNAL, **63**, 3313 (1941).

[2] T. De Vries and B. T. Collins, *ibid.*, **64**, 1224 (1942).

[3] J. H. Mathews, *ibid.*, **48**, 562 (1926).

[4] J. C. Phillips and S. C. Waterton, *J. Chem. Soc.*, 2783 (1930).

[5] W. M. Jones and W. F. Giauque, THIS JOURNAL, **69**, 983 (1947).

[6] E. B. Hodge, *Ind. Eng. Chem.*, **32**, 748 (1940).

[7] M. R. Corelli, *Ann. chim. applicata*, **38**, 335 (1948).

[8] D. E. Holcomb and C. L. Dorsey, Jr., *Ind. Eng. Chem.*, **41**, 2788 (1949).

[9] A. Eucken and L. Meyer, *Z. physik. Chem.*, **B5**, 452 (1929).

[10] M. R. Corelli, *Ann. chim. applicata*, **39**, 591 (1949).

[11] Unpublished results: communicated by E. J. Prosen, National Bureau of Standards, Washington, D. C.

[12] Edward Wichers, THIS JOURNAL, **74**, 2447 (1952).

[13] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

[14] C. J. Thompson, H. J. Coleman and R. V. Helm, *ibid.*, **76**, 3445 (1954).

[15] F. D. Rossini, *Anal. Chem.*, **20**, 110 (1948).

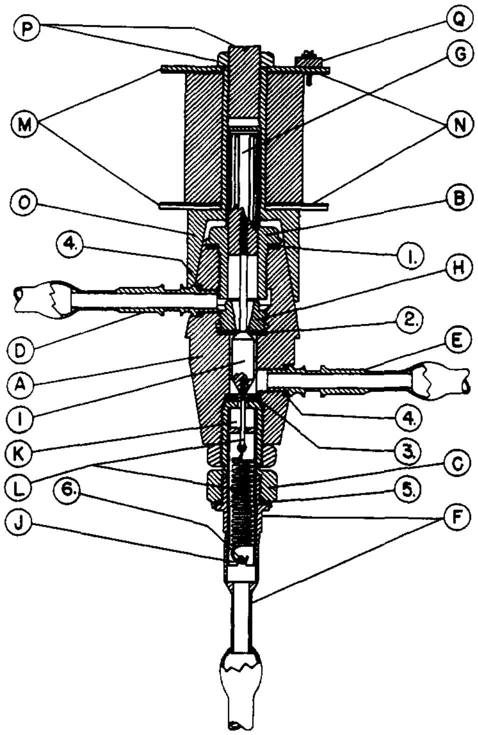

Fig. 1.—Three-way solenoid valve: A, valve body; B, core vacuum seal; C, outlet sealing plug and lock nut; D, normal output tube; E, input tube; F, valve outlet tube; G, solenoid core (pure iron, chromium plated); H, plunger stop; I, valve plunger; J, spring tension tube; K, guide; L, valve opening mechanism; M, pure iron disks; N, bakelite disks; O, solenoid base (brass); P, core stop and nut; Q, terminal block; 1, gasket ("Teflon"); 2, upper plunger seat ("Teflon"); 3, lower plunger seat (gold); 4, gasket ("Teflon"); 5, gasket ("Teflon"); 6, spring hanger. All parts are of stainless steel unless otherwise indicated.

this small value. The sample apparently underwent slight decomposition in storage, but the decomposition products were evidently very volatile and were removed by refluxing.

The Vapor Pressure.—The vapor pressure of nitromethane was determined at selected temperatures from 55 to 136° in the twin ebulliometer system described previously.[16] The heating element of the ebulliometer described in ref. 16 has been enclosed in a glass re-entrant well so that samples come into contact with glass only. The boiling and condensation temperatures of nitromethane and water were observed as they boiled simultaneously at a common pressure. The "observed" vapor pressures, presented in Table I, were obtained from the vapor pressure data for water reported by Osborne, Stimson and Ginnings.[17] The results of this investigation are accurately represented (see columns 4 and 5, Table I) by both the Antoine equation

$$\log_{10} p = 7.28050 - 1446.186/(t + 227.515) \qquad (1)$$

and the Cox equation[18]

$$\log_{10} P = A(1 - 374.347/T) \qquad (2)$$

where $\log_{10} A = 0.845118 - 6.1497 \times 10^{-4}T + 6.0541 \times 10^{-7}T^2$ (p in mm., P in atm., t in °C., and T in °K.). Although the Cox equation is more cumbersome to use for numerical calculations, it is presented here because it is more reliable for use in extrapolations beyond the temperature range of the experiments. The normal boiling point given by both equations is 101.19° (374.35°K.).

