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ENTHALPY MEASUREMENT OF COAL-DERIVED LIQUIDS

Quarterly Technical Progress Report for July—September 1980

By
A. J. Kidnay
V. F. Yesavage

September 15, 1980
Date Submitted

Work Performed Under Contract No. AC22-79ET13395

Colorado School of Mines
Golden, Colorado

U. S. DEPARTMENT OF ENERGY

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Enthalpy Measurement of Coal-Derived Liquids
Quarterly Technical Progress Report
for the Period July - September 1980

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Prepared for
U. S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236

Under Contract DE-AC22-79ET 13395

Abstract

Equipment modifications to a Freon 11 boil-off type calorimeter are described, and using the calorimetric system the enthalpies of thiophene were measured experimentally. Data were taken over a temperature range of 100°F to 750°F at pressures of 50, 100, 200, 400, 600, 825.9 (the critical), 1000, and 1500 psia. Thermodynamic properties derived from the data are compared to values in the literature, and the agreement is exceptionally good. The data are then compared directly to results calculated by means of two correlations: a modification of the BWR equation of state by Kesler and Lee, and a modified SRK equation of state method. Both correlations are found to work well in predicting the enthalpy of thiophene.

Objective and Scope of Work

Thermodynamic property research is justly recognized as invaluable by process and design engineers in the petroleum, chemical, and allied industries. Calorimetric measurements of specific heats or enthalpies, pressure-density-temperature measurements, and phase equilibrium determination, for pure fluids or complex mixtures, are all essential in the optimum design of both physical and chemical processing units.

Coal-derived liquids are a new and vital class of industrial compounds, but have thermodynamic properties that are largely unknown and, presently, unpredictable. The objective of this research is to measure one of the most important thermodynamic properties, the enthalpy, for representative coal-derived liquids over the pressure and temperature regions most likely to be encountered in both liquefaction and processing systems.

The research is divided into three major program areas.

I) Design, construction, and evaluation of a freon boil off calorimeter for temperatures of 70 to 700°F and pressures to 2000 psig.

II) Enthalpy measurements on approximately 10 samples of coal-derived liquids. The samples for measurement will be selected after consultation with the ERDA Bartlesville Energy Research Center.

III) Preparation of engineering correlations for the measured enthalpy data, and comparison with representative data for petroleum and petroleum fractions.

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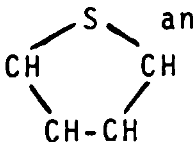
INTRODUCTION

As the United States and the world at large become increasingly aware of our dwindling petroleum resources, it becomes ever more obvious and imperative for alternative sources of energy to be discovered and utilized. At this point in time, one of the best prospects is coal. However, coal in solid form cannot be used in certain applications; several processes have therefore been devised to either gasify or liquefy coal.

This present project, initiated by Dr. Arthur J. Kidnay and Dr. Victor F. Yesavage at the Colorado School of Mines and funded by the United States Department of Energy, is concerned specifically with coal liquids; measuring correlating, and attempting to predict the enthalpies of coal-derived liquids. In the years which have passed since this project was begun, several coal-derived liquids have been run through a flow calorimeter system in order to determine their enthalpy as a function of temperature and pressure, and subsequently the prevalent correlations for predicting petroleum enthalpies were tested for applicability. It was found that these correlations did not predict enthalpies of coal liquids well, and the cause was suspected to be the unusually high proportion of aromatic and associating compounds in coal-derived liquids as compared to petroleum crudes. Thus, an alternative method for correlating and predicting enthalpies for coal liquids has been sought. To this end, numerous pure, aromatic compounds have been measured on this apparatus: benzene, 1-methylnaphthalene, m-cresol, 2,6-lutidine, m-xylene and now thiophene. The two correlations which seem to offer the best hope of success at this time are the Kesler and Lee correlation, and the Soave-Redlich-Kwong equation of state. In this study, measurements of enthalpy for thiophene have been taken and compared to other thermodynamic data existent for the compound. Then, these two correlations are compared to the data and their applicability is evaluated.

Due to the physical limitations of the system, it was necessary to choose a compound for this study whose freezing point is well below 65°F and whose viscosity is low enough at room temperature that it can be readily pumped through the calorimeter. In addition, it was hoped to find a compound whose critical temperature was below 600°F and whose critical pressure was below 1000 psia so that a full range of liquid and vapor data could be obtained.

Thiophene was chosen because it fulfilled all of these criteria, and because it should be representative of cyclic sulfur compounds. Although thiophene itself is seldom found in coal-derived liquids, derivatives thereof are often present, and thiophene's behavior should be indicative of these derivatives. Thiophene's structure is 

and McClellan (1963) gives its dipole moment as 0.51 to 0.55. Thus one would expect it to exhibit some degree of association through dipole-dipole interaction. It was hoped that by measuring the enthalpy of thiophene and comparing the results with predicted values, some idea of the effect of this association would be gained.

THEORETICAL BACKGROUND

The system used for these measurements is built around a flow calorimeter. This particular calorimeter is a reference boil-off type utilizing Freon-11 (trichlorofluoromethane) as the reference fluid, since its boiling point is 65°F, approximately room temperature.

By applying the first law of thermodynamics (assuming steady state) to the flow calorimeter, the enthalpy change of the sample as it passes through the calorimeter may be determined. In the absence of shaft work and heat leaks and ignoring negligible changes in kinetic and potential energy, the following equation remains:

$$(H_{T,P})_{in} - (H_{T,P})_{out} = \frac{Q}{M} \qquad (1)$$

where

$(H_{T,P})_{in}$ = enthalpy of the sample per unit mass at the inlet conditions

$(H_{T,P})_{out}$ = enthalpy of the sample per unit mass at the outlet conditions

Q = heat removed from the sample

M = mass flow rate of the sample

Thus, if Q and M are measured, the difference in enthalpy between sample inlet and outlet conditions may be determined.

