The results in Table I show that the theoretical adsorption isotherm (1) not only has the correct form required by the Gibbs adsorption theorem but also that it yields quite accurate data on surface tension lowering for relative pressures above about 0.05. It should perhaps be noted, however, that this is true in all cases studied only when the repulsive term in the adsorbate–adsorbent interaction is taken into account, two examples being found (Table I, in which equation (1), with $a = 1.0$ instead of 1.5, leads to an improper ($B > -1$) solution of the Gibbs equation.

The method developed in this paper for calculating $\pi_{0.5-1.0}$ is not necessarily restricted to type II (and III) isotherms; it may be applied equally well to isotherms (types IV and V) in which capillary condensation occurs, since the surface pressure π will not be affected by the pore structure of the solid. It is necessary only that the isotherm have a large enough free or unrestricted adsorption region for $x > 0.05$, *e.g.*, $0.05 < x < 0.2$ or $0.05 < x < 0.5$, etc.), to allow one to evaluate the constants E_1,c_1, and v_m.

One will observe that the surface pressure of the film which forms at $x = 0.05$, *i.e.*, $\pi_{0-0.05}$, is generally a large part of the surface pressure of the film at saturation pressures, *i.e.*, $\pi_{0-1.0}$. For example, Table II shows that $\pi_{0-0.05}/\pi_{0-1.0}$ is 0.43 for nitrogen on anatase. Moreover, one cannot be sure of the accuracy of $\pi_{0-0.05}$ determined graphically in view of the uncertainties in the graphical method of extrapolation to $x = 0$ and necessary experimental errors in the adsorption data in the low x region. These considerations thus emphasize the need for further theoretical developments for handling problems in the $0 < x < 0.05$ region.

Summary

The theory of adsorption developed in an earlier publication including, however, the repulsive term previously neglected is shown to agree with several type II isotherms over the entire range of relative pressures from 0.05 to 1.0. Methods are outlined for handling the complex infinite series of the theoretical equation, and the convergence and divergence properties of the equation are discussed.

The Bangham equation derived from the Gibbs adsorption equation for the surface pressure π of an adsorbed film is integrated by means of the theoretical adsorption isotherm. The calculated surface pressures are shown to be in excellent agreement with data determined by Jura and Harkins from graphical integration of the Bangham equation employing the experimental adsorption isotherms. The theory offers a method for evaluation of surface pressure from all types of physical adsorption isotherms including those exhibiting capillary condensation.

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[CONTRIBUTION NO. 13 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Thermodynamic Properties of Thiophene[1]

BY GUY WADDINGTON, J. W. KNOWLTON,[2] D. W. SCOTT, G. D. OLIVER,[3] S. S. TODD,[4] W. N. HUBBARD, J. C. SMITH AND HUGH M. HUFFMAN

The thermodynamic properties of sulfur compounds are of interest for several reasons. From a practical point of view, the increasing interest in the sulfur compounds occurring in or derivable from petroleum makes it important to have an extensive knowledge of the properties of these substances. Such information would be useful in the refining of petroleum and in the preparation of sulfur derivatives of hydrocarbons. Also, the thermodynamic properties of the simpler sulfur compounds are of interest because of the information such data would yield with respect to their molecular structures. Finally, as in the case of hydrocarbons, a study of representative members of a homologous series of sulfur compounds would yield relationships permitting the estimation of properties of compounds which had not been studied.

The study of some sulfur compounds of interest to the petroleum industry has recently been added to the Bureau of Mines program of thermodynamic research. Thiophene, because of its importance and intrinsic interest, was chosen as the first compound to be studied in this field. Listed below, in their order of presentation in this paper, are the several types of investigation carried out: Section (1), low-temperature heat capacity; Section (2), vapor pressure; Section (3), heat of vaporization, vapor heat capacity, gas imperfection, and entropy of the ideal gas; Section (4), heat of combustion and heat of formation; Section (5), thermodynamic functions from spectroscopic and molecular structure data. From these investigations, relatively complete thermodynamic information about thiophene in the low pressure region has been obtained.

The Material.—Two samples of thiophene differing somewhat in their histories were used

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(1) Portions of this paper were presented at the Atlantic City Meeting of the American Chemical Society, April, 1947.

(2) Deceased.

(3) Present address: Carbide and Carbon Chemical Corp., Oak Ridge, Tenn.

(4) Present address: Pacific Experiment Station, Bureau of Mines, Berkeley, California.

in the several investigations. Sample I was a selected cut from the Socony Vacuum Oil Company's pilot plant at Paulsboro, N. J., and was used without further purification for measurements of vapor heat capacities, heats of vaporization, and vapor pressures by the ebulliometric method. The apparent purity of this sample deduced from melting point studies by the time–temperature method was approximately 99.96 mole per cent. Sample II, used for the low-temperature studies, for the measurements of vapor pressures by the static method, and for the measurement of the heat of combustion, was prepared from material similar to Sample I by distillation in an efficient fractionating column at the Laramie Station of the Bureau of Mines.

TABLE I

MELTING POINT OF THIOPHENE

$N_x = 0.0111\Delta T$

% Melted	$T_{(obs.)}$	$T_{(calcd.)}$
16.08	234.7532	234.698
38.13	.8494	.8434
66.95[a]	.8891	.8891
91.40[a]	.9053	.9053
100.00		.9091
Pure		234.950
Triple point		234.95 ± 0.05°K.

Impurity = 0.045 mole %

[a] Computation based on these 2 points.

A mass spectrometer analysis, which was carried out at the Socony Vacuum laboratories, showed Sample II to have the composition: thiophene 99.954 mole %, benzene 0.030 mole %, carbon bisulfide 0.008 mole % and methylthiophene 0.008 mole %.[5] Melting point studies were made in this laboratory by the calorimetric method. The results of these investigations are summarized in Table I. Since thiophene and benzene are known to form solid solutions, too much reliance should not be placed on the value of the purity obtained from the melting point data. Direct determinations of sulfur made during the combustion measurements indicated that the sulfur content was in substantial agreement with theory.

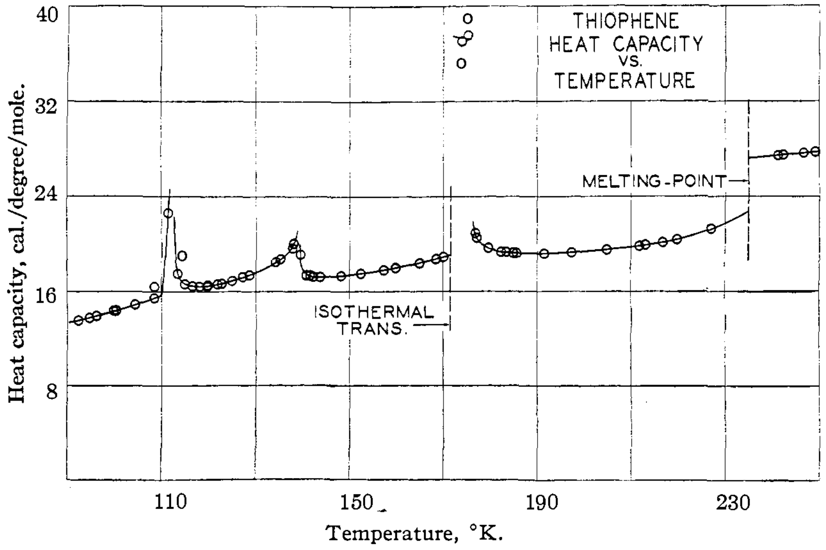

Fig. 1.—Plot of the heat capacity against temperature in the region of anomalous behavior.

Section 1: Low-Temperature Heat Capacity

The Apparatus.—The measurements were made in the apparatus described by Ruehrwein and Huffman.[6] Very briefly, the method was as follows: About 0.5 mole of the material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the environment was maintained at that of the calorimeter to prevent heat interchange. The initial and final temperatures of the calorimeter were measured by means of a platinum resistance thermometer. The electrical measurements required for the determination of the resistance of the thermometer and the electrical energy were made on a "White" double potentiometer in conjunction with a high-sensitivity galvanometer and accurately calibrated resistances. The potential was in terms of a bank of six thermostated saturated cadmium cells, which had been certified by the National Bureau of Standards. Time measurements were made with an electric stop clock, which was operated by an a. c. power supply, the frequency of which was accurate to 0.001%. The precision of the measurements was, in general, better than 0.1%, and above 30° K. it is believed that the accuracy uncertainty should not be greater than 0.2%. The energy measurements were made in terms of the international joule and were converted to calories by dividing by 4.1833.

