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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.<sup>-1</sup> mole<sup>-1</sup>, 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<sup>-1</sup> at 112.5°K. and 1371 cal. mole<sup>-1</sup> at the triple point, 142.64°K., respectively). Results obtained for the heat capacity in the liquid state [ $C_{\text{satd}}$ ], vapor pressure [ $p$ ], heat of vaporization [ $\Delta H_v$ ], heat capacity in the ideal gaseous state [ $C_p^\circ$ ], and second virial coefficient [ $B = (PV - RT)/P$ ] are represented by the following empirical equations: (1)  $C_{\text{satd}}(\text{liq.}) = 37.14 - 4.956 \times 10^{-2}T + 1.481 \times 10^{-4}T^2 - 238.3/T$ , cal. deg.<sup>-1</sup> mole<sup>-1</sup> (150 to 330°K.); (2)  $\log_{10} p$  (mm.) =  $6.87734 - 1113.895/(t + 226.157)$ , (10 to 86°); (3)  $\Delta H_v = 10,066 - 7.214T - 9.864 \times 10^{-3}T^2$ , cal. mole<sup>-1</sup> (290 to 326°K.); (4)  $C_p^\circ = 3.17 + 0.07564T - 3.167 \times 10^{-5}T^2$ , cal. deg.<sup>-1</sup> mole<sup>-1</sup> (317 to 487°K.); and (5)  $B = -318 - 32.8 \exp(1000/T)$ , cc. mole<sup>-1</sup> (290 to 487°K.). The entropy in the ideal gaseous state at 298.16°K., 77.51 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, and the standard heat of formation from graphite, hydrogen and gaseous diatomic sulfur, -33.46 kcal. mole<sup>-1</sup> at 298.16°K., were computed from these data and heat of combustion data reported elsewhere. Values of the functions  $(F^\circ - H_0^\circ)/T$ ,  $(H^\circ - H_0^\circ)/T$ ,  $H^\circ - H_0^\circ$ ,  $S^\circ$  and  $C_p^\circ$  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,<sup>2</sup> of relatively complete tables of the chemical thermodynamic properties of the entire family of alkanethiols.<sup>3</sup> Toward this end, the properties of ethanethiol,<sup>4</sup> 1-pentanethiol<sup>5</sup> and 2-methyl-2-propanethiol<sup>6</sup> 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<sup>7</sup> and the 1951 values of the fundamental physical constants<sup>8</sup> 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  $0.011 \pm 0.003$  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.<sup>9</sup> 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

(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).

(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).

promote thermal equilibration at low temperatures. The observed heat capacities at saturation pressure,  $C_{\text{satd}}$ , of solid and liquid 2-propanethiol are recorded in Table I. The temperature increments used in the experiments were small enough that corrections for non-linear variation of  $C_{\text{satd}}$  with  $T$  were unnecessary (the increments were approximately 10% of the absolute temperature below 50°K., 5 to 6° from 50°K. to the melting point, and 10° in the liquid region). The precision of the heat capacity measurements was usually within 0.1%; above 30°K., the accuracy uncertainty of the values of  $C_{\text{satd}}$  should not exceed 0.2%. The following empirical equation represents the heat capacity data for liquid 2-propanethiol in the temperature range, 150–330°K., with an average deviation of 0.01 and a maximum deviation of 0.04 cal. deg.<sup>-1</sup> mole<sup>-1</sup>:

$$C_{\text{satd}}(\text{liq.}) = 37.14 - 4.956 \times 10^{-2}T + 1.481 \times 10^{-4}T^2 - 238.3/T, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (1)$$

TABLE I  
THE MOLAL HEAT CAPACITY OF 2-PROPANETHIOL, CAL. DEG.<sup>-1</sup>

$T, ^\circ\text{K.}^a$	$C_{\text{satd}}^b$	$T, ^\circ\text{K.}$	$C_{\text{satd}}$	$T, ^\circ\text{K.}$	$C_{\text{satd}}$
Crystals I					
		66.60	11.333	125.43	21.336
		70.10	11.740	127.67	21.869
12.89	0.986	73.07	12.104	132.09	23.138
13.07	1.034	74.38	12.266	133.15	23.434
14.25	1.309	79.74	12.942	138.40	25.777 <sup>c</sup>
14.62	1.409	79.84	12.959		
15.73	1.689	85.54	13.728		
16.26	1.834	86.54	13.860		
17.72	2.240	91.47	14.513	149.26	31.401
18.04	2.329	93.28	14.751	156.82	31.476
20.11	2.929	96.71	15.222	165.17	31.554
20.31	2.986	100.07	15.709	173.39	31.635
22.50	3.618	100.90	15.831	177.26	31.672
22.92	3.742	104.95	16.471	181.57	31.725
25.03	4.338	108.14	16.994	187.03	31.790
25.50	4.469	108.54	17.083	197.13	31.924
27.83	5.097	108.83	17.138	207.43	32.076
28.23	5.191	110.27	17.539	217.51	32.263
31.06	5.902	110.74	17.618	227.51	32.461
34.14	6.589			237.43	32.705
37.57	7.263	Crystals II		247.75	32.986
41.23	7.916			248.98	33.014
45.37	8.560	114.06	19.196	257.97	33.282
50.07	9.237	115.85	19.497	258.45	33.293
54.65	9.841	116.79	19.656	268.79	33.634
55.31	9.931	118.47	19.933	279.95	34.052
55.48	9.946	118.69	19.965	290.98	34.469
60.44	10.571	119.26	20.027	301.86	34.895
61.23	10.678	122.19	20.631	312.27	35.333
66.20	11.292	125.26	21.293	321.63	35.764

<sup>a</sup>  $T$  is the mean temperature of each heat capacity measurement. <sup>b</sup>  $C_{\text{satd}}$  is the heat capacity of the condensed phase under its own vapor pressure. <sup>c</sup> The heat capacity data immediately below the melting point have not been corrected for the effects of hetero-phase premelting.