TABLE I

THE VAPOR PRESSURE OF NITROMETHANE

Boiling point, °C. Water	Nitromethane	p(obsd.)[a] mm.	p(obsd.) − p(calcd.) Eq. 1	Eq. 2
60.000	55.711	149.41	0.00	+0.02
65	61.298	187.57	.00	+ .01
70	66.919	233.72	− .03	− .04
75	72.557	289.13	+ .04	+ .01
80	78.231	355.22	+ .01	− .03
85	83.925	433.56	+ .10	+ .04
90	89.655	525.86	+ .04	− .02
95	95.408	633.99	.00	− .03
100	101.186	760.00	+ .02	+ .02
105	106.994	906.06	− .07	− .01
110	112.826	1074.6	− .1	.0
115	118.681	1268.0	− .1	+ .1
120	124.564	1489.1	− .1	+ .1
125	130.473	1740.8	0.0	+ .1
130	136.404	2026.0	+ .3	.0

[a] From vapor pressure data for water given in ref. 17.

The vapor pressure data published by Hodge[6] and by Holcomb and Dorsey[8] agree with the present results within the probable accuracy uncertainty of the earlier data. The data reported by Corelli[7] are in poor agreement with the results of this investigation. The vapor pressure data obtained by Jones and Giauque[5] near 25° are appreciably higher than values computed by use of eq. 2. The sample of nitromethane used by Jones and Giauque may have contained enough water as impurity to account for the observed discrepancy.

The Heat of Vaporization.—The heat of vaporization and vapor heat capacity of nitromethane were measured in the flow calorimeter system described in previous publications from this Laboratory.[19] Because several changes in the apparatus and method of operation have been made since publication of ref. 19, a brief description of some of the important modifications will be given here. A metal cycling vaporizer has replaced the glass vaporizer described in ref. 19. Although the principle of operation remains the same, it is believed that the use of a metal vaporizer is more sound calorimetrically, since the metal parts equilibrate more rapidly after small temperature fluctuations that occur during some of the measurements. The heating element used for this investigation consisted of glass-insulated Nichrome wire, sheathed by thin-walled copper tubing to prevent contact with the liquid under study. Glass thread wrapped around the copper sheath served to promote smooth ebullition.

All glass stopcocks that come into contact with either liquids or vapors have been replaced by stainless steel, greaseless valves which were designed and constructed in this Laboratory. The 3-way solenoid valve depicted in Fig. 1 is used in heat of vaporization experiments to divert vapor from the flow system to the collection system. The solenoid valve and an electric timer are actuated simultaneously by a single switch. Small bellows-type valves, such as that shown in Fig. 2, are used on sample receivers and at any other points where valves are needed to handle the flow of vapor or liquid.

The procedure used for heat of vaporization experiments has been modified by use of a metering device by means of which liquid from an external reservoir may be admitted to the vaporizer at a precisely controlled rate of flow. With this device, it is possible to maintain a constant quantity of liquid in the vaporizer as material is withdrawn from the system in the experiments. This revised procedure eliminates one of the largest sources of possible systematic error in heat of vaporization measurements—the corrections for change in liquid level in the vaporizer.[19a] The metering apparatus, shown schematically in Fig. 3, consists of a buret to which is attached a length of capillary tubing and a

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(16) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, THIS JOURNAL, **71**, 797 (1949).

(17) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

(18) E. R. Cox, *Ind. Eng. Chem.*, **28**, 613 (1936).