The Results.—The results of the heat capacity measurements are given in Table II and shown graphically in Fig. 1 over the region 90 to 250° K. Inspection of this figure shows that the thermal properties of thiophene vary with temperature in an unusual manner. The material appears to undergo two second-order transitions of the lambda type

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(5) Private communication from D. E. Badertscher.

(6) Ruehrwein and Huffman, THIS JOURNAL, 65, 1620 (1943).

TABLE II

MOLAL HEAT CAPACITY OF THIOPHENE IN CAL./DEG.

T, °K.	ΔT	$C_{\text{sat.}}$	T, °K.	ΔT	$C_{\text{sat.}}$
11.70	1.027	0.842	129.20	5.252	17.459
12.97	1.526	1.131	132.23	12.698	18.153
13.07	1.120	1.155	134.24	5.458	18.448
14.58	1.727	1.494	135.18	8.090	18.717
14.72	2.233	1.539	137.84	1.742	19.852
16.71	2.534	2.006	138.02	1.292	20.034
17.43	3.204	2.195	139.22	1.280	18.214
19.51	3.078	2.719	139.36	1.397	18.129
20.18	2.301	2.895	140.52	1.323	17.373
22.68	3.268	3.523	140.78	1.442	17.384
23.32	3.984	3.691	141.55	5.664	17.413
26.72	4.812	4.501	142.22	1.449	17.230
27.60	4.575	4.703	143.67	1.447	17.228
31.35	4.445	5.518	143.97	9.487	17.288
32.32	4.869	5.716	148.15	7.545	17.303
37.44	5.371	6.691	150.16	17.947	17.420
43.17	6.083	7.618	152.44	7.457	17.508
49.15	5.879	8.604	157.33	10.033	17.836
54.75	6.411	9.347	159.80	7.251	18.016
54.84	5.492	9.357	159.94	5.369	17.965
54.92	5.018	9.377	162.36	6.453	18.196
55.91	6.219	9.509	165.01	5.323	18.391
60.29	5.738	10.039	168.50	1.421	18.708
61.64	7.362	10.184	170.06	1.691	18.866
62.53	7.024	10.311	172.07	1.897	27.45
69.02	7.398	11.002	173.79	1.534	35.23
69.65	7.220	11.087	173.98	1.282	37.15
76.62	7.804	11.811	175.24	1.228	38.98
76.96	7.389	11.856	175.28	1.450	37.58
84.56	8.071	12.699	175.87	2.296	28.61
84.58	7.858	12.701	176.89	2.079	20.89
92.32	7.626	13.542	177.21	2.405	20.528
92.74	8.300	13.584	178.15	2.259	20.075
92.97	5.642	13.604	179.65	2.482	19.689
94.67	5.329	13.775	182.30	2.511	19.325
95.06	6.194	13.828	183.33	6.793	19.313
99.01	6.439	14.258	184.35	10.137	19.287
99.88	5.096	14.368	184.82	2.525	19.245
100.27	4.239	14.401	185.57	6.745	19.229
100.41	8.550	14.430	191.47	5.058	19.199
104.12	3.777	14.854	197.34	6.688	19.307
104.45	4.102	14.894	204.81	8.242	19.530
104.52	15.260	15.079	211.76	8.220	19.848
107.84	3.658	15.349	212.98	8.100	19.912
108.42	3.856	15.417	216.82	6.275	20.133
108.49	7.603	16.423	219.88	8.021	20.390
110.41	1.482	15.756	226.98	6.185	21.294
111.55	2.405	22.604		Liquid	
111.72	1.148	21.975	240.33	4.847	27.456
112.55	0.807	33.89	242.30	5.720	27.503
113.50	1.481	17.526	246.76	8.012	27.675
113.88	1.844	17.202	249.21	8.103	27.731
114.29	4.001	19.093	258.06	9.609	28.057
115.01	1.545	16.572	267.61	9.487	28.403
115.75	1.899	16.444	277.03	9.366	28.775
116.56	1.553	16.422	286.34	9.254	29.128
118.11	1.551	16.395	295.54	9.141	29.500
119.66	1.543	16.465	297.45	6.002	29.599
119.83	7.088	16.493	304.18	7.459	29.857
121.29	19.184	16.608	304.62	9.028	29.881
121.96	3.052	16.623	311.60	7.383	30.187
122.77	5.986	16.669	319.67	8.762	30.527
124.98	2.999	16.920	327.92	7.741	30.863
127.26	7.762	17.199	336.08	8.565	31.255
128.64	5.755	17.375			

having maxima at approximately 112 and 138° K., both transitions involving only small amounts of energy. At approximately 171.6° K. the crystals undergo an isothermal transition involving about 150 calories per mole. Immediately following this isothermal absorption of energy, the heat capacity is abnormally high, but drops rapidly to the normal level in a manner similar to the high temperature side of a lambda-type transition. Similar behavior was observed in an unpublished investigation in the organic laboratory at Stanford University.[7]

Because of this unusual behavior, the transition zones were investigated with considerable care in order to define the shape of the heat-capacity curve as definitely as possible. From the experimental data there can be no doubt of the negative slope of the heat-capacity curve on the high-temperature side of the transitions. Since it was thought that the shape of the curve might be characteristic of the crystals formed at low temperatures, measurements were made on the high-temperature side of each transition without allowing the material to cool below the temperature of maximum heat capacity. The usual practice is to cool the material to a suitably low temperature and then to make measurements at progressively higher temperatures. In the present case a reversal of this procedure was attempted, *i. e.*, measurements of heat capacity were made at progressively lower temperatures. In laboratory parlance this is described as "backing into a transition." These experiments demonstrated that the heat capacity was independent of the history of the sample.

Because of the peculiar behavior between 171 and 184° K., a time–temperature study was made over this region. In this study, electrical energy was supplied to the calorimeter at an approximately steady rate and the temperature of the resistance thermometer recorded at integral minutes. These data have been plotted in Fig. 2 and are in agreement qualitatively and semiquantitatively with the deductions made from the heat-capacity measurements. [These measurements are inherently less reliable than the usual heat capacity measurements for two reasons: (1) Because of the location of the thermometer coil next to the heater coil, in the combination thermometer and heater, the temperature of the thermometer coil would always be higher than the contents of the calorimeter during energy input. However, if the rate of energy input to the heater is constant and the conduction and radiation paths are also constant, this temperature

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(7) Private communication from G. S. Parks.

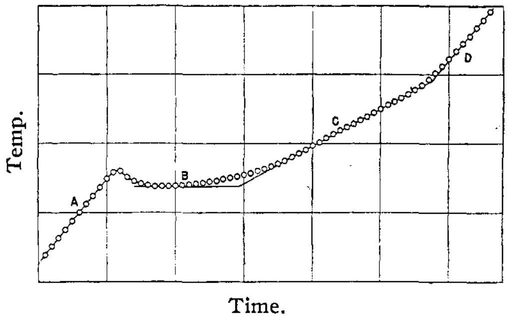

Fig. 2.—Time-temperature study of thiophene between 171 and 184°K. This study includes isothermal transition and the region of abnormally high heat capacity. Units are arbitrary.

head should be constant and the above investigation should give a good picture of the relative temperature change. (2) There will be another uncertainty due to the fact that the system is not in thermodynamic equilibrium during the heating process.] The initial portion of the curve shows a nearly uniform slope which is inversely proportional to $\Delta E/\Delta T$, the heat capacity. The low temperature material tends to superheat, and when the transition begins, the excess energy is absorbed by the transition process and the temperature drops rapidly. For some time thereafter the temperature remains nearly constant, then begins to increase slowly, forming another portion of the curve having a slope which is nearly uniform but considerably smaller than the slope of the initial part of the curve. The curve finally breaks again into another portion of uniform but higher slope. By drawing straight lines through the uniform portions of the curve it may be divided into four parts. In portion (A) the energy absorbed raises the temperature of the low-temperature crystals. In this region the heat capacity calculated from the time-temperature curve is in good agreement with the observed heat capacity values. Portion (B), which is almost flat, corresponds to an isothermal absorption of energy. This is followed by portion (C), which has a small slope and corresponds to the short temperature interval of high heat capacity. Portion (D) corresponds to the temperature range in which the heat capacity of the crystals has an apparently normal value. All of the data are in agreement, so there can be little question in regard to the thermal behavior of the material upon which the measurements were made. Because this behavior is so unusual, the question of the purity of the material has been carefully considered. All of the evidence at this time indicates that the amount of impurity was so small that it would probably have no significant effect on the thermal properties. For this reason it must be concluded that the observed behavior is characteristic of thiophene.