**The Isothermal Transition.**—An isothermal transition involving an extremely small absorption of energy was observed to occur in crystalline 2-propanethiol at about 112.5°K. Two measurements were made of the enthalpy change over a finite temperature interval that included the transition temperature. The heat of transition was determined from these results by subtraction of the energy absorbed non-isothermally, as computed from the heat capacity data. The mean of the two values obtained for the heat of transition was 12.63 ± 0.03 cal. mole<sup>-1</sup>; the precision uncertainty given denotes the deviation of the experimental results from the mean.

**The Triple Point and Sample Purity.**—The triple point and sample purity were determined in a calorimetric study

of the equilibrium melting temperature as a function of the fraction of sample melted.<sup>10</sup> The results of this study are presented in Table II. The equilibrium melting temperatures,  $T_{\text{obsd}}$ , were plotted against the reciprocal of the fraction melted,  $1/F$ . The triple point temperature,  $T_{\text{T.P.}}$ , was determined by linear extrapolation of these data to  $1/F = 0$ . The mole fraction of total impurity in the sample,  $N_2^*$ , was calculated by the relationship  $N_2^*/F = A(T_{\text{T.P.}} - T_{\text{obsd}})$ , where  $A$  is the cryoscopic constant,  $\Delta H_{\text{fusion}}/RT_{\text{T.P.}}$ . This procedure is based on the assumptions that ideal solutions are formed in the liquid phase and that the impurity is insoluble in the solid phase.

TABLE II

## 2-PROPANETHIOL MELTING POINT SUMMARY

Heat of fusion,  $\Delta H_{\text{fusion}} = 1371$  cal. mole<sup>-1</sup>; triple point,  $T_{\text{T.P.}} = 142.64 \pm 0.05^\circ\text{K.}$ ; cryoscopic constant,  $A = (0.0339)$  deg.<sup>-1</sup>; impurity =  $0.011 \pm 0.003$  mole %

Melted, %	$1/F$	Obsd. $T, ^\circ\text{K.}$	Graph. <sup>b</sup>
13.09	7.64	142.6226	142.6177
25.17	3.97	142.6319	142.6299
49.35	2.03 <sup>a</sup>	142.6364 <sup>a</sup>	142.6364
70.48	1.42 <sup>a</sup>	142.6384 <sup>a</sup>	142.6384
91.63	1.09 <sup>a</sup>	142.6395 <sup>a</sup>	142.6395
100.00	1.00		142.6398
Pure	0.00		142.6431 <sup>c</sup>

<sup>a</sup> A straight line through these points was extrapolated to  $1/F = 0$  to obtain the triple point temperature,  $T_{\text{T.P.}}$ .

<sup>b</sup> Temperatures read from the straight line of footnote <sup>a</sup>; deviations from  $T_{\text{obsd}}$  indicate departure from assumed conditions. <sup>c</sup> Triple point temperature.

**The Heat of Fusion.**—The heat of fusion of 2-propanethiol was measured in the manner described for the heat of transition. For use in computation of the energy absorbed non-isothermally, the heat capacity data just below the melting point were corrected for the effect of hetero-phase premelting. The result of each of two direct measurements was 1371 cal. mole<sup>-1</sup>, and the same value was computed from data obtained in the melting point study. The spread of the 3 values was 0.4 cal. mole<sup>-1</sup>.

**The Thermodynamic Properties of 2-Propanethiol in the Solid and Liquid States.**—Values of the entropy, heat content and free energy function of 2-propanethiol in the solid and liquid states at saturation pressure were computed from the thermal data presented in the foregoing sections. The results at selected temperatures from 10 to 330°K. are presented in Table III. These values were calculated by appropriate numerical integration of values of  $C_{\text{satd}}$  read at integral temperatures from a large scale plot of the data of Table I. Corrections for the effects of hetero-phase premelting have been applied to the data in Table III.

**The Vapor Pressure.**—The vapor pressure of 2-propanethiol from 11 to 86° was measured with the twine bulliometer system described in an earlier publication from this Laboratory.<sup>11</sup> The ebulliometer described in ref. 11 has been modified by enclosing the heating element in a glass re-entrant well so that samples of corrosive compounds come into contact with glass only. The boiling and condensation temperatures of water and 2-propanethiol were measured as both compounds boiled simultaneously at the same pressure. The "observed" vapor pressures, presented in Table IV, were obtained from the vapor pressure data for water given by Osborne, Stimson and Ginnings.<sup>12</sup> At both the beginning and end of the measurements, the difference in the boiling and condensation temperatures of 2-propanethiol was only 0.003° at 760 mm. pressure. This small, constant difference is evidence that the sample was essentially free of impurity of different volatility and that no change in purity occurred during the experiments. An

(10) S. S. Todd, G. D. Oliver and H. M. Huffman, *THIS JOURNAL*, **69**, 1519 (1947).