(19) (a) G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947); (b) G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

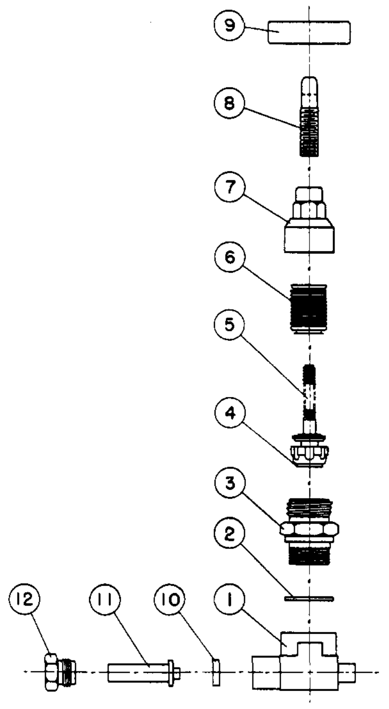

Fig. 2.—Vacuum bellows valve: 1, valve body; 2, "Teflon" gasket; 3, bellows housing; 4, "Teflon" seat; 5, valve stem and seat; 6, bellows; 7, bellows cap (brass); 8, stem nut; 9, stem handle; 10, "Teflon" gasket; 11, connection for Kovar-glass seal; 12, seal nut. All parts are of stainless steel unless otherwise indicated.

specially designed stainless steel solenoid valve. The rate of flow of liquid is controlled by the choice of the size of capillary tubing and by adjustments of the pressure of helium gas above the liquid in the buret. The solenoid valve is used to admit liquid from the meter to the liquid return line of the flow calorimeter system, and is actuated by the same switch that actuates the 3-way diversion valve and the electric timer.

At each of 4 temperatures from 318 to 374°K., 3 measurements of the heat of vaporization were made with the apparatus and procedure described above. The results of these experiments are summarized in Table II. At 334.80°K., 3 measurements were also made with the procedure described in ref. 19a, and the results obtained differed from the value recorded in Table II by less than 0.05%. It is believed that the accuracy uncertainty of the heat of vaporization data presented in Table II is no greater than 0.1%. The following empirical equation represents these data within 1 cal. mole^{-1}

$$\Delta H_v = 11{,}730 - 4.9977T - 1.2400 \times 10^{-2}T^2 \text{ cal. mole}^{-1} \quad (318 \text{ to } 374\text{°K.}) \quad (3)$$

TABLE II

THE MOLAL HEAT OF VAPORIZATION AND GAS IMPERFECTION OF NITROMETHANE

T, °K.	ΔH_v (obsd.), cal.	$-B$, cc. Obsd.[a]	$-B$, cc. Calcd.[b]	V,[b] cc.
318.30	8883 ± 1[c]	3102	3007	206,590
334.80	8667 ± 2	2463	2380	107,390
353.36	8416 ± 2	1931	1893	55,900
374.44	8120 ± 1	1499	1515	29,040

[a] Calculated from observed values of ΔH_v and P by the use of the Clapeyron equation. [b] Calculated by use of eq. 4 and 7. [c] Maximum deviation from the mean of 3 determinations.

The heat of vaporization of nitromethane has been measured by other investigators near the normal boiling point[1,3,4] (about 374°K.) and at 298.16°K.[5] The earlier results obtained near the normal boiling point are 1 to 2% higher than the value obtained in this research. Jones and Giauque's[5] datum obtained at 298.16°K. is 0.1% higher than the value calculated by eq. 3; as in the case of the discrepancy in vapor pressures noted above, Jones and Giauque's value for the heat of vaporization may be high as a result of the possible water impurity in their sample.

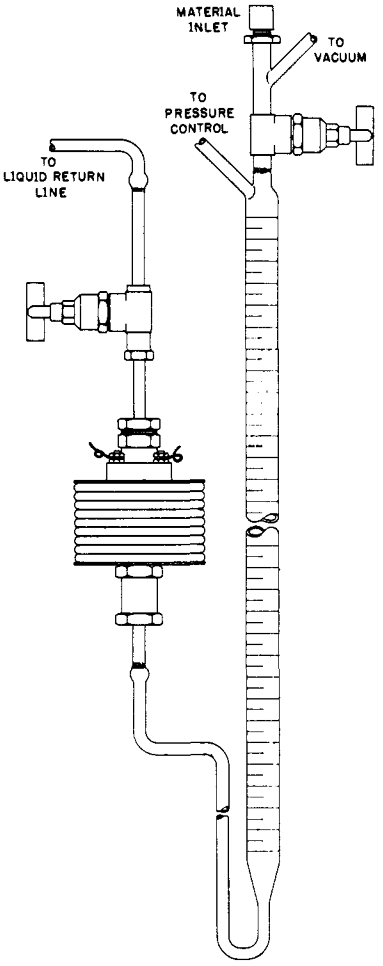

Fig. 3.—Liquid introducer for vapor heat capacity apparatus.