The value for the heat of the isothermal transition at 171.6° K. is rather arbitrary because of the uncertainties in the heat capacity of the high-temperature form and also of the temperature of transition. Check measurements were made of the energy requirements over a selected temperature interval, including the isothermal transition and the high heat capacities, and good agreement was obtained. This indicates that the transition was reproducible. The arbitrary distribution of the energy absorbed as heat of transition and heat capacity should have no significant effect on the entropy. The value assigned for the heat of transition is 152.4 cal./mole.

Two measurements were made of the heat of fusion. The experimental values were 1214.4 and 1216.6 giving a mean value $\Delta H° = 1215.5 \pm 1.1$ cal./mole.

Section 2: Vapor Pressure.—The vapor pressure of thiophene was measured from 0 to 40° by a static method and from 40 to 120° by an ebulliometric method.

The apparatus used for the static vapor pressure measurements is shown schematically in Fig. 3. A sample container, A, and a mercury manometer, B (shown in isometric projection in the insert of Fig. 3), are contained in a constant-temperature water-bath, C, having a plate glass window, D, through which the manometer may be observed. When a sample is to be introduced into or removed from the sample container, the mercury in the manometer may be lowered into the mercury reservoir, E, by applying suction through the stopcock, F. The glass tube connecting the mercury reservoir with the manometer enters the bottom of the constant-temperature bath

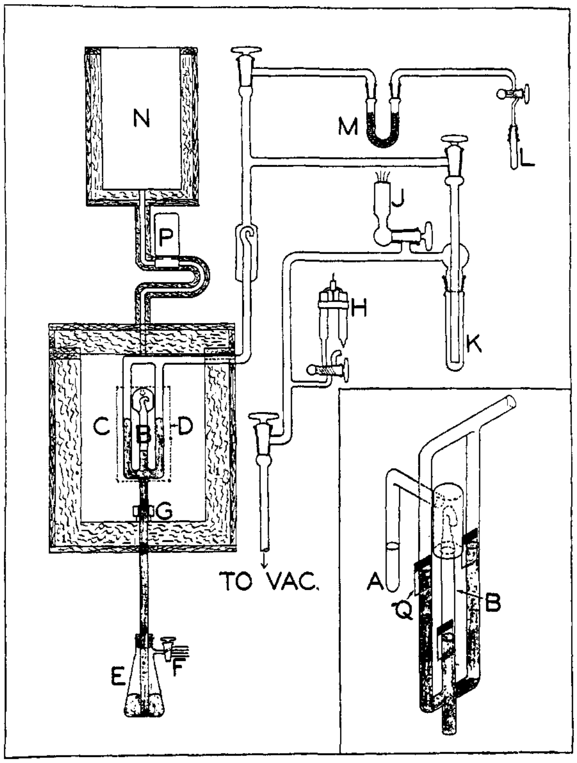

Fig. 3.—Apparatus for vapor pressure measurements by the static method.

through the packing gland, G. The two outer arms of the manometer are connected to a high-vacuum system. The Pirani gage, H, and ionization gage, J, included in this high-vacuum system, may be isolated by stopcocks when not in use and are protected from mercury vapor and other condensible materials by the refrigerated trap, K.

The procedure used for introducing and outgassing the sample is as follows: Approximately 5 ml. of the substance to be investigated is placed in the bulb, L, where it is frozen. The space over the solid is evacuated to a pressure of 10^{-5} mm. or less. The material is then distilled under its own vapor pressure into the sample container, A, during which operation the vapor passes through the U-tube, M, containing a suitable drying agent. The sample is again frozen and the space over it evacuated. The material is subjected to several additional bulb-to-bulb distillations between the sample container, A, and the bulb, L, and back again, and after each of these distillations it is frozen and any residual gas is pumped out. After the final distillation into the sample container, the material is melted, and about 20% of it is pumped off and caught in the trap, K (from where it is subsequently transferred to bulb L for storage). A series of vapor-pressure measurements is now made with the 80% of the sample remaining. Following these measurements, an additional 60% of the original sample is pumped off and a second series of vapor-pressure measurements is made with the 20% of the sample remaining. If the vapor pressures measured on 80% of the sample and on 20% are found to be in good agreement, this is taken as evidence that the sample was adequately outgassed and contained only negligible amounts of impurities of different volatility.

The constant-temperature bath is controlled by electrical heating when operating above room temperature and by intermittent addition of cold water from the container, N, by means of the solenoid valve, P, when operating below room temperature. In this type of apparatus, with both the sample container and manometer in the same constant-temperature bath, it is essential that there be no temperature gradients which will cause sample to distill from the sample container to the mercury surface of the manometer. For this reason, the various elements in the constant-temperature bath are so arranged that any small gradients, not eliminated by vigorous stirring, are in such a direction that the manometer is never colder than the sample container. The tube for addition of cold water is in the rear of the bath. Two immersion heaters, one a steady heater for compensating most of the heat loss of the bath, and the other an auxiliary heater used in heating the bath rapidly from one operating temperature to another, are located in the front of the bath, between the window and the manometer (but not obscuring the view of the mercury columns). The intermittent heater used for controlling the bath temperature and the stirrer are located in a 3-inch-diameter tower in one corner of the bath (not shown). A sensitive mercury-in-glass thermoregulator and a calorimetric-type platinum resistance thermometer, calibrated and certified by the National Bureau of Standards, are both in close proximity to the sample container. The resistance of the thermometer is measured by means of a G-2 Mueller bridge and a sensitive galvanometer. The bath is controlled to ± 0.01° at 15°, ± 0.005° at 40°, and ± 0.01° at 75°. When making measurements at 0°, the water is drained from the bath, and the sample container is surrounded by a Dewar flask containing crushed ice.

The manometer is read by means of a Gaertner M904 cathetometer certified by the National Bureau of Standards. The vernier of the cathetometer scale is graduated in 0.05-mm. divisions, and it is possible to estimate visually between vernier divisions to 0.01 mm. Each meniscus is observed against a background, Q, made from a rectangle of white plastic with a black strip across the top. The black reflects in the mercury surface and makes the outline of the meniscus clearly visible against the white background. The backgrounds are so mounted that they may be adjusted for vertical height by means of rods extending up through the lid of the constant-temperature bath. The manometer is illuminated by "Lumiline" incandescent lamps on each side of the window.

To test the window of the constant-temperature bath for any optical imperfections that would introduce errors into the pressure readings, a standard meter bar was mounted behind the window in the place ordinarily occupied by the manometer. Cathetometer readings of the distance between graduations on the standard meter bar showed that there were no optical imperfections in the window that would affect the pressure readings significantly. The walls of the manometer arms were also tested for optical imperfections by taking "blank" pressure readings with the sample container evacuated. The pressure readings obtained did not differ significantly from zero.

When taking pressure readings, the meniscus heights are always read in order from one side to the other at approximately equal time intervals and the readings for the two outer arms are averaged. This procedure automatically corrects for any regular variation of meniscus height with time or with position, such as might be caused by a temperature drift of the mercury reservoir or by failure of the axis of the cathetometer telescope to rotate in an exactly horizontal plane. Capillary depression corrections, taken from the tables of Cawood and Patterson,[8] are applied and the readings are reduced to 0° and standard acceleration of gravity. The acceleration of gravity at this location is calculated from the latitude and altitude to be 979.82 cm./sec.^{2}, and the standard acceleration of gravity is taken as 980.665 cm./sec.^{2}. Corrections for the vapor pressure of mercury are applied to the values obtained at the higher temperatures where this correction becomes significant.