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

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

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-PROPANE-THIOL IN THE SOLID AND LIQUID STATES<sup>a</sup>

<i>T</i> , °K.	$-(F_{\text{satd}} - H_0^{\circ})/T$ , cal. deg. <sup>-1</sup>	$(H_{\text{satd}} - H_0^{\circ})/T$ , cal. deg. <sup>-1</sup>	$H_{\text{satd}} - H_0^{\circ}$ , cal.	$S_{\text{satd}}$ , cal. deg. <sup>-1</sup>	$C_{\text{satd}}$ , cal. deg. <sup>-1</sup>
Crystals I					
10	0.04	0.12	1.22	0.16	0.48
15	.14	.40	5.92	.53	1.50
20	.31	.84	16.88	1.15	2.90
25	.55	1.40	35.0	1.95	4.33
30	.86	2.00	60.0	2.86	5.65
35	1.22	2.60	91.1	3.82	6.76
40	1.60	3.18	127.4	4.78	7.71
45	2.01	3.73	168.0	5.74	8.51
50	2.42	4.25	212.3	6.67	9.23
60	3.28	5.19	311.2	8.47	10.52
70	4.14	6.04	422.5	10.18	11.73
80	5.01	6.82	545.9	11.83	12.98
90	5.85	7.58	682.3	13.43	14.32
100	6.70	8.32	832.4	15.02	15.70
110	7.52	9.07	997.4	16.59	17.41
112.5	7.73	9.26	1042.0	16.99	18.25
Crystals II					
112.5	7.73	9.37	1054	17.10	18.93
120	8.35	10.01	1201	18.36	20.21
130	9.18	10.88	1414	20.06	22.45
140	10.03	11.81	1654	21.84	25.86
142.64	10.24	12.09	1724	22.33	26.87
Liquid					
142.64	10.24	21.70	3095	31.94	31.34
150	11.35	22.17	3326	33.52	31.42
160	12.80	22.75	3640	35.55	31.51
170	14.19	23.27	3956	37.46	31.60
180	15.53	23.74	4273	39.27	31.71
190	16.83	24.16	4590	40.99	31.83
200	18.08	24.54	4909	42.62	31.96
210	19.29	24.90	5230	44.19	32.12
220	20.45	25.24	5552	45.69	32.31
230	21.58	25.55	5876	47.13	32.52
240	22.68	25.84	6202	48.52	32.77
250	23.73	26.13	6532	49.86	33.04
260	24.76	26.40	6863	51.16	33.34
270	25.77	26.66	7198	52.43	33.68
273.16	26.08	26.74	7305	52.82	33.79
280	26.74	26.92	7537	53.66	34.05
290	27.69	27.17	7880	54.86	34.43
298.16	28.45	27.37	8162	55.82	34.74
300	28.61	27.42	8226	56.03	34.82
310	29.52	27.66	8576	57.18	35.23
320	30.40	27.91	8931	58.31	35.69
325.72 <sup>b</sup>	30.89	28.05	9135	58.94	35.96
330	31.26	28.15	9290	59.41	36.15

<sup>a</sup> The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure. <sup>b</sup> The normal boiling point.

Antoine equation, eq. 2, was obtained from the data of Table IV by a least squares adjustment.<sup>13</sup>

$$\log_{10} p(\text{mm.}) = 6.87734 - 1113.859/(t + 226.157) \quad (2)$$

where  $t$  is in °C. Values of the vapor pressure computed from eq. 2 are given in the last column of Table III. The normal boiling point from eq. 2 is 52.56°.

(13) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **55**, 219 (1945).

TABLE IV

THE VAPOR PRESSURE OF 2-PROPANE-THIOL

Boiling point, °C.	Pressures, mm.	
	Water	2-Propanethiol
60.000	10.697	149.41
65	15.770	187.57
70	20.899	233.72
75	26.071	289.13
80	31.282	355.22
85	36.536	433.56
90	41.833	525.86
95	47.175	633.99
100	52.558	760.00
105	57.985	906.06
110	63.461	1074.6
115	68.979	1268.0
120	74.540	1489.1
125	80.143	1740.8
130	85.795	2026.0

<sup>a</sup> Calculated from eq. 2.

**The Heat of Vaporization.**—The heat of vaporization and vapor heat capacity of 2-propanethiol were determined in the flow calorimeter system previously described.<sup>14</sup> The glass vaporizer used differed from that described in ref. 14 in that the heating element and leads were enclosed in glass to prevent contact with the corrosive thiol. The tube shielding the heating element was wrapped with glass thread to promote steady ebullition.

The results of triplicate determinations of the heat of vaporization at each of three temperatures from 290 to 326°K. are recorded in Table V. The accuracy uncertainty of these data should not exceed 0.1%. The following empirical equation may be used for interpolation in the temperature range of the measurements

$$\Delta H_v = 10,066 - 7.214T - 9.864 \times 10^{-3}T^2, \text{ cal. mole}^{-1} \quad (290-326^\circ\text{K.}) \quad (3)$$

TABLE V

THE MOLAL HEAT OF VAPORIZATION AND GAS IMPERFECTION OF 2-PROPANE-THIOL

<i>T</i> , °K.	$p$ , <sup>a</sup> mm.	$\Delta H_v$ , cal.	$B_{\text{obsd.}}$ , cc.	$B_{\text{calcd.}}$ , <sup>b</sup> cc.
290.41	200.0	7139 ± 3 <sup>c</sup>	-1356	-1343
306.20	380.0	6932 ± 3	-1180	-1176
325.72	760.0	6670 ± 3	-1016	-1024

<sup>a</sup> Calculated from eq. 2. <sup>b</sup> Calculated from eq. 5. <sup>c</sup> Maximum deviation of the experimental results from the mean.

**The Vapor Heat Capacity.**—Measurements of the vapor heat capacity were made at 2 or more pressures at each of 5 temperatures between 317 and 449°K. and at one pressure at 487°K. The results are listed in Table VI. From 317 to 449°K. values of the heat capacity in the ideal gaseous state,  $C_p^\circ$ , were determined from the data at finite pressures by linear extrapolations to zero pressure.<sup>14</sup> To determine  $C_p^\circ$  at 487°K., the variation of  $C_p$  with  $P$  was estimated from the data at lower temperatures. It is believed that the accuracy uncertainty of the tabulated values of  $C_p^\circ$  (obsd.) is less than 0.2%. The following empirical equation represents the experimental values of  $C_p^\circ$  within 0.02 cal. deg.<sup>-1</sup> mole<sup>-1</sup>

$$C_p^\circ = 3.17 + 0.07564T - 3.167T^2, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (317-487^\circ\text{K.}) \quad (4)$$

At 449 and 487°K., tests for thermal decomposition of the sample were made as described in an earlier paper.<sup>15</sup> No effect of decomposition was detected.