The Vapor Heat Capacity.—A new flow calorimeter has replaced that described in ref. 19a, but the design was modified in only one important respect. The platinum–tungsten soldered joints in the thermometer circuit were placed out of the direct flow of effluent vapor so as to eliminate thermal e.m.f.'s such as those encountered in the thermometer circuit of the earlier calorimeter.

Measurements of the vapor heat capacity of nitromethane were made at 2 to 4 pressures from $^1/_4$ to 1 atm. at each of 6 temperatures from 363 to 523°K. The results are presented in the third column of Table III. Near 520°K., experiments were made to detect possible thermal decomposition of the compound. In these experiments, 3 measurements of the apparent vapor heat capacity were made at a constant flow rate and constant initial temperature, but with temperature increments of 4, 8 and 12°. When plotted against temperature, the three values of the apparent heat capacity so obtained deviated by less than 0.05% from a straight line. If significant thermal decomposition had occurred, the plot would probably have been curved, since the rate of chemical reaction usually increases exponentially with temperature. Furthermore, the results of heat of vaporization measurements made at the conclusion of the experiments were in excellent agreement with those made at the beginning of the investigation. For these reasons, it is believed that the results of this study were not affected by thermal decomposition of the sample.

Table III

The Molal Vapor Heat Capacity of Nitromethane in Cal. Deg.$^{-1}$

T, °K.	P, atm.	C_p(obsd.)	C_p(eq.)[a]	C_p°(calcd.)[b]
363.20	0.5012	17.264	17.244	
	.3750	16.844	16.836	
	.2501	16.463	16.443	
	0	15.71	15.69	15.69
383.25	1.0029	18.464	18.479	
	0.7501	17.865	17.888	
	.5012	17.317	17.335	
	.2501	16.783	16.803	
	0	16.28	16.30	16.29
413.25	1.0029	18.431	18.436	
	0.5012	17.777	17.786	
	.2501	17.472	17.478	
	0	17.17	17.18	17.18
443.25	1.0029	18.822	18.806	
	0.5012	18.435	18.408	
	.2501	18.233	18.217	
	0	18.05	18.03	18.04
483.25	1.0029	19.615	19.562	
	0.2501	19.244	19.226	
	0	19.12	19.12	19.12
523.25	1.0029	20.461	20.425	
	0.2501	20.221	20.218	
	0	20.14	20.15	20.15

[a] Calculated from eq. 5 to 7. [b] Calculated from spectroscopic and molecular structure information.

The data recorded in Table III confirm the observations of previous investigators[1,2] that the variation with pressure of the vapor heat capacity of nitromethane is abnormally large. However, the present more precise data show in addition that a linear relationship between vapor heat capacity and pressure (at constant temperature) is not valid for nitromethane. For this reason, it was necessary to use a method for correlating the heat capacity data different from that usually employed in this Laboratory.[20]

Gas Imperfection and Correlation of the Heat Capacity Data.—Numerical constants of an equation of state for nitromethane vapor were obtained from the experimental data presented in this paper by use of the Clapeyron equation and the thermodynamic relationship, $(\partial^2 V/\partial T^2)_P = -(1/T)(\partial C_p/\partial P)_T$. In terms of the latter relationship and the equation of state

$$PV = RT(1 + B/V) \qquad (4)$$

the vapor heat capacity is given, with slight approximations,[21] by

$$C_p = C_p^\circ - PT(d^2B/dT^2) + 2[P^2/R][B(d^2B/dT^2)][1 - 3BP/RT] \qquad (5)$$