To test the performance of the apparatus, the vapor pressure of benzene was measured at six temperatures between 0° and 35°. The results obtained, when compared with values calculated from the equation given in the A.P.I. Tables,[9] showed an average deviation of 0.03 mm. of Hg and a maximum deviation of 0.06 mm.

The results obtained for thiophene are listed in the first part of Table III. Each value listed is the average of five or more pressure readings taken within a period of about an hour. Three readings of the bath temperature were taken within the same period, and if these were significantly different from the integral temperature, the appropriate corrections were applied to the pressure readings.

In the ebulliometric vapor-pressure measurements, the boiling temperature of thiophene was compared directly with the boiling temperature of water in a closed system filled with nitrogen gas, the pressure of which could be adjusted to any predetermined value between 100 and 2500 mm. The boiling temperature of each liquid was measured in a differential ebulliometer, Fig. 4, which is a modification of one described by Swietoslawski.[10] The strain-free platinum resistance thermometer used to measure the boiling points had been calibrated and certified by the National Bureau of Standards. Its resistance was measured with the same bridge and galvanometer used with the static vapor pressure apparatus.

At atmospheric pressure, the boiling and condensation temperatures of the thiophene sample

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(8) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

(9) American Petroleum Institute Research Project 44 at the National Bureau of Standards, Selected Values of Properties of Hydrocarbons. Table No. 5k (Part 1), alkyl benzenes, C_6 to C_8, vapor pressures and boiling points, at 10 to 1500 mm., dated June 30, 1944.

(10) W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, New York, 1945, p. 11.

TABLE III

VAPOR PRESSURE OF THIOPHENE

STATIC METHOD

t, °C.	Vapor pressure, mm. 80% of sample	20% of sample	Calcd. (eq. 1)
0	21.44	21.41	21.39
15	48.73	48.64	48.68
20	62.67	62.59	62.60
25	79.71	79.67	79.68
30	100.49	100.47	100.45
35	125.51	125.45	125.50
40	155.53	155.47	155.47

EBULLIOMETRIC METHOD

Boiling point, °C. Water	Thiophene	Vapor pressure, mm. Obs.	Calcd. (eq. 1)
60	39.061	149.41	149.43
65	44.560	187.57	187.67
70	50.094	233.72	233.84
75	55.663	289.13	289.22
80	61.276	355.22	355.26
85	66.931	433.56	433.53
90	72.629	525.86	525.76
95	78.370	633.99	633.84
100	84.155	760.00	759.80
105	89.985	906.06	905.88
110	95.860	1074.6	1074.5
115	101.776	1268.0	1268.0
120	107.738	1489.1	1489.3
125	113.741	1740.8	1741.0
130	119.787	2026.0	2026.3

differed by only 0.003°. This result indicates that the sample did not contain sufficient impurities of different volatility to have any significant effect on the boiling point measurements.

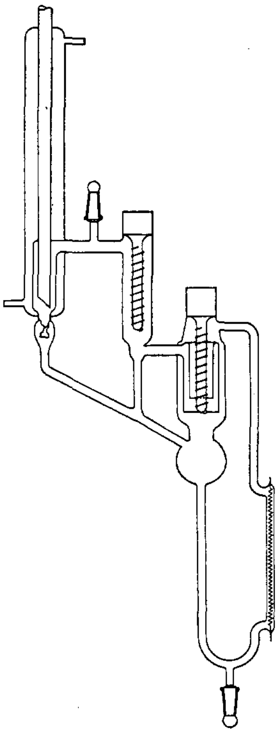

Fig. 4.—Differential ebulliometer.

The vapor pressure data obtained by the ebulliometric method are listed in the second part of Table IV. The pressures corresponding to the observed boiling points of water were obtained from the tables of Osborne, Stimson and Ginnings.[11]

The vapor pressure data obtained by both methods were fitted to an Antoine equation by the least squares treatment of Willingham, Taylor, Pignocco, and Rossini.[12] In weighting the individual points, the expected standard deviation of each temperature measurement was arbitrarily taken as 0.01° and the expected standard deviation of each pressure measurement by the static method was arbitrarily taken as 0.10 mm. The equation obtained is

$$\log_{10} P = 6.95926 - 1246.038/(221.354 + t) \quad (1)$$

Values of the vapor pressure calculated by means of this equation are included in Table III for comparison with the observed values. In the deviation plot, Fig. 5, the results of prior investigations of the vapor pressure of thiophene[13] are compared with those reported here.

Section 3: Heat of Vaporization, Vapor Heat Capacity, Gas Imperfection, and Entropy of the Ideal Gas

Heat of Vaporization and Vapor Heat Capacity.—The heat of vaporization of thiophene was determined at three temperatures, and the heat capacity of the vapor was measured at two or more pressures at each of five temperatures between 70 and 200°. The cycling vaporizer and flow calorimeter, described in previous publications from this laboratory,[14] were used for these measurements. The heat of vaporization data are given in Table IV; the accuracy of these values is estimated to be about 0.1%. The following empirical equation may be used for interpolation over the temperature range of the experiments

$$\Delta H_{\mathrm{vap.}} = 9543 + 2.740T - 0.02349T^2 \quad (2)$$

Table V lists the vapor heat-capacity data. The values of $C_p°$ (obs.) were obtained at each temperature by linear extrapolation to zero pressure, of plots of heat capacity *vs.* pressure. Al-

TABLE IV

HEAT OF VAPORIZATION OF THIOPHENE

1 cal. = 4.1833 int. joules; mol. wt. = 84.132

t, °C.	No. expts.	$\Delta H_{\mathrm{vap.}}$, cal./mole
45.36	4	8032 ± 7[a]
63.08	3	7808 ± 3[a]
84.16	3	7522 ± 3[a]

[a] Maximum deviation

TABLE V

VAPOR HEAT CAPACITY OF THIOPHENE, CAL./DEG/MOLE

1 cal. = 4.1833 int. joules; mol. wt. = 84.132; 0° C. = 273.16° K.

T, °K.	343.95	371.20	402.30	436.20	471.15
C_p (759 mm.)		22.03	23.47	24.96	26.41
C_p (378 mm.)	20.43	21.80			
C_p (192 mm.)	20.25	21.67	23.24	24.81	26.31
$C_p°$ (obs.)	20.05	21.55	23.17	24.76	26.27
$C_p°$ (calcd.)[a]	19.91	21.36	22.92	24.48	25.96
$C_p°$ (obs.) − $C_p°$ (calcd.)	0.14	0.19	0.25	0.28	0.31

[a] Harmonic oscillator-rigid rotator approximation.

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[11] Osborne, Stimson and Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

[12] Willingham, Taylor, Pignocco and Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

[13] (a) Milazzo, *Gazz. chim. ital.*, **74**, 58 (1944); (b) Nasini, *Proc. Royal Soc.* (*London*), **A123**, 704 (1929); (c) Fawcett and Rasmussen, THIS JOURNAL, **67**, 1705 (1945).