**Gas Imperfection and the Second Virial Coefficient.**—The second virial coefficient  $B$ , in the equation of state  $PV = RT + BP$ , was evaluated at 3 temperatures from the experi-

(14) G. Waddington, S. S. Todd and H. M. Huffman, *THIS JOURNAL*, **69**, 2275 (1947).

(15) D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, R. E. Pennington and Guy Waddington, *ibid.*, **74**, 2478 (1952).

TABLE VI  
 THE MOLAL VAPOR HEAT CAPACITY OF 2-PROPANETHIOL IN CAL. DEG.<sup>-1</sup>

$T$ , °K.	317.20	333.20	358.20	402.20	449.20	487.20
$C_p$ (760.0 mm.)		25.583	26.694	28.757	30.853	
$C_p$ (380.0 mm.)	24.441	25.204				
$C_p$ (200.0 mm.)	24.229	25.040	26.322	28.552	30.786	32.527
$C_p^o$ (obsd.)	23.99	24.84	26.19	28.48	30.76	32.50
$C_p^o$ (calcd.) <sup>a</sup>	23.98	24.85	26.18	28.46	30.76	32.50
$(\partial C_p/\partial P)_T$ (obsd.)	0.90	0.74	0.50	0.28	0.09	
$(\partial C_p/\partial P)_T$ (calcd.) <sup>b</sup>	0.95	0.72	0.48	0.26	0.15	0.10

<sup>a</sup> Calculated from spectroscopic and molecular structure data. <sup>b</sup> Calculated by use of eq. 5; units of  $(\partial C_p/\partial P)_T$  are cal. deg.<sup>-1</sup> mole<sup>-1</sup> atm.<sup>-1</sup>.

mental heat of vaporization and vapor pressure data by use of the Clapeyron equation in the form  $B = [\Delta H_v/T(dP/dT)] - RT/P + V_L$ , where  $V_L$  is the molal volume of the liquid. The relationship  $(\partial C_p/\partial P)_T = -T(d^2B/dT^2)$  and the observed variation of  $C_p$  with  $P$  were used to obtain values of  $(d^2B/dT^2)$  at 5 temperatures. These data for  $B$  and  $(d^2B/dT^2)$  were correlated by means of the empirical equation

$$B = -318 - 32.8 \exp(1000/T), \text{ cc. mole}^{-1} (290-487^\circ\text{K.}) \quad (5)$$

where  $T$  is in °K. The constants of eq. 5 were evaluated by the method outlined in a previous publication.<sup>16</sup> Values of  $B$  and  $(\partial C_p/\partial P)_T$  obtained from the experimental data and those calculated from eq. 5 are compared in Tables V and VI, respectively.

**The Entropy.**—Values of the entropy of 2-propanethiol in both the saturated liquid ( $S_{\text{satd}}$ ) and ideal gaseous states ( $S^o$ ) were computed from the data given in preceding sections. The results at selected temperatures from 290.41 to 325.72°K. are summarized in Table VII.

TABLE VII

THE MOLAL ENTROPY OF 2-PROPANETHIOL, CAL. DEG.<sup>-1</sup>

0-13°K.	Debye extrapolation <sup>a</sup>		0.353	
13-112.5°	Crystals I, graphical, $\int C_{\text{satd}} d \ln T$		16.633	
112.5°	Transition, 12.63/112.5		0.112	
112.5-142.64°	Crystals II, graphical, $\int C_{\text{satd}} d \ln T$		5.230	
142.64°	Fusion, 1371/142.64		9.612	
142.64-298.16°	Liquid, graphical, $\int C_{\text{satd}} d \ln T$		23.878	
$S_{\text{satd}}$ , liq., 298.16°K. ( $\pm 0.10$ ) <sup>b</sup>			55.82	
$T$ , °K.		290.41	306.20	325.72
$S_{\text{satd}}$ , liq. <sup>c</sup>		54.91	56.75	58.94
$\Delta H_v/T^d$		24.58	22.64	20.48
$P(dB/dT)^e$		0.08	0.11	0.16
$R \ln (p/760)^f$		-2.65	-1.38	0.00
$S^o$ , gas(obsd.) ( $\pm 0.15$ ) <sup>b</sup>		76.92	78.12	79.58
$S^o$ , gas(calcd.) <sup>g</sup>		76.92	78.13	79.60

<sup>a</sup> A Debye function for 5.5 degrees of freedom with  $\theta = 120.4^\circ$  was used for this extrapolation. <sup>b</sup> Estimated accuracy uncertainty. <sup>c</sup> Interpolated from Table III. <sup>d</sup> Entropy of vaporization; from Table V. <sup>e</sup> Entropy of gas imperfection; from eq. 5. <sup>f</sup> Entropy of compression; calculated from eq. 2. <sup>g</sup> Calculated from spectroscopic and molecular structure data.

**The Heat of Formation.**—The heat of combustion of 2-propanethiol was determined in the rotating-bomb combustion calorimeter previously described.<sup>17</sup> Complete experimental details of the measurements will be published in a subsequent paper on bomb-calorimetric studies of the three

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

(17) (a) W. N. Hubbard, C. Katz and Guy Waddington, *J. Phys. Chem.*, **58**, 142 (1954); (b) W. N. Hubbard, D. W. Scott, and Guy Waddington, *ibid.*, **58**, 152 (1954).