In order to determine accurately the value of Q, the sample must be brought into contact with the Freon 11 within the calorimeter. The Freon is at its bubble point, 65°F, so that any heat given up by the sample goes to vaporize the Freon. If the Freon flow rate is sufficient so that no superheating occurs, and if the contact time within the calorimeter is long enough to cool the sample down completely (to 65°F), Q may be determined simply by multiplying the latent heat of vaporization of Freon at 65°F by the amount of Freon vaporized. This amount may be measured if the vaporized Freon is immediately cooled, condensed, and collected in a chilled collection flask for weighing. If the Freon obtained in this manner and the sample passing through the calorimeter are collected simultaneously and then weighed, Q and M may be inserted into equation (1) and the enthalpy change calculated as follows:

$$(H_{T,P})_{in} - (H_{T,P})_{out} = \frac{Q}{M} = \frac{M_{Fr}\lambda_{Fr}}{M} \qquad (2)$$

where

M_{Fr} = mass of Freon 11 collected

λ_{Fr} = latent heat of vaporization of Freon 11 at 65°F: 79.18 BTU/lb_m

One constraint which has been assumed in the above calculations, yet which should be mentioned, is that there be no significant heat leak into or out of the calorimeter or the line between the inlet temperature thermometer and the calorimeter. Before taking any thiophene data, heptane was run in the system and measurements taken at a wide variety of flow rates to assure this was the case. Even so, some care must be taken, for if the sample flow rate is extremely low, even a small heat leak might become significant. Conversely, the flow rate of the sample must not be too high, or the rate of Freon boil-off will be too large for the system to handle. The calorimeter used in this study was designed for a sample flow rate of approximately 30 cm^3 to 60 cm^3 per minute.

By the method described above, enthalpy data were taken for a wide range of temperatures at a number of isobars. The enthalpy difference between inlet and outlet conditions was corrected to outlet conditons of 1 atmosphere and 65^{o}F, the conditions arbitrarily selected as the reference point where the enthalpy of the sample is zero. In the two-phase regions, only the enthalpy of the overall mixture was measured.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

Much has been written on the equipment originally built for this project and on the myriad of modifications which have since been made. Sufficient information may be obtained from the theses by Andrew (1978), McConnell (1976), and Sharma (1977). The most recent modifications, which have improved the performance of the system markedly, are described in the thesis by G. D. Mohr (1980). Operating procedure is discussed by Hinman (1979).

Two equipment changes have been made subsequent to Mohr's thesis. A 500 psig Heise gauge was put in place of a 2000 psig Heise gauge on the inlet side of the system, providing greater accuracy at pressures less than 500 psig. A pressure gauge was also inserted into the nitrogen line between the supply bottle and the pressure regulator valve. This allows a greater degree of control when setting the system pressure by indicating more accurately the pressure in the supply line. Fig. 1 shows the flow calorimeter, and Fig. 1a is the system as it now stands.