[14] (a) Waddington, Todd and Huffman, THIS JOURNAL, **69**, 22 (1947); (b) Waddington and Douslin, *ibid.*, **69**, 2275 (1947).

though the accuracy of vapor heat capacity measurements of polyatomic molecules is difficult to assess, the accuracy uncertainty of the $C_p°$ values given here is believed to be about ±0.2%. Over the range of temperatures studied, $C_p°$ is given without significant loss of accuracy by the empirical relationship

$$C_p° = -7.017 + 0.10045T - 6.325 \times 10^{-5}T^2 \quad (3)$$

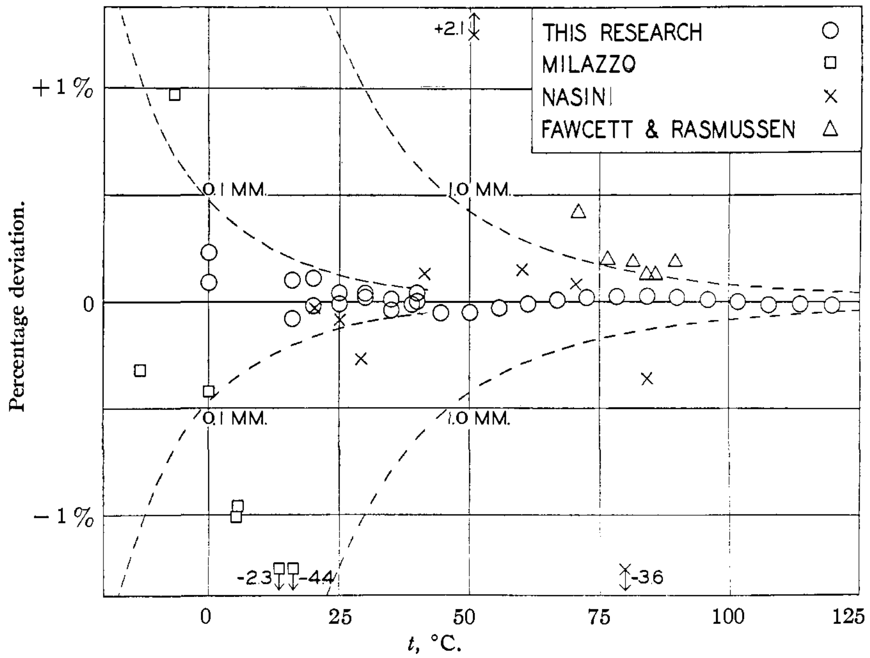

Fig. 5.—Deviation plot of vapor pressure data for thiophene, comparing the results of this research with those of previous investigators (ref. 13). Equation 1 was used for the base line. The dashed lines represent the percentage deviations arising from absolute deviations of 0.1 mm. and 1.0 mm., respectively.

Gas Imperfection and the Second Virial Coefficient.—Values of the second virial coefficient, B, in the equation of state $PV = RT + BP$ were calculated from the heat of vaporization and vapor pressure data by means of the relation

$$B = \frac{\Delta H_{\text{vap.}}}{T(\mathrm{d}P/\mathrm{d}T)} - \frac{RT}{P} + V_l \quad (4)$$

where V_l is the molal volume of the liquid. Use of the experimental data for the pressure dependence of the vapor heat capacity in the equation $(\partial Cp/\partial P)_T = -T(\partial^2 B/\partial T^2)_P$ yielded values of the second derivative of B with respect to temperature. These results were used to obtain the following empirical equation for the second virial coefficient of thiophene vapor

$$B(\text{liters}) = -0.435 - 0.0172 \exp. (1200/T) \quad (5)$$

The method of evaluating the constants has been discussed previously.[15]

In Table VI the observed values of the second virial coefficient and of $(\partial Cp/\partial P)_T$ are compared with those calculated from Eq. 5.

TABLE VI

SECOND VIRIAL COEFFICIENT AND $(\partial Cp/\partial P)_T$ FOR THIOPHENE

t, °C.	B, liters Obs.	Calcd.	t, °C.	$(\partial Cp/\partial P)_T$, cal./deg./mole/atm. Obs.	Calcd.
45.36	−1.173	−1.179	70.79	0.77	0.78
63.08	−1.025	−1.045	98.04	.48	.48
84.16	−0.957	−0.930	129.14	.31	.30
			163.04	.20	.20
			197.99	.13	.13

Entropy from Calorimetric Data.—The calorimetric data have been used to calculate the entropy in the usual way. In the transition regions the heat capacity curves are not necessarily accurate because of rapid curvature. However, the curves have been made in such a way that $\int_{T_x}^{T_y} C_p \mathrm{d}T$ gives the observed enthalpy change; hence there will be no significant error in the entropy.

Since the heat-capacity measurements were carried out up to 340° K., it was possible, with a small extrapolation, to obtain the entropy of the liquid at the temperatures corresponding to those at which the heat of vaporization had been measured. The entropy calculations are summarized in Table VII.

TABLE VII

THE MOLAL ENTROPY OF THIOPHENE, CAL./DEG.

$S_{0-12°\text{K.}}$ (Debye, 4° freedom, $\Theta = 102.7$) = 0.322
$\Delta S_{12-171.6}$ (graphical) = 23.265
$\Delta S_{171.6}$ (152.4/171.6) = 0.888
$\Delta S_{171.6-234.94}$ (graphical) = 6.896
$\Delta S_{234.94}$ (1215.5/234.94) = 5.174
$\Delta S_{234.94-298.16}$ (graphical) = 6.755
$S_{298.16}$ Liq. = 43.30 ± 0.10

T, °K.	318.52	336.24	357.32
Entropy of liquid at 298.16°K.	43.30	43.30	43.30
$\Delta S_{298.16-T}$ (graphical)	1.98	3.66	5.58
Vaporization, $\Delta H_{\text{vap.}}/T$	25.22	23.22	21.05
Compression, $R \ln (P/760)$	−2.72	−1.38	0.00
Gas imperfection[a]	+0.05	+0.08	+0.11
Entropy of ideal gas at 1 atm.	67.83 ±0.20	68.88 ±0.20	70.40 ±0.20

[a] For calculating the correction for gas imperfection, which is given by $P(\partial B/\partial T)_P$, in terms of the second virial coefficient, eq. 5 was used.

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[15] Scott, Waddington, Smith and Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

The uncertainties in the experimental heat capacity measurements in certain temperature regions are probably higher than usual because of the rapid curvature and slow approach to equilibrium. Nevertheless it is believed that the experimentally determined entropy of the liquid is reliable to ±0.1 cal./deg./mole, and that of the gas is reliable to ± 0.20 cal./deg./mole.

Section 4: Heat of Combustion and Heat of Formation

Calorimetric Method.—The calorimetric method has been described previously.[16]

Certain modifications in the apparatus as described by Hubbard, Knowlton and Huffman[17] had been made, but the operating principles were unchanged. All of the combustions were carried out in a platinum-lined bomb having a volume of 0.330 liter. The general method of Huffman and Ellis[16] for the combustion of sulfur compounds was followed; that is, an atmosphere of air was left in the bomb to supply nitrogen required for the complete oxidation of sulfur to sulfur trioxide and no (liquid) water was introduced into the bomb before the combustion. The combustion samples were contained in thin-walled glass ampules drawn down to a capillary neck which was not sealed.

The ampules were filled by the following procedure. The weighed empty ampules were placed neck down in the receiver of an all-glass distilling apparatus. The system was then evacuated and the thiophene allowed to distill into the receiver under its own vapor pressure. When a sufficient quantity had been distilled, air was admitted to the system and the pressure forced liquid into the ampules. Shortly before a combustion experiment an ampule was taken from the receiver, external material was removed, and a small amount of thiophene was forced out of the ampule so as to bring the liquid level, at room temperature, below the fine part of the capillary, to avoid losses due to expansion caused by temperature fluctuations subsequent to weighing. Because of the fineness of the opening and the small surface exposed, there appeared to be no significant evaporation of sample or solution of air during the experimental period. The method was tested by burning benzene in both sealed and unsealed ampules. In both cases very satisfactory agreement was obtained with the accepted value for its heat of combustion.

Calibration.—The energy equivalent of the system was determined by the combustion of benzoic acid NBS standard sample #39f having the certified value of 26,428.4 NBS international joules per gram for the isothermal heat of combustion under standard conditions.[18] Since the conditions of this investigation were not quite standard, this value was corrected to 26,426.6 NBS int. joules/g. Joules were converted to conventional calories by dividing by 4.1833. The average value of the energy equivalent of the system, from eight calibration experiments, was found to be 3225.7 cal./degree, with an average deviation of 0.004% and a maximum deviation of 0.017%.

Corrections and Analytical Procedures.—The reactions involved in the combustion of sulfur compounds are rather complex and require corrections not usually applied in C, H, O combustions. Under the conditions of the experiment, part of the nitrogen in the bomb is fixed. Hence it is necessary to determine both the type of nitrogen compound and the quantity so that proper calorific corrections may be applied for these secondary reactions. Because of the large heat of dilution of sulfuric acid, it is necessary to know its concentration with considerable certainty. Finally, because there is a difference in the amount of water vapor initially present in the bomb and the amount existing over the sulfuric acid solution in the final state, a correction must be applied for its condensation.