$C_3H_6S$  isomers. It was found that the standard heat of formation,  $\Delta H_f^o(\text{liq.})$ , of liquid 2-propanethiol from C(graphite),  $H_2(\text{gas})$  and S(rhombic) is  $-25.12 \pm 0.15$  kcal. mole<sup>-1</sup> at 298.16°K. The standard heat of formation in the ideal gaseous state,  $\Delta H_f^o(\text{gas})$ , was computed from  $\Delta H_f^o(\text{liq.})$  by addition of the heat of vaporization, 7.038 kcal. mole<sup>-1</sup>, and correction for gas imperfection, 0.039 kcal. mole<sup>-1</sup>, as computed from eq. 3 and 5, respectively.

Values of the standard free energy,  $\Delta F_f^o$ , and logarithm of the equilibrium constant,  $\log_{10} K_f$ , for the formation of both liquid and gaseous 2-propanethiol were calculated from the values for the heat of formation and entropy (Tables VII and XI) and the thermodynamic functions for graphite,<sup>18</sup> hydrogen<sup>18</sup> and rhombic sulfur.<sup>19</sup> The heat and free energy of formation of  $S_2(\text{gas})$  from rhombic sulfur<sup>20</sup> were used in calculating  $\Delta H_f^o$ ,  $\Delta F_f^o$  and  $\log_{10} K_f$  for the formation of 2-propanethiol in the ideal gaseous state at 298.16°K. from C(graphite),  $H_2(\text{gas})$ , and  $S_2(\text{gas})$ . These data are presented in Table VIII.

TABLE VIII

THE MOLAL HEAT AND FREE ENERGY AND THE LOGARITHM OF THE EQUILIBRIUM CONSTANT FOR THE FORMATION OF 2-PROPANETHIOL AT 298.16°K.

State <sup>a</sup>	Reference state <sup>b</sup>	$\Delta H_f^o$ , kcal.	$\Delta F_f^o$ , kcal.	$\log_{10} K_f$
Liquid	S(rhombic)	$-25.12 \pm 0.15^c$	-1.05	0.77
Gas	S(rhombic)	$-18.04 \pm 0.16^c$	-0.44	0.32
	$S_2(\text{gas})$	-33.46	-10.00	7.33

<sup>a</sup> Standard state of 2-propanethiol. <sup>b</sup> Reference state of elemental sulfur in the reactions: (A)  $3C(\text{graphite}) + 4H_2(\text{gas}) + S(\text{rhombic}) \rightarrow C_3H_6S(\text{liq. or gas})$ ; (B)  $3C(\text{graphite}) + 4H_2(\text{gas}) + \frac{1}{2}S_2(\text{gas}) \rightarrow C_3H_6S(\text{gas})$ . <sup>c</sup> The uncertainty interval given is twice the "over-all" standard deviation. See F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

### Calculation of Thermodynamic Functions

To extend the experimental thermal data to higher temperatures, calculations of the thermodynamic functions of 2-propanethiol were made by the appropriate methods of statistical mechanics. For these computations it was necessary to (1) make a vibrational assignment from spectroscopic data, (2) calculate the moments and reduced moments of inertia of the molecule from molecular structure information, and (3) determine the heights of the potential barriers to internal rotation from the calorimetric entropy and heat capacity data. Details of the calculations are discussed in the following sections.

**The Vibrational Assignment.**—The vibrational assignment was based on spectroscopic data ob-

(18) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **54**, 143 (1945).

(19) "Selected Values of Chemical Thermodynamic Properties" Circular of the National Bureau of Standards, 500, Washington, D. C., 1952; Series I, Table 14-1.

(20) W. H. Evans and D. D. Wagman, *J. Research Natl. Bur. Standards*, **49**, 141 (1952).

tained by several investigators.<sup>21,22</sup> The Raman data furnished by Dr. E. J. Rosenbaum, Sun Oil Company, and the infrared data furnished by Mr. T. G. Burke, Carbide and Carbon Chemicals Company, and by the Bureau of Mines, Laramie, Wyoming, were obtained from measurements made with portions of the Standard Sample of 2-propanethiol, API-USBM serial No. 11. The spectral data are summarized in Table IX. The infrared spectra from 250 to 400  $\text{cm}^{-1}$  are shown in Fig. 1.<sup>22a</sup>

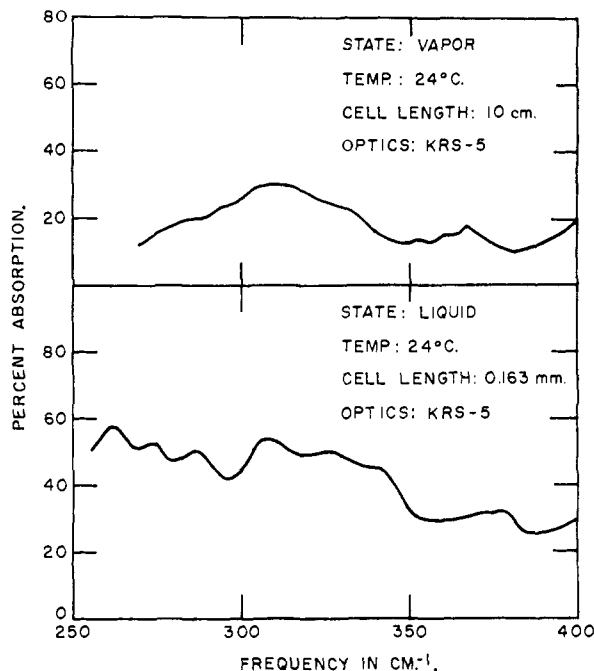


Fig. 1.—The infrared spectra of 2-propanethiol from 250 to 400  $\text{cm}^{-1}$ .