where V is the molal volume of the vapor, B is the second virial coefficient, and C_p° is the heat capacity in the ideal gaseous state. The last term in eq. 5 is usually neglected, but for the highly polar nitromethane molecule, B is large, and the last term of eq. 5 must be retained to represent accurately the vapor heat capacity data. Equation 5 was fitted to the observed vapor heat capacity data by an iterative process in which the numerical constants of the following expressions were determined

$$C_p^\circ = 2.352 + 4.2882 \times 10^{-2}T - 1.694 \times 10^{-5}T^2, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (6)$$

$$B = -300 - 12.97 \exp(1700/T), \text{ cc. mole}^{-1} \qquad (7)$$

The constant, -300, in eq. 7 was adjusted to give agreement between values of V computed with eq. 4 and 7 and the "observed" values computed by use of the Clapeyron equation and the experimental heat of vaporization and vapor pressure data. In Table II, the "observed" values of B are compared with those calculated by use of eq. 7. In Table III the experimental vapor heat capacity data are compared with values of C_p computed by use of eq. 5, 6 and 7. The deviations between calculated and "observed" values of B (Table II) are less than 0.1% of the molal volume; the deviations between calculated and experimental values of C_p (Table III) are, with one exception, less than 0.15%, and the average deviation is less than 0.1%. Because eq. 4 to 7 accurately represent the calorimetric data, it is believed that the accuracy uncertainty of values of C_p° computed by use of eq. 6 should not exceed 0.2%. Furthermore, the satisfactory results obtained by use of the equation of state 4 show that, although the second virial coefficient of nitromethane is unusually large, the third virial coefficient may be neglected at the low pressures involved in this study. It should be emphasized that eq. 4 to 7 are not expected to be reliable for extrapolations much beyond the ranges of temperature and pressure of the experiments.

Pitzer and Gwinn[1] and De Vries and Collins[2] have made more limited studies of the vapor heat capacity of nitromethane. The values of $C°_p$ reported by these investigators deviate from the curve represented by eq. 6 by as much as 1%, the probable accuracy uncertainty of the earlier data. Pitzer and Gwinn[1] also report the results of some vapor density measurements and give a representation for B in the equation of state, $PV = RT + BP$. Their results are consistent with the equation of state presented in this paper. However, the vapor density measurements of Eucken and Meyer[9] and Corelli[10] are not in good agreement with the gas imperfection data of this investigation or those of Pitzer and Gwinn.[1]

The Chemical Thermodynamic Properties

The vapor heat capacity data obtained in this research, the value of the entropy reported by Jones and Giauque,[5] and the value of the standard heat of formation recently determined at the National Bureau of Standards[11] form a sound basis for computing the chemical thermodynamic properties of nitromethane by the appropriate methods of statistical mechanics. The assignment of fundamental vibrational frequencies proposed by Smith, Pan and Nielsen[22] was used in these calculations. This assignment differs from that proposed by Wells and Wilson[23] only in the choice of the two methyl-rocking frequencies. Use of the assignment of Smith, *et al.*, results in a more satisfactory simultaneous fit to the calorimetric entropy and vapor heat capacity data.[24]

In computing the moments of inertia of nitromethane, the following molecular structure parameters were used: N–O bond distance, 1.21 Å.[25a]; C–N bond distance, 1.46 Å.[25a]; C–H bond distance, 1.09 Å.[25b]; O–N–O bond angle, 127°[25a]; and H–C–N and H–C–H bond angles, 109° 28′.[25b] The results obtained for the principal moments of inertia were $I_A = 67.61 \times 10^{-40}$, $I_B = 76.44 \times 10^{-40}$ and $I_C = 138.75 \times 10^{-40}$ g. cm.^{2}. The method of Pitzer and Gwinn[26] was used to compute the reduced moment of inertia for internal rotation of nitromethane, 4.886×10^{-40} g. cm.^{2}.

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[20] *E.g.*, ref. 19 and D. W. Scott, Guy Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

[21] The exact relationship is $C_p = C_p^\circ - RT^2(d^2B/dT^2)/V + R[B - T(dB/dT)]^2/[V^2 + 2BV]$.