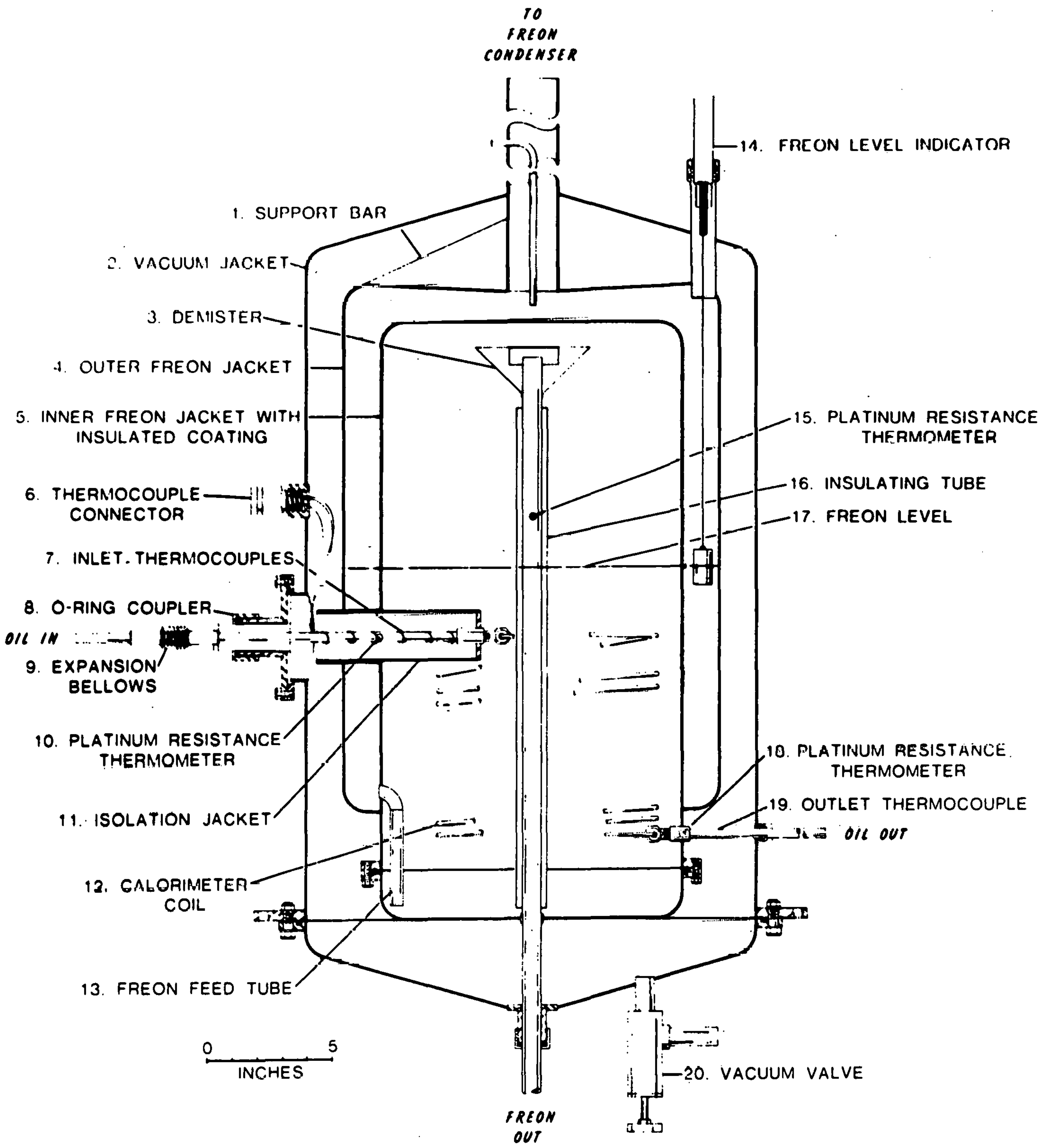


FIGURE 1 FLOW CALORIMETER

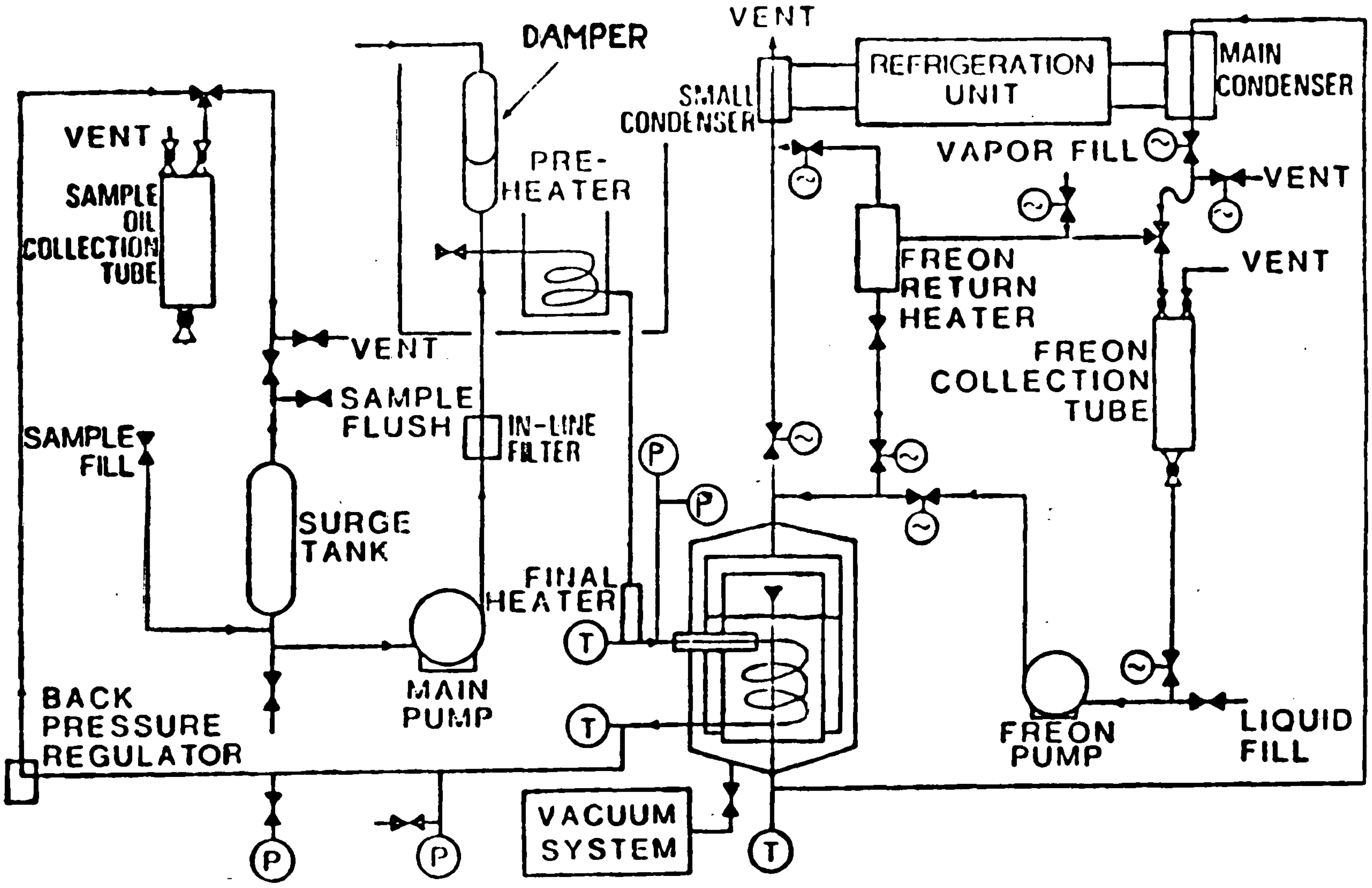


FIGURE 1a. FLOW DIAGRAM OF EXPERIMENTAL APPARATUS

EXPERIMENTAL RESULTS

The thiophene was purchased from the Aldrich Chemical Company, Inc. The specified purity is 99+%, and the property specifications are listed as follows: molecular weight 84.14; boiling point 85^{o}C;n_D^{20} = 1.5278; d = 1.051. The critical properties are T_c = 579.4^{o}K; P_c = 56.2 atm, from Reid (1977 p. 639).

Before beginning experimentation with thiophene, numerous runs were made with n-heptane; at 154 psia;the results, given in Table 1, were compared with a plot of previous measurements made in this lab as well as with data at 150 psia published in Thinh (1974). The excellent agreement indicated the system was working well. All three 2000 psig Heise pressure gauges were checked against each other, and it was discovered that one was substantially in error. This gauge was shipped back to the factory for recalibration and a 500 psig Heise gauge installed in its place. The resulting system contained the 500 psig gauge as an inlet gauge, a 2000 psig outlet gauge, and a 2000 psig gauge used as backup and as an inlet gauge for pressures above 500 psig. Finally, the platinum resistance thermometer used to measure the sample inlet temperature was checked against one kept as a reference, and once again agreement indicated good working condition.

Table 1

Heptane Enthalpy Check Data

Pressure psia	Temperature	H This Investigation	H Previous Investigation
154	279.2	124.3	124.3
	302.3	140.3	140.2
	345.3	168.0	170.1
	429.4	321.7	322.2
	524.8	382.2	385.4
	601.3	435.0	438.3

Following this thorough evaluation of the system, the n-heptane was drained out and the system was flushed, first with benzene, then with thiophene. After each flush, the entire system was purged with nitrogen. Only then was the system charged with fresh thiophene.

Enthalpy Measurements of Thiophene

Enthalpy data for thiophene were taken over a range of temperatures from 100°F to 750°F along isobars of 50, 100, 200, 400, 600, 825.9 (the critical), 1000, and 1500 psia. The outlet enthalpies were corrected to 65°F using a liquid heat capacity for thiophene of 0.30 BTU/lb_m°F, which was obtained from Fig. 2. This correction never amounted to more than 0.26 BTU/lb_m. The outlet pressure was corrected to 1 atmosphere using the Kesler and Lee correlation (1975):

$$\left(\frac{H - H^*}{RT_c}\right) = \left(\frac{H - H^*}{RT_c}\right)^0 + \omega \left(\frac{H - H^*}{RT_c}\right)^1$$

These corrections are tabulated with the data, and never exceeded 2.73 BTU/lb_m.