The vibrational assignment for 2-propanethiol is consistent with those for related molecules—particularly that for isobutane.<sup>2a</sup> Since 2-propanethiol belongs (effectively) to symmetry group  $C_s$ , its vibrations may be divided into two classes— $A'$ , symmetrical with respect to the plane of symmetry, and  $A''$ , unsymmetrical with respect to the plane of symmetry. The vibrational modes belonging to class  $A'$  produce polarized Raman displacements and type A or C vapor phase infrared bands<sup>23</sup>; the  $A''$  vibrations produce depolarized Raman lines and type B infrared bands. The polarization data of Radinger and Wittek<sup>21c</sup> and resolvable band contours of the vapor phase infrared spectral data of Trotter and Thompson<sup>22d</sup>

(21) Raman data: (a) E. J. Rosenbaum, Sun Oil Company, Norwood, Pa., to be published by American Petroleum Institute Research Project 44 in the Catalog of Raman Spectral Data; (b) A. Dadiou, A. Pongratz and K. W. F. Kohrausch, *Sitzber. Akad. Wiss. Wien, Math. naturw.*, **161**, 267 (1932); (c) G. Radinger and H. Wittek, *Z. physik. Chem.*, **B45**, 329 (1940).

(22) Infrared data: (a) (25–40  $\mu$ , gas and liquid) T. G. Burke, Carbide and Carbon Chemicals Co., Oak Ridge, Tenn.; (b) (14–25  $\mu$ , liquid) U. S. Bureau of Mines, Laramie, Wyoming, to be published by American Petroleum Institute Research Project 44 in the Catalog of Infrared Spectral Data; (c) (2–15  $\mu$ , liquid) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data, Serial No. 1296; (d) (2–15  $\mu$ , gas) I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 481 (1946).

(23) R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

were consistent and served as the basis for the assignment to symmetry classes given in Table IX.

TABLE IX  
THE VIBRATIONAL SPECTRA AND ASSIGNMENT FOR 2-PROPANETHIOL<sup>a</sup>

Raman, <sup>b</sup> liq. $\Delta\bar{\nu}$ , $\text{cm}^{-1}$	$\rho$	Infrared, <sup>c</sup> liq. $\bar{\nu}$ , $\text{cm}^{-1}$	Funda- mental $\bar{\nu}$ , $\text{cm}^{-1}$	Assignment Description
		262 s		
		274 w		
		287 w		
311 (5)		308 s	310	CCS bend, $A''$
		326 w		
336 (20)	p	ca. 340 sh	336	CCS bend, $A'$
		ca. 370 sh		
		378 w		
414 (10)	p		414	CCC bend, $A'$
571 (5)				893 – 310 = 583, $A''$
616 (40)				CS stretch, $A'$
632 (75)	0.17	ca. 620 sh	624	{ see text.
		628 s		{
787 (5)				1084 – 310 = 774, $A''$
804 (15)				1131 – 336 = 795, $A''$
855 (15)		861 m	858	CSH bend, $A'$
892 (20)	0.43	894 m	893	CC stretch, $A'$
		929 m	929	$\text{CH}_3$ rock, $A''$
		ca. 955 sh		336 + 624 = 960, $A'$
955 (5)				1334 – 336 = 998, $A''$
994 (5)				
1062 (10)	0.4	1063 s	1063	$\text{CH}_3$ rock, $A'$
1082 (10)		1085 s	1084	CC stretch, $A''$
1098 (10)				1450 – 336 = 1114, $A''$
1131 (10)			1131	$\text{CH}_3$ rock, $A''$
1142 (10)				1450 – 310 = 1140, $A'$
1160 (15)	p	1161 s	1161	$\text{CH}_3$ rock, $A'$
1202 (10)				310 + 893 = 1203, $A''$
1243 (10)	p	1250 s	1257	{ CH wag, $A'$
1265 (10)	p	ca. 1267 sh		{ see text
1286 (0)				414 + 858 = 1272, $A'$
1314 (10)		ca. 1307 sh		414 + 893 = 1307, $A'$
1334 (0)			1334	CH wag, $A''$
		1368 s	1368	$\text{CH}_3$ bend, $A''$
		1385 s	1386	$\text{CH}_3$ bend, $A'$
1387 (5)		1451 s	1450 [4]	$\text{CH}_3$ bend, $A'$ and $A''$
1449 (35)	0.80	ca. 1464 sh		336 + 1131 = 1467, $A''$
		2564 s	2568	SH stretch, $A'$
2572 (90)	p		2950 [7]	CH stretch, $A'$ and $A''$

<sup>a</sup> Above 1500  $\text{cm}^{-1}$ , only those frequencies assigned as fundamentals are tabulated. <sup>b</sup> Ref. 21. <sup>c</sup> Ref. 22.

Since the infrared spectrum from 250 to 400  $\text{cm}^{-1}$  is very complex, the assignment of the skeletal bending modes was made principally on the basis of the Raman data. It is probable that the infrared spectrum in this region is complicated by bands due to the torsional modes of the thiol and methyl groups. From the potential barriers to internal rotation described in a later section, it was found that the methyl torsional frequency should appear near 250  $\text{cm}^{-1}$  and that the first harmonic of the thiol torsion should appear near 350  $\text{cm}^{-1}$ .<sup>24</sup> Because of the poor resolution of the vapor phase infrared data (a result of the low vapor pressure of 2-propanethiol at room temperature) and because of the strong interaction effects on the spectrum of the liquid, a more detailed analysis was not attempted.

Two doublets in the spectra were interpreted as the results of Fermi resonance. The assumption of resonance between a fundamental near 624  $\text{cm}^{-1}$  and the overtone,  $2 \times 310 = 620$ , and between a fundamental near 1250  $\text{cm}^{-1}$  and the overtone,  $2 \times 624 = 1248 \text{ cm}^{-1}$ , accounts for the

(24) E. B. Wilson, Jr., *Chem. Revs.*, **27**, 17 (1940).

observed doublets. Most of the frequencies not assigned as fundamental vibrations appeared only as weak Raman displacements in the careful investigation by Rosenbaum.<sup>22a</sup> Since the CH<sub>3</sub> bending and CH stretching frequencies were not all resolved, average values were used for these thermodynamically unimportant modes.