[22] D. C. Smith, Chi-Yuan Pan and J. R. Nielsen, *J. Chem. Phys.*, **18**, 706 (1950).

[23] A. J. Wells and E. B. Wilson, Jr., *ibid.*, **9**, 314 (1941).

[24] However, in violation of the probable effective selection rules for nitromethane one of the frequencies assigned by Smith, *et al.*, to a methyl-rocking mode has been reported as polarized in the Raman spectrum [see J. P. Mathieu and D. Massignon, *Ann. Phys.*, **16**, 5 (1941)].

[25] (a) L. O. Brockway, J. Y. Beach and L. Pauling, This Journal, **57**, 2693 (1935); (b) assumed.

[26] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942)

TABLE IV

THE MOLAL THERMODYNAMIC PROPERTIES OF NITROMETHANE[a]

T, °K.	$-(F° - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H° - H_0^\circ)/T$, cal. deg.$^{-1}$	$H° - H_0^\circ$, kcal.	$S°$, cal. deg.$^{-1}$	C_p°, cal. deg.$^{-1}$	ΔH_f°,[b] kcal.	ΔF_f°,[b] kcal.	$\log_{10} K_f$[b]
0	0	0	0	0	0	−14.55	−14.55	+∞
273.16	54.49	10.07	2.751	64.56	12.95	−17.62	− 2.90	2.32
298.16	55.39	10.34	3.083	65.73	13.70	−17.86	− 1.66	1.22
300.00	55.45	10.36	3.108	65.81	13.76	−17.88	− 1.56	1.14
400	58.59	11.60	4.640	70.19	16.80	−18.69	+ 4.02	−2.20
500	61.32	12.92	6.460	74.24	19.56	−19.32	9.77	−4.27
600	63.79	14.22	8.532	78.01	21.92	−19.69	15.73	−5.73
700	66.08	15.47	10.83	81.55	23.90	−20.11	21.56	−6.73
800	68.23	16.63	13.30	84.86	25.56	−20.33	27.51	−7.52
900	70.25	17.70	15.93	87.95	26.97	−20.45	33.51	−8.14
1000	72.16	18.69	18.69	90.85	28.17	−20.48	39.52	−8.64
1100	73.98	19.60	21.56	93.58	29.19	−20.46	45.52	−9.04
1200	75.73	20.44	24.53	96.17	30.07	−20.37	51.50	−9.38
1300	77.39	21.21	27.57	98.60	30.82	−20.26	57.49	−9.66
1400	78.99	21.92	30.69	100.91	31.48	−20.11	63.48	−9.91
1500	80.53	22.58	33.87	103.11	32.05	−19.94	69.43	−10.12

[a] To form an internally consistent set of values of the thermodynamic properties and to retain the higher accuracy of increments with temperature of a given property, the values in this table are given to more significant figures than are justified by their absolute accuracy. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of nitromethane by the reaction: C(graphite) + 3/2 H_2(gas) + O_2(gas) + 1/2N_2(gas) → CH_3NO_2(gas).

Previous investigations[1,2,5] of the thermodynamic properties of nitromethane have shown that the height of the potential barrier to internal rotation is in the range 0 to 1000 cal. mole^{-1}. The data of this study place an upper limit of 250 cal. mole^{-1} on the barrier height. However, if a reasonable estimate is made of the effect of anharmonicity on C_p°, the present data are consistent with an assumption of free internal rotation. In a recent study of the microwave spectrum of nitromethane, Tannenbaum, Johnson, Myers and Gwinn[27] found the barrier height to be only 6.00 ± 0.03 cal. mole^{-1}, which is effectively zero for thermodynamic purposes.

The effect of anharmonicity on the thermodynamic functions was estimated by the empirical method described in an earlier paper.[28] Best agreement between calculated and observed values of C_p° was obtained with $\nu = 500$ cm.$^{-1}$ and $Z = 0.064$ cal. deg.$^{-1}$ mole^{-1}, where ν and Z are the empirically chosen frequency and anharmonicity parameters defined in ref. 28.