Two problems which occurred during the process of data-taking should be mentioned here. First, the low temperature data points (those below 100°F) are not reliable. To obtain any Freon flow, the pump governing the sample flow rate had to be operating near its maximum capacity. Even so, the Freon flow was so small that it was highly susceptible to small pressure buildups in the Freon system (due to vaporizing Freon), and was therefore somewhat irregular. Consultation with previous experimenters confirmed this to be unavoidable at such low temperatures. Second, in the midst of taking the 600 psia data, the system began exhibiting drastic temperature instability. After checking the final heater and its control system for irregularities, it became apparent that the problem resided in a fluctuating flow rate rather than in any part of the heating system. The diaphragms in the dual-diaphragm pump, and the check valves attached thereto, were replaced. The temperature problem was thereby remedied, so the 600 psia vapor and two-phase data were retaken with a fresh charge of thiophene. This 600 psia isobar shows more curvature above and below the two-phase region than any of the lower isobars, so several points at lower pressures, both liquid and vapor, were taken to discover if the system had somehow changed its behavior. After proving satisfactorily that such was not the case, it is felt that this curvature is simply due to the impurities in the sample which affect the enthalpy to a greater extent as the pressure and temperature approach the critical values. With these two exceptions, little difficulty was encountered in the data-taking process.

The experimental data obtained are presented in Tables 2 through 9, and are also displayed graphically in Fig. 2. Previous experience with this system as noted in Hinman (1979), indicates that the error in the enthalpy data is less than 1% of the measured ΔH at any temperature. The temperatues are accurate to within ±0.1 ^{o}F. Pressures below 500 psia are accurate to within ±0.5 psia, and above 500 are accurate to within ±2.0 psia. From these data, several comparisons, crossplots, and correlations may be made. These will be discussed in the next section.

Table 2

THIOPHENE ENTHALPY DATA

50 PSIA

Run No.	Phase	Temperature Inlet (°F)	Pressure (psia) Inlet	Pressure (psia) Outlet	ΔH Expt BTU/lb_m	Pressure Correction BTU/lb_m	ΔH Corrected BTU/lb_m
35	L	127.3	49.1	24.9	19.7	0.02	19.7
1	L	146.7	50.0	32.0	25.9	0.17	26.1
22	L	186.7	50.0	22.5	42.6	0.02	42.6
2	L	211.1	50.0	30.0	52.6	0.17	52.8
25	L	222.5	49.8	28.7	58.0	0.02	58.0
23	L	243.0	49.8	23.0	63.8	0.02	63.8
29	L	247.5	49.9	32.4	66.4	0.02	66.4
30	L	261.4	50.2	32.9	72.6	0.05	72.7
3	L-V	264.3	50.0	29.0	81.3	0.02	81.3
26	L-V	266.1	50.7	27.9	93.9	0.02	93.9
4	L-V	266.3	50.0	30.0	143.6	0.02	143.6
27	L-V	267.9	51.4	22.9	164.3	0.02	164.3
32	V	270.9	50.0	24.9	223.1	0.02	223.1
28	V	277.7	50.7	22.4	226.1	0.02	226.1
36	V	337.2	50.6	20.9	243.2	0.01	243.2
5	V	355.7	49.5	32.0	248.0	0.02	248.0
33	V	368.2	50.8	24.9	253.9	0.02	253.9
34	V	407.2	50.6	24.4	265.6	0.02	265.6
37	V	461.1	49.5	21.4	283.9	0.02	283.9
38	V	500.3	49.3	20.9	299.0	0.02	299.0
39	V	540.9	50.0	21.2	310.7	0.02	310.7
40	V	582.8	50.0	18.9	325.6	0.02	325.6
41	V	623.2	50.8	18.4	342.2	0.02	342.2
42	V	663.7	51.2	11.9	357.3	0.00	357.3
43	V	705.1	49.2	20.2	373.0	0.02	373.0
44	V	733.8	50.2	21.4	383.8	0.02	383.8

Table 3

THIOPHENE ENTHALPY DATA

100 PSIA

Run No.	Phase	Temperature Inlet ($^\circ$F)	Pressure (psia)		ΔH Expt BTU/lb$_m$	Pressure Correction BTU/lb$_m$	ΔH Corrected BTU/lb$_m$
			Inlet	Outlet			
45	L	219.7	99.9	81.9	54.8	0.17	55.0
46	L	265.7	101.4	83.9	74.3	0.17	74.5
47	L	280.8	100.4	83.9	80.9	0.17	81.1
53	L	303.3	99.6	81.8	90.7	0.17	90.9
48	L	318.7	99.4	79.9	97.8	0.17	98.0
54	L	321.1	100.6	81.8	98.3	0.17	98.5
49	L-V	323.0	99.4	77.9	161.4	0.17	161.6
50	L-V	323.5	100.2	77.9	172.9	0.17	173.1
55	L-V	323.8	100.5	81.8	106.9	0.17	107.1
51	L-V	324.2	100.6	77.9	184.9	0.17	185.1
56	L-V	324.4	100.2	80.8	204.7	0.17	204.9
52	V	325.5	100.8	77.4	235.9	0.17	236.1
57	V	356.5	100.6	80.8	246.0	0.17	246.2
58	V	381.3	99.3	79.8	254.4	0.17	254.6
59	V	425.7	99.3	79.8	269.7	0.17	269.9
60	V	462.0	99.4	79.8	281.3	0.17	281.5
61	V	502.7	100.7	80.8	294.9	0.17	295.1
62	V	551.8	99.1	79.8	313.6	0.17	313.8
63	V	611.4	99.8	79.8	334.5	0.17	334.7
64	V	659.9	100.0	79.8	355.0	0.17	355.2
65	V	728.0	100.0	79.8	380.0	0.17	380.2

Table 4

THIOPHENE ENTHALPY DATA

200 PSIA

Run No.	Phase	Temperature Inlet (°F)	Pressure (psia) Inlet	Pressure (psia) Outlet	ΔH Expt BTU/lb_m	Pressure Correction BTU/lb_m	ΔH Corrected BTU/lb_m
66	L	269.6	200.5	182.4	75.7	0.32	76.0
67	L	306.6	200.4	182.8	90.4	0.32	90.7
68	L	355.7	199.6	183.8	109.7	0.32	110.0
82	L	388.5	199.5	187.8	123.6	0.34	123.9
71	L-V	391.7	198.4	183.8	159.3	0.32	159.6
72	L-V	392.6	199.5	185.8	207.6	0.34	207.9
69	L-V	393.3	199.6	183.8	236.4	0.32	236.7
70	V	393.6	200.3	183.8	254.8	0.32	255.1
73	V	426.4	200.3	185.8	262.9	0.34	263.2
74	V	450.6	200.5	185.8	273.0	0.34	273.3
75	V	483.7	199.1	185.8	284.3	0.34	284.6
76	V	531.4	199.8	186.3	300.2	0.34	300.5
77	V	577.8	200.2	186.8	319.5	0.34	319.8
78	V	624.1	198.8	184.8	335.7	0.34	336.0
79	V	662.9	199.7	184.8	352.2	0.34	352.5
80	V	709.0	200.0	185.1	370.5	0.34	370.8
81	V	728.3	199.6	184.8	378.6	0.34	378.9