The assignment of frequencies to particular vibrational modes involves some uncertainties, but the set of fundamentals chosen is believed to be adequate for use in calculating thermodynamic functions.

TABLE X

POTENTIAL BARRIERS TO INTERNAL ROTATION IN SOME THIOL COMPOUNDS

Compound	Potential barrier, <sup>a</sup> cal. mole <sup>-1</sup> CH <sub>3</sub> -C	SH-C
Methanethiol	..	1460 <sup>b</sup>
Ethanethiol	3310	1640
2-Propanethiol	3950	1390
2-Methyl-2-propanethiol	5100	1360

<sup>a</sup> Potential barrier is  $V_0$  of the equation  $V(\phi) = \frac{1}{2}V_0(1 + \cos 3\phi)$ . <sup>b</sup> Reported by H. Russell, D. W. Osborne and D. M. Yost, THIS JOURNAL, **64**, 165 (1942).

describe the restricted internal rotations of 2-propanethiol. The heights of the CH<sub>3</sub> and SH barriers required to fit the calorimetric data are 3950 and 1390 cal. mole<sup>-1</sup>, respectively. A comparison of these barrier heights with those found in previous studies of thiol compounds is given in Table X. It is interesting to note that the thiol barriers of the four compounds studied to date are the same within the probable limits of error of the tabulated results. Thus, an average value for the thiol barrier,  $1500 \pm 150$  cal. mole<sup>-1</sup>, may be used with some confidence in future studies of higher aliphatic thiols.

**The Effect of Anharmonicity and Comparison with Experimental Data.**—The effect of anharmonicity of normal molecular vibrations was determined from the vapor heat capacity data by the method described in an earlier paper.<sup>27</sup> Best agreement with the experimental data was obtained with  $\nu = 600$  cm.<sup>-1</sup> and  $Z = 0.124$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>. The parameters  $\nu$  and  $Z$ , defined in ref. 27, were evaluated simultaneously with the determination of the heights of the potential barriers to internal rotation.

TABLE XI

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-PROPANETHIOL<sup>a</sup>

T, °K.	$(F^\circ - H_0^\circ)/T$ , cal. deg. <sup>-1</sup>	$(H^\circ - H_0^\circ)/T$ , cal. deg. <sup>-1</sup>	$H^\circ - H_0^\circ$ , kcal.	$S^\circ$ , cal. deg. <sup>-1</sup>	$C_p^\circ$ , cal. deg. <sup>-1</sup>	$\Delta H_f^\circ$ , <sup>b</sup> kcal.	$\Delta F_f^\circ$ , <sup>b</sup> kcal.	log <sub>10</sub> K <sub>f</sub> <sup>b</sup>
0	0	0	0	0	0	-27.95	-27.95	Infinite
273.16	-61.45	14.11	3.854	75.56	21.61	-33.09	-11.95	9.56
298.16	-62.72	14.79	4.410	77.51	22.94	-33.46	-10.00	7.33
300.00	-62.82	14.84	4.452	77.66	23.04	-33.49	-9.86	7.18
400	-67.45	17.56	7.024	85.01	28.35	-34.83	-1.77	0.97
500	-71.65	20.20	10.10	91.85	33.06	-35.92	+6.63	-2.90
600	-75.56	22.68	13.61	98.24	37.02	-36.77	15.21	-5.54
700	-79.22	24.99	17.49	104.21	40.38	-37.40	23.93	-7.47
800	-82.71	27.09	21.67	109.80	43.26	-37.85	32.73	-8.94
900	-86.03	29.02	26.12	115.05	45.74	-38.15	41.55	-10.09
1000	-89.16	30.81	30.81	119.97	47.92	-38.28	50.44	-11.02

<sup>a</sup> 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. <sup>b</sup> The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of 2-propanethiol by the reaction:  $3C(\text{graphite}) + 4H_2(\text{gas}) + \frac{1}{2}S_2(\text{gas}) \rightarrow C_3H_7S(\text{gas})$ .

**The Moments and Reduced Moments of Inertia.**—Since the molecular structure of 2-propanethiol has not been determined experimentally, it was necessary to use the molecular dimensions of closely related compounds for computing the moments of inertia. The following bond distances and bond angles were assumed: C-C bond distance, 1.54 Å.; C-S bond distance, 1.815 Å.<sup>25</sup>; C-H bond distance, 1.09 Å.; S-H bond distance, 1.34 Å.<sup>25</sup>; C-S-H bond angle 100°<sup>25</sup>; and all other bond angles, 109° 28'. On the basis of this assumed molecular structure, the product of the three principal moments of inertia was calculated to be  $5.107 \times 10^{-114}$  g.<sup>3</sup> cm.<sup>6</sup>. The reduced moments of inertia of the methyl and thiol groups were computed by the general method of Kilpatrick and Pitzer.<sup>26</sup> The values obtained were  $5.135 \times 10^{-40}$  and  $2.764 \times 10^{-40}$  g. cm.<sup>2</sup> for the two equivalent methyl groups and the thiol group, respectively.

**The Potential Barriers to Internal Rotations.**—Simple cosine-type potential barriers were used to

(25) T. M. Shaw and J. J. Windle, *J. Chem. Phys.*, **19**, 1063 (1951).

(26) J. E. Kilpatrick and K. S. Pitzer, *ibid.*, **17**, 1064 (1949).