Qualitative tests indicated that nitrogen was fixed in the form of nitric acid and nitrous acid. The NO_2^- ion was determined by the colorimetric method of Treadwell and Hall[19] and the total nitrogen was determined as ammonia after reduction by Devarda's method.[20] It was assumed that all of the nitrogen was in the form of nitrous and nitric acid; hence nitric acid was taken as the difference between total nitrogen and nitrous acid nitrogen. The heat effects (ΔE) associated with the formation of nitrous and nitric acid were taken as 6.4 and −14.96 kcal. per mole, respectively.

The concentration of the sulfuric acid was calculated from the stoichiometric relations of the materials entering into the reaction. In a number of cases the sulfate ion was determined gravimetrically and the amount found was on the average 99.8% of the calculated amount. The data of Huffman and Ellis[16] were used to correct the observed heats to one corresponding to a standard sulfuric acid concentration. The correction for the condensation of water vapor was determined from measurements of the humidity, the volume of the bomb, the known heat of vaporization of water, and the vapor pressure of aqueous sulfuric acid.[21]

The results of the six combustions are summarized in Table VIII. In addition to the final results this table shows the magnitude of the various correction terms used.

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(16) (a) Huffman and Ellis, THIS JOURNAL, **57**, 41 (1935); (b) Stiehler and Huffman, *ibid.*, **57**, 1734 (1935); (c) Huffman, *ibid.*, **60**, 1171 (1938).

(17) Hubbard, Knowlton and Huffman, *ibid.*, **70**, 3259 (1948).

(18) Jessup, *J. Research Natl. Bur. Standards*, **29**, 247 (1942).

(19) Treadwell and Hall, "Analytical Chemistry," 9th ed., John Wiley and Sons, Inc., New York, N. Y., 1946, p. 306.

(20) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 639.

(21) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1926, p. 303.

TABLE VIII

SUMMARY OF THIOPHENE COMBUSTIONS

For the Isothermal Reaction at 25°: $C_4H_4S(l) + 13/2\ O_2(g) + 0.7\ H_2O(l) = 4\ CO_2(g) + [H_2SO_4 \cdot 1.7H_2O](l)$

Mass of thiophene g. (in vac.)	Mass of oil, g. (in air)	$C_p \times \Delta t$ total cal.	$\frac{n_{H_2O}}{n_{H_2SO_4}}$	Calories correction[a] $Q_{diln.}$	$Q_{cond.}$	Q_{HNO_2}	Q_{HNO_3}	$Q_{fuse + oil + ign.}$	Ash found, mg.	$-\Delta U_B/M$, cal./g.	Dev., cal./g.
0.74153	0.05190	6454.62	1.45	+ 6.71	−3.63	+2.84	−3.08	− 597.23	5.2	7910.6	−2.1
.75114	.04007	6396.36	1.34	+10.11	−3.03	+2.26	−4.17	− 465.11	6.0	7910.7	−2.0
.71659	.06929	6459.56	1.60	+ 2.32	−2.58	+2.10	−4.48	− 791.19	6.2	7914.1	+1.4
.71031	.07539	6478.65	1.66	+ 1.05	−2.54	+2.45	−5.29	− 861.06	6.7	7909.9	−2.8
.71005	.7431	6469.56	1.65	+ 1.18	−2.68	+2.52	−4.96	− 848.64	6.8	7918.1	+5.4
.68715	.09056	6466.65	1.82	− 2.71	−2.47	+2.30	−2.17	−1029.80	5.4	7912.6	−0.1
							Average			7912.7 ± 2.3 = 0.03%	
							Max. spread		8.2 cal./g. = 0.1%		

[a] $Q_{diln.}$ = correction for dilution of H_2SO_4, $Q_{cond.}$ = correction for condensation of water, Q_{HNO_2} = correction for nitrous acid, Q_{HNO_3} = correction for nitric acid.

In Table IX are given the derived data for thiophene. It should be borne in mind that $-\Delta U_R$ and $-\Delta H_R$ apply to the combustions only when the composition of the aqueous sulfuric acid corresponds to $H_2SO_4 \cdot 1.7H_2O$ and that the Washburn correction has not been applied.

TABLE IX

THIOPHENE, MOL. WT. = 84.132; DERIVED DATA AT 298.16°

in kcal./mole

ΔU_R	ΔH_R	$\Delta H°_f$(liq.)	$\Delta H°_f$(gas)
−665.71	−667.19	19.52	27.82

ΔU_R and ΔH_R refer to the reaction in which H_2O/H_2SO_4 = 1.7. $\Delta H_f°$ refers to the formation from the elements.

Discussion.—The above value for the heat of formation of thiophene is to be looked upon as a preliminary value only, for several reasons that will be discussed below. The corrections for the fixed nitrogen were based on the assumption of the formation of aqueous nitrous acid and nitric acid. Actually this assumption may not be warranted as is borne out by the following evidence. According to the above assumption the products of the combustion of the sulfur and the nitrogen are all acidic. Hence from the total nitrogen and sulfur known to be present it is possible to calculate the moles of acid to be expected. This calculated value was always greater than the value found from titration by approximately 0.4–0.5 millimole or 2 to 3%. Because the gravimetric sulfur analyses accounted for practically 100% of the theoretical SO_4^{--} ion and no known cations were present, it is believed that the discrepancy is due to nitrogen being fixed in some form other than nitrous acid or nitric acid. This problem is being investigated.

Furthermore, a small amount of solid material is found after each combustion when the solutions formed in the combustion are evaporated to dryness. Presumably this solid residue comes from the reaction of the products of combustion with either platinum or glass or both. The amount of residue is far too small to account for the discrepancy between calculated and found hydrogen ion. A series of combustions made in an illium bomb showed about twice as much residue and the combustion values were definitely higher.

The heat of combustion of thiophene has also been studied by Moore, Renquist and Parks[22] in an illium bomb. Their value for $-\Delta U_B/M$ corrected for the change in the heat of combustion of benzoic acid[18] and a change in calibration[23] is 7918.3 ± 2.5 calories per gram and in good agreement with the value 7916.8 obtained in this laboratory using an illium bomb.

In the opinion of the authors, the data obtained in this Laboratory using the platinum bomb are probably the most reliable. In spite of the uncertainty attached to their experimental quantities, it seems desirable to publish these results as being the best available and because of the need of a value of the heat of formation for thermodynamic calculations.

Section 5: Thermodynamic Functions from Spectroscopic and Molecular Structure Data

Vibrational Assignment.—With the aid of the vapor-heat-capacity data, a complete, although not entirely certain, vibrational assignment for thiophene was made. No complete vibrational assignment has been proposed heretofore, but Thompson and Temple[24] have assigned 14 of the 21 fundamental frequencies. The assignment given here is based primarily on the Raman data of Reitz[25] and the infrared data of Thompson and Temple, as given in Table X, although all of the other available spectroscopic data[26] were consid-

(22) Moore, Renquist and Parks, THIS JOURNAL, **62**, 1505 (1940).

(23) Private communications from G. S. Parks.

(24) Thompson and Temple, *Trans. Faraday Soc.*, **41**, 27 (1945).

(25) Reitz, *Z. physik. Chem.*, **B33**, 179 (1936); *B38*, 275 (1937).

(26) (a) Venkateswaren, *Indian J. Physics*, **5**, 145 (1930); *Phil. Mag.*, **15**, 263 (1933). (b) Bhagavantam, *Indian J. Physics*, **7**, 79 (1932). (c) Venkateswaren and Bhagavantam, *Indian J. Physics*, **7**, 585 (1933). (d) Bonino and Monzani-Ansidei, *Z. physik. Chem.*, **B25**, 327 (1934); *Atti. accad. Lincei, Classe sci. fis. mat. nat.*, **24**, 207 (1936); *Ricerca sci.*, **7**, I, 315 (1936). (e) Coblentz, "Investigation of Infrared Spectra," Publ. Carnegie Inst. of Wash., D. C. No. 35 Part I (1905). (f) Manzoni-Ansidei and Rolla, *Atti. accad. Lincei, Classe sci. fis. mat. nat.*, **27**, 410 (1938). (g) Barnes and Brattain, *J. Chem. Phys.*, **3**, 446 (1935). (h) American Petroleum Institute Research Project 44 at the National Bureau of Standards. Catalog of Infared Spectrograms. Serial No. 364, Thiophene (liquid), contributed by the Socony-Vacuum Oil Company, Paulsboro, New Jersey. (i) Barnes, Liddel and Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 659 (1943).

ered. The assignment is given in Table XI; the numbering of the modes of vibration follows that used by Lord and Miller[27] for the analogous molecule pyrrole.