Table 5

THIOPHENE ENTHALPY DATA

400 PSIA

Run No.	Phase	Temperature Inlet (°F)	Pressure (psia) Inlet	Pressure (psia) Outlet	ΔH Expt BTU/lb_m	Pressure Correction BTU/lb_m	ΔH Corrected BTU/lb_m
84	L	340.2	400.1	390.4	105.6	0.71	106.3
85	L	404.2	401.1	391.9	132.7	0.71	133.4
167	L	404.7	400.9	390.9	134.5	0.71	135.2
86	L	428.3	400.7	390.9	143.7	0.71	144.4
88	L	458.9	399.6	387.8	158.0	0.84	158.8
90	L-V	474.9	400.7	388.8	196.6	0.71	197.3
119	L-V	475.6	400.8	388.5	177.2	0.86	178.1
91	L-V	476.9	399.6	386.8	227.7	0.69	228.4
92	L-V	479.4	400.0	389.8	254.1	0.71	254.8
164	V	486.5	401.9	389.9	276.5	0.71	277.2
165	V	488.0	401.9	389.9	275.7	0.71	276.4
168	V	508.0	398.0	385.0	284.5	0.69	285.2
166	V	511.4	401.9	390.4	287.6	0.71	288.3
120	V	537.7	400.3	387.0	299.4	0.84	300.2
94	V	553.2	400.1	386.9	302.8	0.69	303.5
95	V	588.9	400.3	386.9	314.0	0.69	314.7
121	V	589.6	400.0	387.0	315.5	0.69	316.2
96	V	629.3	400.4	387.4	331.4	0.69	332.1
97	V	666.9	400.2	386.9	346.9	0.69	347.6
98	V	710.5	400.5	387.9	364.1	0.71	364.8

Table 6

THIOPHENE ENTHALPY DATA

600 PSIA

Run No.	Phase	Temperature Inlet (°F)	Pressure (psia) Inlet	Pressure (psia) Outlet	ΔH Expt BTU/lb_m	Pressure Correction BTU/lb_m	ΔH Corrected BTU/lb_m
6	L	390.1	600	571	128.4	1.03	129.4
7	L	442.2	600	571	151.6	1.03	152.6
13	L	507.4	600	592	186.8	1.08	187.9
14	L	526.7	600	590	198.6	1.06	199.7
125	L-V	530.0	600	587	207.8	1.06	208.9
12	L-V	530.5	600	592	212.8	1.08	213.9
122	L-V	531.2	600	589	238.8	1.06	239.9
8	L-V	532.9	600	592	234.5	1.08	235.6
15	L-V	534.8	600	588	259.6	1.06	260.7
9	L-V	535.9	600	589	273.1	1.06	274.2
126	V	537.3	600	588	280.4	1.06	281.5
113	V	542.1	598	584	285.1	1.06	286.2
127	V	546.0	598	586	288.1	1.06	289.2
112	V	555.3	599	586	295.1	1.06	296.2
111	V	572.2	599	586	304.2	1.06	305.3
106	V	581.0	599	588	306.8	1.06	307.9
128	V	581.6	600	587	309.3	1.06	310.4
109	V	600.2	601	590	314.1	1.06	315.2
129	V	634.0	601	586	326.9	1.06	328.0
114	V	640.8	600	587	330.3	1.06	331.4
115	V	686.0	600	587	349.5	1.06	350.6
103	V	734.7	600	592	370.4	1.08	371.5

Table 7

THIOPHENE ENTHALPY DATA

825.9 PSIA

Run No.	Phase	Temperature Inlet (°F)	Pressure (psia)		ΔH Expt BTU/lb$_m$	Pressure Correction BTU/lb$_m$	ΔH Corrected BTU/lb$_m$
			Inlet	Outlet			
16	L	478.0	826	816	167.6	1.48	169.1
130	L	529.3	826	815	199.4	1.48	200.9
17	L	538.5	826	817	204.0	1.48	205.5
131	L	549.3	826	815	212.4	1.48	213.9
132	L	564.4	826	815	222.5	1.48	224.0
18	L	576.1	826	816	239.4	1.48	240.9
133	L	579.5	826	815	245.3	1.48	246.8
134	L	589.1	827	815	280.0	1.48	281.5
135	L	603.6	828	816	296.1	1.48	297.6
136	L	636.0	827	816	317.3	1.48	318.8
137	L	678.0	828	816	337.5	1.48	339.0
138	L	725.2	828	817	363.0	1.48	364.5

Table 8

THIOPHENE ENTHALPY DATA

1000 PSIA

Run No.	Phase	Temperature Inlet (°F)	Pressure (psia) Inlet	Pressure (psia) Outlet	ΔH Expt BTU/lb_m	Pressure Correction BTU/lb_m	ΔH Corrected BTU/lb_m
142	L	402.3	1001	990	131.4	1.80	133.2
143	L	462.3	1001	991	162.3	1.80	164.1
144	L	530.0	1001	991	200.6	1.80	202.4
140	L	567.6	999	990	224.0	1.80	225.8
141	L	597.5	998	989	253.2	1.80	255.0
148	L	606.7	1000	994	273.5	1.80	275.3
145	L	626.4	1001	991	294.9	1.80	296.7
146	L	644.7	1000	992	313.0	1.80	314.8
149	L	652.2	999	992	315.3	1.80	317.1
150	L	687.5	998	992	336.6	1.80	338.4
151	L	735.1	999	992	359.8	1.80	361.6