Values of C_p° computed with the vibrational assignment of Smith, Pan and Nielsen,[29] with assumption of free internal rotation, and with empirical anharmonicity corrections are given in Table III. From the data of Table III it may be seen that the calculated and experimental results agree within 0.1% over the range of temperature of the experiments. The calculated value of $S°$ at 298.16°K. and one atmosphere pressure is 65.73 cal. deg.$^{-1}$ mole^{-1}, in exact agreement with Jones and Giauque's experimental datum. Because excellent agreement was obtained between the calculated and calorimetric data, this method of computation was used in calculating thermodynamic functions to 1500°K.

As an independent check on the accuracy of the flow calorimetric data, values of C_p° were also computed with anharmonicity corrections calculated by conventional methods from anharmonicity coefficients obtained from spectroscopic data. The results were less than 0.2% lower than the experimental data in Table III. If the effects of vibration–vibration and rotation–vibration interactions could be computed, the discrepancy would probably be smaller. The empirical method of computing anharmonicity corrections was chosen chiefly because it is more convenient, but it is also believed to be more reliable than the computation from limited spectroscopic data.

The Chemical Thermodynamic Properties.—Values of the following thermodynamic functions at selected temperatures from 0 to 1500°K. are presented in Table IV: $(F° - H_0^\circ)/T$, $(H° - H_0^\circ)/T$, $H° - H_0^\circ$, $S°$ and C_p°.

The standard heat of formation of liquid nitromethane from the elements, ΔH_f°(liq.), has recently been found to be −27.03 ± 0.15 kcal. mole^{-1} at 298.16°K.[11] The standard heat of formation in the ideal gaseous state, ΔH_f°(gas), was computed from this value of ΔH_f°(liq.) by addition of the standard heat of vaporization, 9.171 kcal. mole^{-1}, as calculated with the aid of eq. 3, 5 and 7. The value of ΔH_f°(gas) so obtained, −17.86 kcal. mole^{-1} at 298.16°K., was used with the values of the thermodynamic functions of nitromethane from Table IV and of the thermodynamic functions of C(graphite),[30] H_2(gas),[30] O_2(gas)[30] and N_2(gas)[30] to compute values of the standard heat, ΔH_f°, standard free energy, ΔF_f°, and common logarithm of the equilibrium constant, $\log_{10} K_f$, for the formation of nitromethane from the elements. Values of these thermodynamic properties at selected temperatures from 0 to 1500°K. are recorded in Table IV

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(27) E. Tannenbaum R. D. Johnson, R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **22**, 949 (1954).

(28) J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and Guy Waddington, THIS JOURNAL, **76**, 2661 (1954).

(29) The vibrational contributions to the thermodynamic functions were taken from H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D. C., 1949.

(30) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

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2-Propanethiol: Experimental Thermodynamic Studies from 12 to 500°K. The Chemical Thermodynamic Properties from 0 to 1000°K.

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Experimental studies were made of the thermodynamic properties of 2-propanethiol. The entropy of the liquid at saturation pressure at 298.16°K., 55.82 cal. deg.$^{-1}$ mole^{-1}, was computed from calorimetric values of the heat capacity in the solid and liquid states (13 to 322°K.) and of the heats of transition and fusion (12.63 cal. mole^{-1} at 112.5°K. and 1371 cal. mole^{-1} at the triple point, 142.64°K., respectively). Results obtained for the heat capacity in the liquid state [C_{satd}], vapor pressure [p], heat of vaporization [ΔH_{v}], heat capacity in the ideal gaseous state [C_p°], and second virial coefficient [$B = (PV - RT)/P$] are represented by the following empirical equations: (1) $C_{\mathrm{satd}}(\mathrm{liq.}) = 37.14 - 4.956 \times 10^{-2}T + 1.481 \times 10^{-4}T^2 - 238.3/T$, cal. deg.$^{-1}$ mole^{-1} (150 to 330°K.); (2) $\log_{10} p\ (\mathrm{mm.}) = 6.87734 - 1113.895/(t + 226.157)$, (10 to 86°); (3) $\Delta H_{\mathrm{v}} = 10{,}066 - 7.214\ T - 9.864 \times 10^{-3}T^2$, cal. mole^{-1} (290 to 326°K.); (4) $C_p^\circ = 3.17 + 0.07564T - 3.167 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (317 to 487°K.); and (5) $B = -318 - 32.8 \exp(1000/T)$, cc. mole^{-1} (290 to 487°K.). The entropy in the ideal gaseous state at 298.16°K., 77.51 cal. deg.$^{-1}$ mole^{-1}, and the standard heat of formation from graphite, hydrogen and gaseous diatomic sulfur, −33.46 kcal. mole^{-1} at 298.16°K., were computed from these data and heat of combustion data reported elsewhere. Values of the functions $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0$, S° and C_p° at selected temperatures to 1000°K. were calculated from spectroscopic and molecular structure information. The heights of the potential barriers hindering internal rotation required for these calculations were evaluated from the calorimetric entropy and vapor heat capacity data. Values of the heat, free energy and equilibrium constant of formation of 2-propanethiol were computed from the calculated thermodynamic functions and the experimental value of the heat of formation at 298.16°K.