TABLE X

SPECTRA OF THIOPHENE[a]

Raman (Reitz[25]) $\Delta\nu$	I	ρ	Infrared (Thompson and Temple[24]) Vapor	Liquid	Assignment
375	0	(dp)			832–453 = 379
453	3	dp			23
565	1	dp			18
604	6	0.34	605	605	1
686	2	1.01			19
			710	710	22
748	4	1.00			20
832	7	0.08	836	836	3 and 24
866	1	1.00	872	870	10
898	1/2	dp	909	904	11
1032	10	0.11	1035	1035	2
1079	9	0.43	1077	1080	4
			1252	1255	14
				1290	12
1358	9	0.13			5
1404	12	0.35	1405	1405	6
				1479	Combination
				1565	Combination
				1590	15
2996	1	p			7 and 16
3078	8b	p(Hg)		3110	Resonance 8 and 17
3108	10	0.33 (Hg)			3 (1032) = 3096

[a] Omitting the region 1700–2800 cm.$^{-1}$

TABLE XI

VIBRATIONAL ASSIGNMENT FOR THIOPHENE

Class A_1 No.	Class A_1 ν, cm.$^{-1}$	Class A_2 No.	Class A_2 ν, cm.$^{-1}$	Class B_2 No.	Class B_2 ν, cm.$^{-1}$	Class B_1 No.	Class B_1 ν, cm.$^{-1}$
1	604	18	565	22	710	10	872
2	1032	19	686	23	453	11	909
3	832	20	748	24	(832)[a]	12	1290
4	1079					14	1252
5	1358					15	1590
6	1404					16	(2996)
7	2996					17	(3093)
8	3093						

[a] Parentheses denote frequencies used for the second time.

In class A_1, the assignment of the frequencies below 1600 cm.$^{-1}$ follows that of Thompson and Temple. These frequencies appear as strong polarized lines in the Raman effect, and their assignment is unambiguous. There are two C–H stretching frequencies in this symmetry class, but three polarized Raman lines are observed in the 3000 cm.$^{-1}$ region of the spectrum. The frequency 2996 cm.$^{-1}$ was assigned to ν_7 and the doublet 3078–3108 cm.$^{-1}$ was interpreted as Fermi resonance between ν_8 and $3(\nu_2)$. The average value, 3093 cm.$^{-1}$, was used for v_8.

In assigning the frequencies in class A_2, use was made of the fact that the vibrations in this symmetry class do not involve motion of the sulfur atom, and consequently the frequencies should not differ greatly from those of the corresponding vibrations in pyrrole. The A_2 frequencies in pyrrole occur at 510, 711, and 868 cm.$^{-1}$;[27] the evident choices for thiophene are the frequencies 565, 686 and 748 cm.$^{-1}$ observed in the Raman effect. In conformity with the selection rules for A_2 frequencies, these do not appear in the infrared.

In class B_2, Thompson and Temple assigned the strong infrared band at 710 cm.$^{-1}$ to ν_{22}. The out-of-plane ring bending frequency, ν_{23}, would be expected in the region of the spectrum below 500 cm.$^{-1}$; the choice is between the Raman lines at 375 and 453 cm.$^{-1}$. Thompson and Temple suggest that the former is the difference tone 832 − 453 = 379 cm.$^{-1}$. Additional evidence for this interpretation is the fact that if 375 cm.$^{-1}$ is assumed to be a fundamental frequency, no reasonable assignment of the other frequencies can be made to agree with the gas heat capacity data. This leaves the 453 cm.$^{-1}$ Raman line for ν_{23}. The remaining B_2 frequency, ν_{24}, arises from an out-of-plane hydrogen bending mode which would be expected to involve little motion of the hetero-atom or group in the series pyrrole, pyrrole-N-d, furan and thiophene. Hence it would be expected to have roughly the same value in all of these molecules. In pyrrole and pyrrole-N-d, ν_{24} is found at 838 and 833 cm.$^{-1}$, respectively,[28] and the B_2 frequency of furan at 837 cm.$^{-1}$ is very likely also ν_{24}. In thiophene a B_2 frequency in this region of the spectrum would be obscured in both the Raman and infrared spectra by the A_1 frequency, ν_3, at 832 cm.$^{-1}$, and the value 832 cm.$^{-1}$ was used for ν_{24}, as well as for ν_3.

Thompson and Temple have assigned the observed frequencies 872, 1252, and 1590 cm.$^{-1}$ to class B_1; these probably are the ring frequencies ν_{10}, ν_{14}, and ν_{15}. As all the C–H stretching frequencies of thiophene have not been resolved, the same values were used for ν_{16} and ν_{17} in class B_1 as for ν_7 and ν_8 in class A_1, namely, 2996 and 3093 cm.$^{-1}$. This leaves only the two C–H bending frequencies, ν_{11} and ν_{12}, to be assigned. The weak Raman line at 898 cm.$^{-1}$ (corresponding to the infrared band for thiophene vapor at 909 cm.$^{-1}$) was used for ν_{11}; it is depolarized and hence cannot be the overtone of ν_{23}. To fix the remaining frequency, ν_{12}, use was made of the gas heat capacity data. Assuming all the other frequencies assigned correctly, the gas heat capacity data require ν_{12} to be approximately 1300 cm.$^{-1}$. Liquid thiophene has a weak infrared band at 1290 cm.$^{-1}$. Although this can be interpreted as a combination band (453 + 832 = 1285) it seems more probable that it is the fundamental frequency, ν_{12}, and it was so assigned.

In Table V the observed values of $C_p°$ are compared with those calculated by means of the harmonic oscillator-rigid rotator approximation, using the vibrational assignment of Table XI. If the

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[27] Lord and Miller, *J. Chem. Phys.*, **10**, 328 (1942).

[28] Actually, Lord and Miller assign these frequencies to ν_{23}, but it seems more probable that they correspond to ν_{24}, and that the lowest B_2 frequencies, 565 and 450 cm.$^{-1}$, correspond to ν_{23}.

vibrational assignment is correct, the values of $C_p°$(obs.) − $C_p°$ (calcd.) in the last line of Table V represent the contribution to the heat capacity of anharmonicity and other factors neglected in the harmonic oscillator–rigid rotator treatment. In the case of benzene,[15] for which there can be little doubt as to the correctness of the vibrational assignment, values of $C_p°$(obs.) − $C_p°$ (calcd.) were found which were similar both in magnitude and in temperature dependence to those found here for thiophene.

Entropy from Molecular Structure Data.—The calorimetric values of the entropy are compared in Table XII with those calculated from molecular structure data. In these calculations the values of the fundamental constants given by Wagman, *et al.*[29] were used. The moments of inertia, calculated from the geometrical data of Schomaker and Pauling[30] and 1941 atomic weights, are $I_x = 156.5 \times 10^{-40}$, $I_y = 262.1 \times 10^{-40}$, and $I_z = 105.6 \times 10^{-40}$ g. sq. cm. The symmetry number is 2. The vibrational assignment of Table XI was used.

TABLE XII

T, °K.	Entropy, cal./deg./mole Calorimetric	Molecular structure
318.52	67.83	67.81
336.24	68.88	68.84
357.32	70.04	70.05

The close agreement of the two sets of entropy values shows that crystalline thiophene approaches zero entropy at the absolute zero. It is also a confirmation of the planar structure (C_{2v} symmetry) for the thiophene molecule.

Statistically Calculated Thermodynamic Functions.—The free-energy function, heat-content function, entropy, and heat capacity of gaseous thiophene have been calculated for various temperatures up to 1500° K. The values obtained are listed in Table XIII.