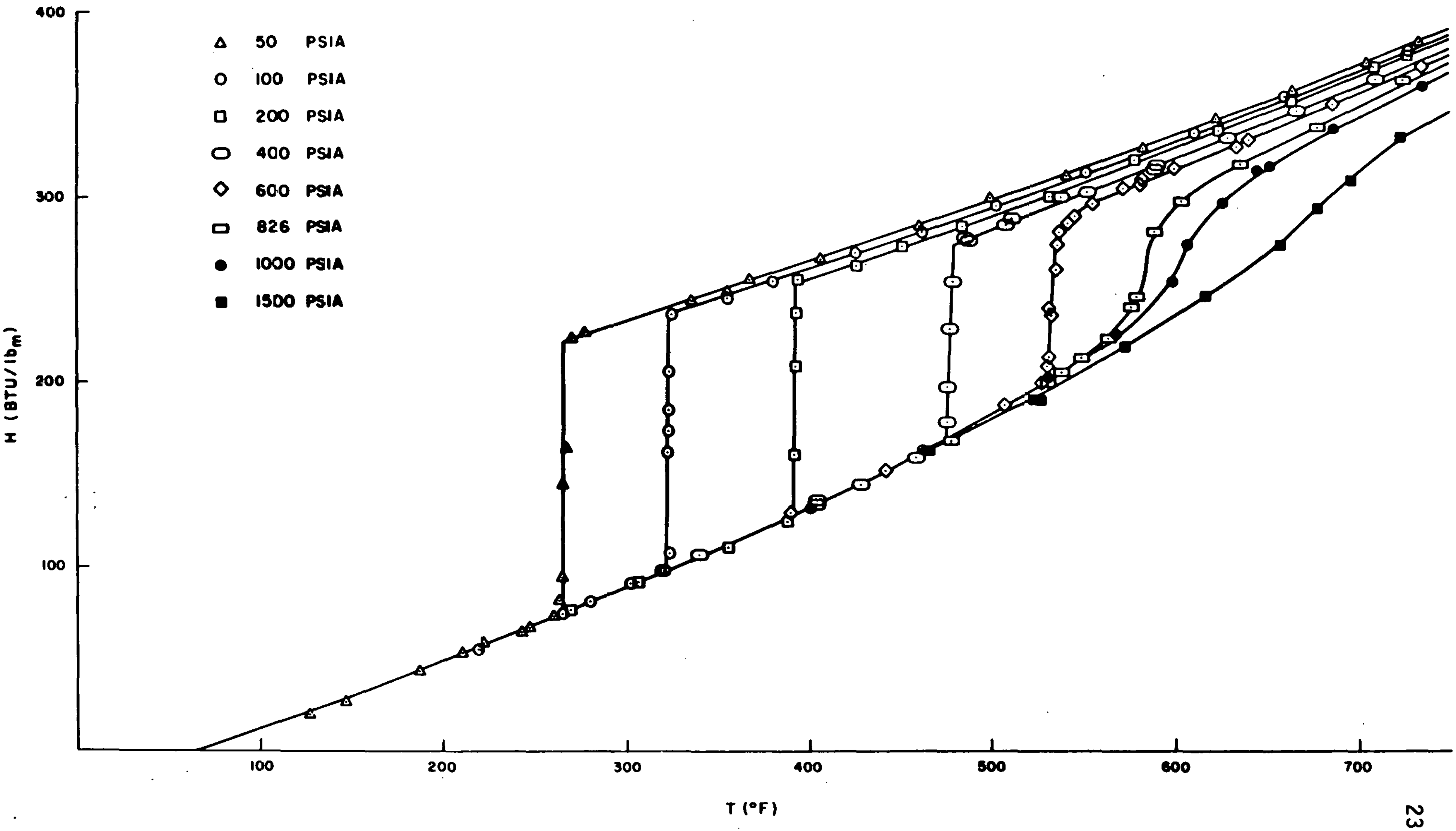
Table 9

THIOPHENE ENTHALPY DATA

1500 PSIA

Run No.	Phase	Temperature Inlet (°F)	Pressure (psia) Inlet	Pressure (psia) Outlet	ΔH Expt BTU/lb$_m$	Pressure Correction BTU/lb$_m$	ΔH Corrected BTU/lb$_m$
153	L	465.3	1501	1481	162.1	2.68	164.8
155	L	522.9	1500	1490	190.2	2.71	192.9
154	L	526.1	1501	1487	189.0	2.71	191.7
156	L	572.1	1499	1490	218.1	2.71	220.8
157	L	615.9	1499	1487	244.9	2.71	247.6
158	L	656.7	1499	1485	273.3	2.71	276.0
161	L	676.5	1501	1493	293.1	2.71	295.8
163	L	695.9	1496	1488	308.3	2.71	311.0
162	L	722.5	1503	1496	330.9	2.73	333.6