Calculated values of  $C_p^\circ$  and  $S^\circ$  are compared with the experimental data in Tables VI and VII, respectively. It may be seen that the values of  $C_p^\circ$  agree within 0.1% over a 170° temperature range; and the values of  $S^\circ$  agree within 0.02 cal. deg.<sup>-1</sup> mole<sup>-1</sup> over a 35° temperature range.

**The Chemical Thermodynamic Properties.**—The vibrational assignment, moments of inertia, barrier heights and anharmonicity corrections described in the preceding paragraphs were used to compute values of the following thermodynamic functions at selected temperatures from 0 to 1000°K.:  $(F^\circ - H_0^\circ)/T$ ,  $(H^\circ - H_0^\circ)/T$ ,  $H^\circ - H_0^\circ$ ,  $S^\circ$  and  $C_p^\circ$ .<sup>28</sup> The calculated thermodynamic functions, the

(27) 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).

(28) (a) 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., July, 1949; (b) restricted internal rotation contributions were computed from the tables published by K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

value of  $\Delta H_f^\circ$  at 298.16°K. (Table VIII) and the thermodynamic functions of C(graphite),<sup>18</sup> H<sub>2</sub>(gas)<sup>18</sup> and S<sub>2</sub>(gas)<sup>20</sup> were used in computing values of  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$  and  $\log_{10} K_f$  at selected temperatures from 0 to 1000°K. The calculated values of these eight thermodynamic properties are recorded in Table XI.

**Acknowledgments.**—The authors wish to thank

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BARTLESVILLE, OKLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

## The Electronic Structure of Conjugated Sulfur Compounds. I. Thiophene and Isothianaphthene

BY JOSEPH DE HEER

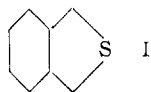
RECEIVED MARCH 11, 1954

The electronic structure of thiophene and isothianaphthene has been calculated by means of a molecular orbital scheme as developed by Longuet-Higgins. Our results suggest a marked difference in homolytic and heterolytic reactivity of certain centers in these molecules. This is in general accordance with experiment. Some experimental data, which only recently have become available, are briefly reviewed. The popular attempts to relate all properties of conjugated sulfur compounds to isosteric polyenes are criticized.

### 1. General Introduction

It has been emphasized for quite some time that there is often a close similarity in physical and chemical properties between aromatic hydrocarbons and the corresponding compounds in which a —CH=CH— group is replaced by a sulfur atom. Thus, following Victor Meyer who pioneered in this field, many investigators have mentioned such similarities between benzene and thiophene.<sup>1</sup>

Recently, Dann, *et al.*,<sup>2,3</sup> have reported an investigation of the isothianaphthene (benzo[c]-thiophene) ring system (I).



In particular they investigated the diene additions of certain compounds containing this ring system. The results suggest not only a detailed discussion of the reactivity of this molecule, but also a reconsideration of the properties of thiophene itself. It becomes obvious that similarities between benzene and thiophene are largely confined to those properties relating to size, shape, molecular weight, etc. The experimental evidence, which will be reviewed in section 6 of this paper, suggests strongly that heterolytic reactivity (relating to nitration, sulfonation, etc.) and homolytic reactivity (*e.g.*, diene additions<sup>4</sup>) should be clearly distinguished.

In this paper we present a theoretical discussion of these reactivities as related to the electronic structure of thiophene and isothianaphthene, on the basis of a molecular orbital theory developed by Longuet-Higgins.<sup>5</sup> A few brief, semi-quantitative,

remarks about the ultraviolet spectra of these compounds will be included.

**2. Free Valencies, Charge Densities and Self-polarizabilities, as a Measure for the Homolytic and Heterolytic Reactivity in Aromatic Hydrocarbons.**—Strictly speaking the reactivity of aromatic hydrocarbons (as of all molecules) should be discussed in terms of their *dynamic* behavior in going into a transition state with a specific reagent. Where such a procedure is too involved, useful indications may be obtained by considering certain *static* properties of these molecules, in particular with reference to their  $\pi$  electron system.

(a) **Free Valencies.**—In this paper free valencies are obtained on the basis of the molecular orbital method, following a procedure originally outlined by Coulson.<sup>6,7</sup> As is well known, these quantities, which indicate the "availability" of electrons at the various positions in a hydrocarbon, are a measure for the homolytic reactivity of these centers.

(b) **Charge Densities and Self-polarizabilities.**—To a first approximation the  $\pi$  electron charge densities at all centers in aromatic and olefinic hydrocarbons are equal to 1. This is equally true for the carbon centers in thiophene, when its electronic structure is described by the Longuet-Higgins theory<sup>5</sup> (see section 3 below). Therefore, in all these molecules, charge densities cannot determine the difference in heterolytic reactivity of the various positions. Here the important quantities are the "self-polarizabilities"<sup>8,9</sup> of the centers concerned. In fact, these polarizabilities determine quantitatively the susceptibility to what most physical organic chemists call, following Ingold, an "electromeric effect."

**3. Electronic Structure of Thiophene.**—Up till 1939, it was generally assumed that in thiophene

(1) For a survey, see H. D. Hartough, "Thiophene and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952.

(2) O. Dann, M. Kokorudz and R. Gropper, *Chem. Ber.*, **86**, 1449 (1953); **87**, 140 (1954).

(3) O. Dann and H. Distler, *ibid.*, **87**, 365 (1954).

(4) According to C. K. Ingold ("Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953), diene additions are largely, but not wholly, homolytic.

(5) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

(6) See, *e.g.*, *Faraday Soc. Discs.*, **2**, 9 (1947).

(7) See appendix I for a brief discussion of this procedure and suggested alternatives.

(8) C. A. Coulson and H. C. Longuet-Higgins, *La Revue Sci.*, **85**, 929 (1947).

(9) See appendix II for an explicit definition of self-polarizabilities and a brief summary of the relevant arguments of reference 8.