As part of American Petroleum Institute Research Project 48A, this Laboratory is conducting studies of the thermodynamic properties of organic sulfur compounds that occur in crude petroleum or are encountered in refining processes. One of the most important types of sulfur compounds under investigation is the family of alkanethiols (mercaptans), and it is planned to determine the thermodynamic properties of key members of this family. The data obtained will provide a sound basis for the construction, by approximate statistical mechanical methods,[2] of relatively complete tables of the chemical thermodynamic properties of the entire family of alkanethiols.[3] Toward this end, the properties of ethanethiol,[4] 1-pentanethiol[5] and 2-methyl-2-propanethiol[6] have already been determined. This paper presents the results of detailed studies of the thermodynamic properties of 2-propanethiol, the first of the series of secondary alkanethiols. The closely integrated experimental and computational investigations will be discussed in the following order: (1) low-temperature calorimetric studies; (2) vapor pressure studies; (3) measurements of the heat of vaporization and vapor heat capacity; (4) determination of the heat of formation; (5) calculation of thermodynamic functions from spectroscopic, molecular structure and calorimetric data.

Experimental

Physical Constants.—The 1951 International Atomic Weights[7] and the 1951 values of the fundamental physical constants[8] were used for all computations. The calorimetric data are based on a molecular weight of 76.160 for 2-propanethiol and the following definitions: 0° = 273.16°K.; 1 cal. = 4.1840 abs. j. = 4.1833 int. j.

The Material.—The 2-propanethiol used was part of the Standard Sample of Sulfur Compound, API-USBM serial No. 11, prepared and purified at the Laramie (Wyo.) Station of the Bureau of Mines. In calorimetric melting point studies to be described below, the material was found to contain 0.011 ± 0.003 mole % liquid-soluble, solid-insoluble impurity. Before use in the experimental studies, the sample was dried, in the vapor phase, with anhydrous magnesium perchlorate and transfers to appropriate receivers were made by vacuum distillations. At no time in the handling of the material or in the experiments were the samples in contact with gases other than helium.

The Heat Capacity in the Solid and Liquid States.—The low temperature thermal properties of 2-propanethiol were measured in an adiabatic cryostat similar to that described by Ruehrwein and Huffman.[9] About 0.6 mole of the compound was sealed in a cylindrical platinum calorimeter equipped with horizontal, perforated, heat-distributing disks of gold. A small amount of helium (about 30 mm. pressure at room temperature) was put in the calorimeter to

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

(2) *E.g.*, (a) K. S. Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946); J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

(3) The compilation and tabulation of selected values of the properties of organic sulfur compounds will be part of the program of American Petroleum Institute Research Project 44.

(4) J. P. McCullough, D. W. Scott, H. L. Finke, M. E. Gross, K. D. Williamson, R. E. Pennington, Guy Waddington and H. M. Huffman, This Journal, **74**, 2801 (1952).

(5) H. L. Finke, D. W. Scott, M. E. Gross, Guy Waddington and H. M. Huffman, *ibid.*, **74**, 2804 (1952).

(6) J. P. McCullough, D. W. Scott, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **75**, 1818 (1953).

(7) Edward Wichers, *ibid.*, **74**, 2447 (1952).

(8) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

(9) R. A. Ruehrwein and H. M. Huffman, *ibid.*, **65**, 1620 (1943).