FIG. 2 - THIOPHENE ENTHALPY



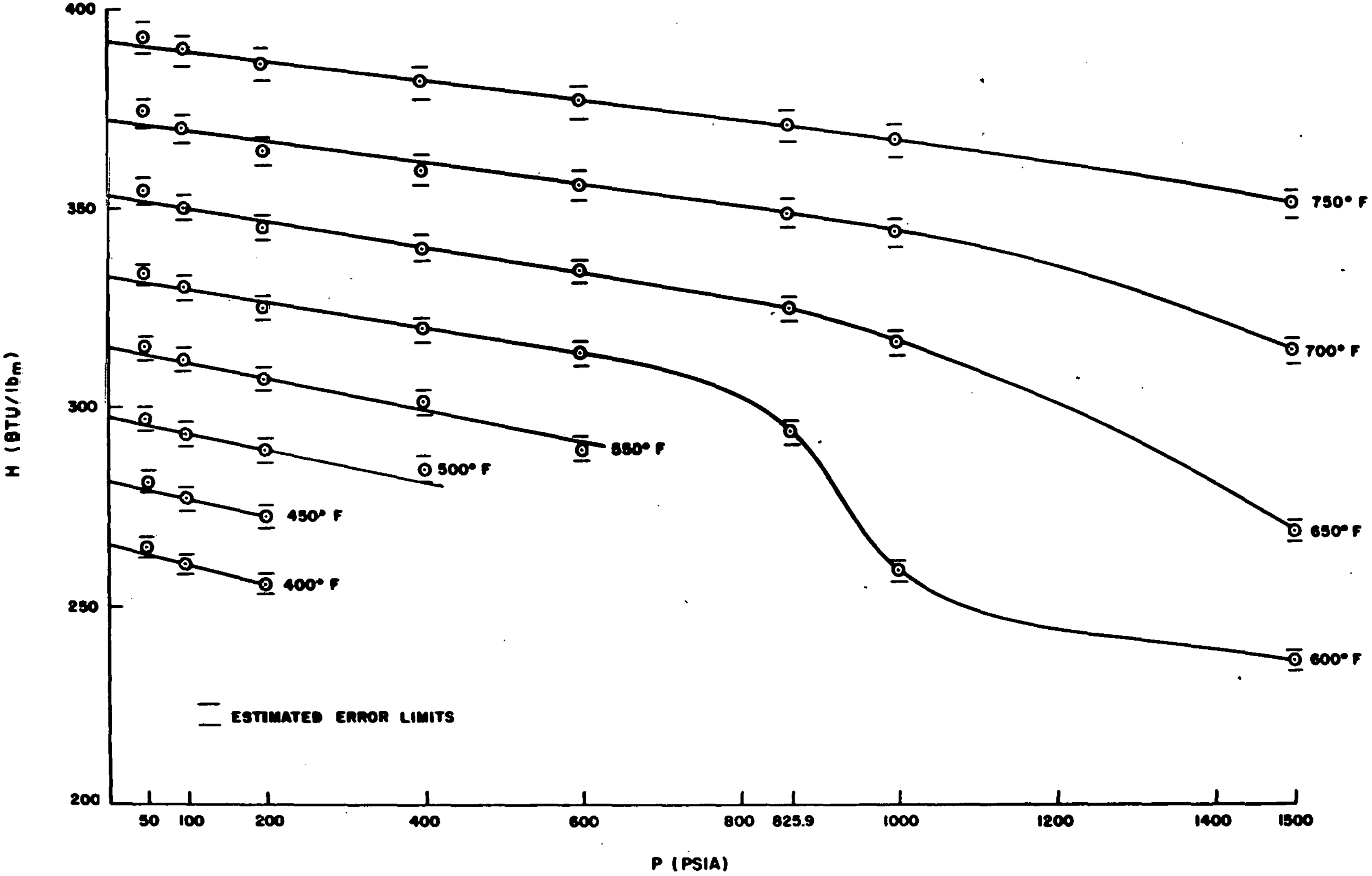
COMPARISON OF THIOPHENE MEASUREMENTS WITH EXPERIMENTAL LITERATURE VALUES

Although there is a significant amount of data in the literature dealing with thiophene, none of it is actual enthalpy data. Instead, there is an abundance of heat capacity, heat of vaporization, virial coefficient, and vapor pressure data, but most of it at lower temperatures than those of this study. A comparison of literature values with derived values from these data will indicate the quality of the data.

Enthalpy Cross-Plot

After fitting the vapor phase isobaric enthalpy data to the expression $H = a + bT + cT^2$, where a, b, and c are constants, isothermal cross-plots of the data were constructed in Figure 3 for temperatures ranging from 400°F to 750°F in increments of 50°F. Error bars indicating a 1% error in the enthalpy are included on the plot. Since Figure 3 is a cross-plot of values estimated by a least-squares fit of the data, the expected scatter in the data should increase. Such is the case: the values at 50 psia are high relative to the higher pressures, causing an upward curvature in the isotherms of Figure 3. This should not be true. Thiophene can be represented with the virial equation; at lower pressures all virial coefficients beyond the second should be negligible. If so, the plot of H vs P

FIG. 3 - THIOPHENE ENTHALPY CROSSPLOT



at constant T should be a straight line in this region. If straight lines are fitted to the data points below 600 psia, as is done in Figure 3, the slope of the resultant lines follow the same trend as the virial equation indicates, but with steeper negative slopes. The steeper slope is most likely due to using higher pressure points (100 psia to 600 psia) to arrive at a slope, instead of the 50 psia to 200 psia points. The low pressure points obviously cannot be exclusively used since the 50 psia points are consistently high.

A comparison between the calculated and observed slopes is presented in Table 10. The columns marked "Calc. 1" and "Calc. 2" are both calculated by means of the virial equation, but the former uses Pitzer's general correlation for the virial coefficient and its derivatives as given in Smith and Van Ness (1975), while the latter uses the correlation for the thiophene virial coefficient offered by Waddington et al. (1949). A discussion of these calculations is given in Appendix A.

As further check on these data, the straight lines of the isotherms were extrapolated back to zero pressure and the enthalpy difference between each isotherm and the 400 °F isotherm calculated. These values are given in Table 11, along with the same quantities calculated using the ideal gas heat capacity expression from Reid et al. (1977, pp.

TABLE 10

EFFECT OF PRESSURE ON THIOPHENE ENTHALPY AT LOW PRESSURES

Temperature °F	T_R	$\left(\frac{\partial H}{\partial P}\right)_T$ $\left(\frac{BTU}{lb_m\ psia}\right)$		
		Calc. 1	Calc. 2	Observed
400.0	0.8243	-0.034	-0.042	-0.051
450.0	0.8723	-0.032	-0.037	-0.045
500.0	0.9202	-0.029	-0.034	-0.042
550.0	0.9681	-0.027	-0.031	-0.040
600.0	1.016	-0.026	-0.029	-0.033
650.0	1.064	-0.024	-0.028	-0.031
700.0	1.112	-0.022	-0.026	-0.028
750.0	1.160	-0.021	-0.025	-0.026

TABLE 11

THIOPHENE ENTHALPY DIFFERENCES BETWEEN VARIOUS TEMPERATURES AT ZERO PRESSURE

Temperature °F	$(H_T - H_{400})_{calc}$ BTU/lb_m	$(H_T - H_{400})_{obs}$ BTU/lb_m
450.0	16.1	16.1
500.0	32.8	32.3
550.0	50.1	50.0
600.0	68.0	66.9
650.0	86.5	88.3
700.0	105.4	106.8
750.0	124.8	126.6

629, 640). The observed values deviate no more than ± 2% from those calculated.

Vapor Pressure

Due to the presence of impurities in the sample, the two-phase data at each isobar do not fall on a truly vertical line. Instead, each two-phase region covers a span of several degrees. In order to obtain the boiling point, the temperature at the top and bottom of each two-phase region were averaged. The results should be accurate to within ± 0.5%. These temperatures were converted to °R, and a plot of log P^s (the system pressure at that isobar) vs 1/T was made. On the same plot, data from the American Petroleum Institute Research Project 44 (1953) and from Waddington et al (1949) were entered. The data are given in Table 12, and the resulting graph in Figure 4. The figure illustrates how closely the data of this study correlate with those of the other two sources. A straight line constructed through all the data reveals very little scatter among the data sets.