TABLE XIII

THERMODYNAMIC FUNCTIONS OF THIOPHENE

T, °K.	$(H_0^0 - F_T^0)/T$, cal./deg./mole	$H_T^0 - H_0^0$, kcal./mole	S_T^0, cal./deg./mole	$C_p{}^0{}_T$, cal./deg./mole
298.16	55.98	3.172	66.62	17.32
300	56.05	3.204	66.72	17.43
400	59.45	5.224	72.51	22.81
500	62.62	7.728	78.08	27.10
600	65.64	10.59	83.32	30.46
800	71.27	17.22	92.80	35.27
1000	76.42	24.61	101.03	38.56
1500	87.52	45.24	117.68	43.33

These thermodynamic functions were calculated on the basis of the harmonic oscillator–rigid rotator approximation and may be somewhat in error, especially at the higher temperatures, because of neglect of the contributions of anharmonicity and other factors. Some values in the table are given to more significant figures than are warranted by their absolute accuracy, in order to retain the internal consistency of the several thermodynamic functions.

Acknowledgments.—The authors are indebted to J. S. Ball of the Petroleum and Oil-Shale Experiment Station, Bureau of Mines, Laramie, Wyo., and to the Socony Vacuum Oil Co., Paulsboro, N. J., for the samples of purified thiophene used in this work, and for analytical data on the samples. Helpful discussion of certain features of the vibrational assignment with Dr. Kenneth S. Pitzer of the University of California is gratefully acknowledged.

Summary

The heat capacity of thiophene was measured over the temperature range 11–340° K. The solid has two lambda-type transitions at approximately 112 and 138° K., an isothermal transition at approximately 171.6° K., and a short region of anomalously high heat capacity on the high-temperature side of the latter transition. The heat of transition (152.4 cal./mole), heat of fusion (1215.5 ± 1.1 cal./mole), and the triple point (234.95 ± 0.05° K.) were measured.

The vapor pressure of thiophene was measured over the temperature range 0 to 120°, and the following equation was found to fit the vapor-pressure data: $\log_{10} P(\text{mm.}) = 6.95926 - 1246.038/(221.354 + t)$. The normal boiling point is 84.16°.

The heat of vaporization was measured at three different temperatures, and the values found were 8032, 7808 and 7522 cal./mole at 45.36, 63.08 and 84.16°, respectively.

The heat capacity of thiophene vapor was measured at five different temperatures in the range 343 to 472° K. The experimental values for $Cp°$, the heat capacity in the ideal gas state, may be represented by the equation $Cp° = -7.017 + 0.10045T - 6.325 \times 10^{-5}T^2$. An equation for the second virial coefficient, B, in the equation of state $PV = RT + BP$, was obtained from thermal data. The equation is B (liters) $= -0.435 - 0.0172 \exp. (1200/T)$.

The entropy of liquid thiophene at 298.16° K. is 43.30 ± 0.10 cal./deg./mole. The entropy of the ideal gas at the normal boiling point (357.32° K.) and 1 atmosphere pressure is 70.04 ± 0.20 cal./deg./mole.

The heat of combustion of thiophene was determined. For the reaction at 298.16° K., $C_4H_4S(l) + 13/2\ O_2(g) + 0.7H_2O = 4\ CO_2(g) + H_2SO_4{\cdot}1.7H_2O$, $\Delta H_R = -667.19$ kcal./mole. The heat of formation of liquid thiophene is 19.52 kcal./mole and the heat of formation of the gas is 27.82 kcal./mole, both at 298.16° K.

A complete vibrational assignment was proposed for thiophene. Using this vibrational as-

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[29] Wagman, Kilpatrick, Taylor, Pitzer and Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[30] Schomaker and Pauling, THIS JOURNAL, **61**, 1769 (1939).

signment and other molecular structure data, values of the free energy function, heat-content function, entropy and heat capacity were calculated by the methods of statistical mechanics for various temperatures up to 1500° K.

Bartlesville, Okla. Received October 1, 1948

[Contribution from the Department of Chemistry, University of Chicago]

Solubilization of Polar–Non-polar Substances in Solutions of Long Chain Electrolytes[1a]

By William D. Harkins and Hans Oppenheimer

I. Introduction

Earlier work in this Laboratory[1b,2] on the effects of long chain alcohols and amines on both the X-ray bands and the critical micelle concentration of soap solutions indicates that their effects are very different from those of the hydrocarbons. This suggests that the locus in which the alcohols dissolve is also different, and thus that the relations exhibited in the solubilization of the alcohols should be different from those of the hydrocarbons.

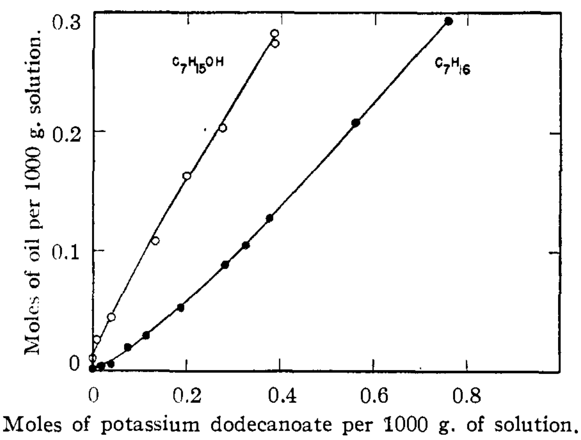

Fig. 1a.—Solubility of normal primary heptyl alcohol and of normal heptane in solutions of potassium dodecanoate.

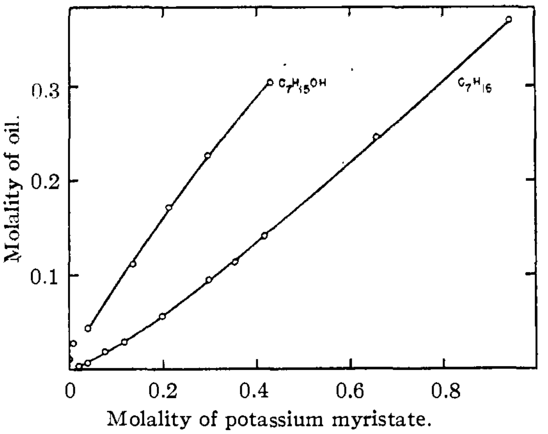

Fig. 1b.—Solubility of normal primary heptyl alcohol and of normal heptane in solutions of potassium tetradecanoate.

In Fig. 1a it is shown that the solubility in aqueous solutions of heptanol in aqueous solutions of potassium dodecanoate is twice as great as that of heptane at the higher soap concentrations. At low concentrations the ratio is much larger. In this figure the concentrations are given in moles per 1000 g. of the solution, but since the density of the soap solutions is, at all concentrations, very close to unity, these are very close to the molar concentrations. In Fig. 1b the concentrations are expressed in terms of molality, but the general relations remain as before.

The curve which represents the *non-polar* solubilization is, in both figures, convex toward the concentration axis. This is the usual relationship: the rate of increase of the non-polar solubilization with soap concentration, increases with soap concentration.

That which represents heptanol is concave toward the axis. Both curves are most highly curved just above the critical micelle concentration.

These curves indicate that, according to expectation, these two types of compounds exhibit two types of solubilization. These are considered further in a later section.

II. Experimental Methods

The solubility of the mercaptans was determined by an amperometric method, according to Kolthoff.[3]

That of the amines, alcohols and acids was found by use of a turbidimetric method, in which a photometer was used to determine the turbidity. It was assumed as a criterion of solubility that as the saturation point is exceeded, the excess oil is emulsified and the solutions therefore become increasingly turbid.

To determine the solubility of an alcohol in a soap solution at one given concentration the following procedure was adopted. The soap solution was weighed into a glass ampule, a weighed amount of oil was added, and the ampule was sealed. At a constant soap concentration a series of ampules was prepared, each successive ampule

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[1a] This investigation was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Rubber Reserve, in connection with the Government's synthetic rubber program.

[1b] M. L. Corrin and W. D. Harkins, *J. Chem. Phys.*, **14**, 640 (1946).

[2] W. D. Harkins, R. W. Mattoon and R. Mittelmann, *ibid.*, **14**, 763 (1947).

[3] I. M. Kolthoff and V. A. Stanger, "Volumetric Analysis," Interscience Pub., New York, N. Y., 1942, p. 264.