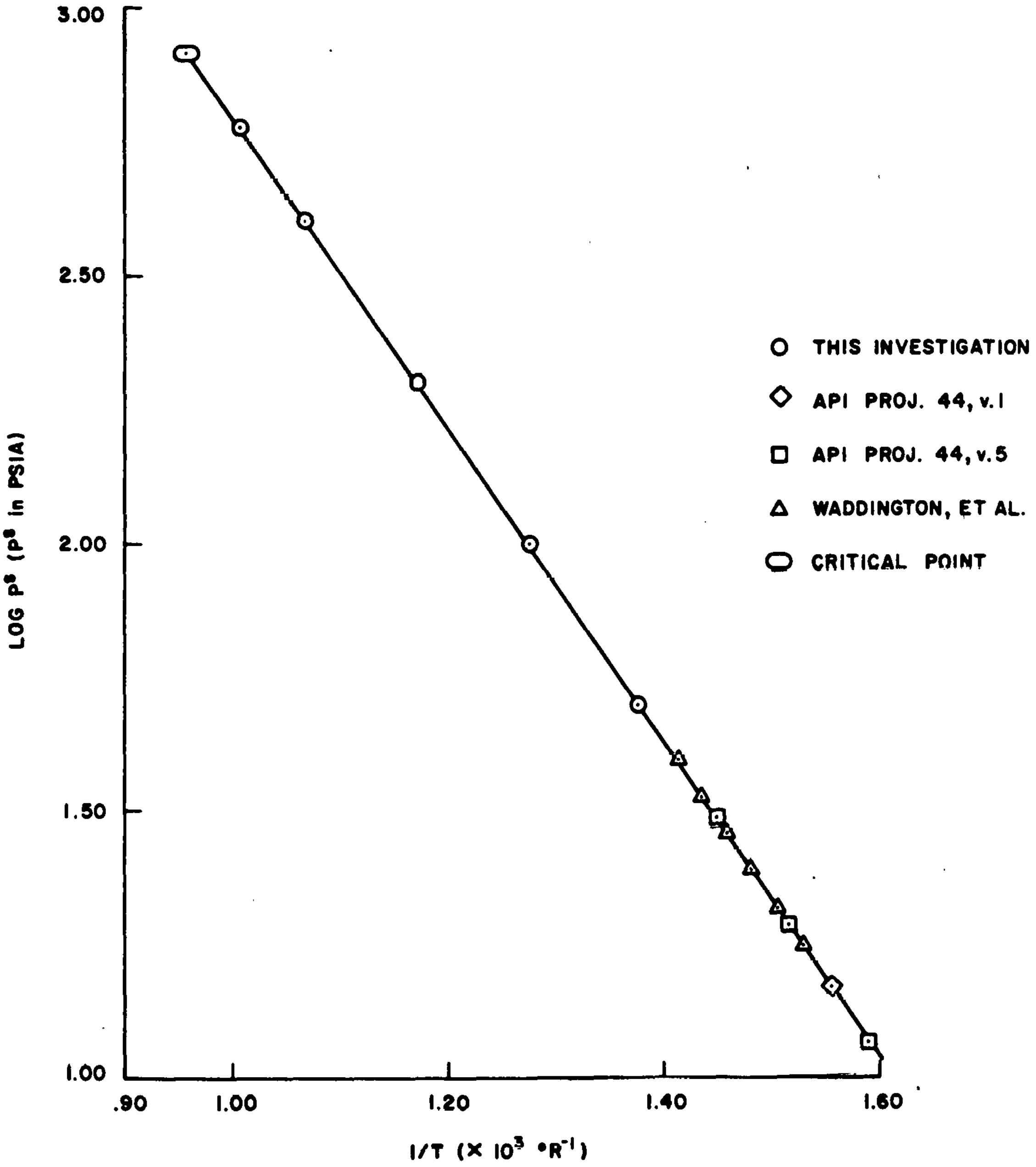
Heats of Vaporization

The impurities in the sample are much more noticeable when attempting to calculate heats of vaporization. For the higher pressures, it is often difficult to determine exactly where the two-phase region begins and ends. Thus

TABLE 12
THIOPHENE VAPOR PRESSURE

Temperature	$1/T$ $x10^{3}\,{}^{\circ}R^{-1}$	P^{s} psia	log P^{s}	Source
266.8	1.377	50.0	1.699	This Investigation
323.5	1.277	100.0	2.000	" "
392.8	1.173	200.0	2.301	" "
477.1	1.068	400.0	2.602	" "
532.9	1.008	600.0	2.778	" "
583.2	0.9589	825.9	2.917	Reid et al (1977, p. 639)
183.5	1.555	14.70	1.167	API Proj. 44 (1953, Table 114a-E)
170.0	1.588	11.60	1.064	API Proj. 44 (1953, Table 114K-E)
200.0	1.516	19.32	1.286	" "
230.0	1.450	30.56	1.485	" "
194.0	1.530	17.52	1.244	Waddington et al, (1949, p. 802)
204.6	1.506	20.78	1.318	" "
215.3	1.482	24.52	1.390	" "
226.0	1.459	28.79	1.459	" "
236.8	1.436	33.66	1.527	" "
247.7	1.414	39.18	1.593	" "

FIG. 4 - THIOPHENE VAPOR PRESSURE



for the 600 psia isobar, the top of which is particularly curved, the heat of vaporization was calculated from the definite discontinuity in the liquid phase to the intersection of the measured vapor and two-phase lines. No attempt was made to square off the vapor corner by extrapolation of the vapor phase data. The inaccuracies inherent in so doing would not improve the results. Once again, the heats of vaporization obtained were tabulated and plotted, along with available data from API Research Project 44 (1953) and Waddington et al (1949) in Table 13 and Figure 5. A nice smooth curve is formed, although here the margin for error is much greater, from ± 2% at 50 psia to as much as ± 5% for the 600 psia value. Error bars in Figure 5 indicate these error ranges.

Vapor Phase Heat Capacity

The equations generated by the previously mentioned least-squares fit of the vapor phase enthalpy data are shown in Table 14. The derivative of each second order equation was taken in order to obtain an equation for C_p. The heat capacity was then calculated at selected temperatures for each vapor isobar, and the results as shown in Table 15 plotted as a function of pressure in Figure 6. Since the heat capacity values are slopes of fitted curves, they are none too accurate; the error is estimated at ± 5%.

TABLE 13

THIOPHENE HEATS OF VAPORIZATION

Temperature ^{o}F	H_{vapor} BTU/lb_m	H_{liquid} BTU/lb_m	ΔH_{vap} BTU/lb_m	Source
266.8	221.8	74.3	147.5	This Investigation
323.5	235.8	97.2	138.6	" "
392.8	253.7	127.7	126.0	" "
477.1	273.8	167.6	106.2	" "
532.9	280.4	198.7	81.7	" "
583.2			0.0	Reid et al, (1977, p. 639)
77.0			176.9	API Proj. 44(1953,Table 23-14-2-(9.2020)-m)
183.5			160.9	" " " "
113.7			171.8	Waddington, et al, (1949,p. 802)
145.6			167.0	" " " "
183.6			160.9	" " " "

FIG. 5 - THIOPHENE HEAT OF VAPORIZATION

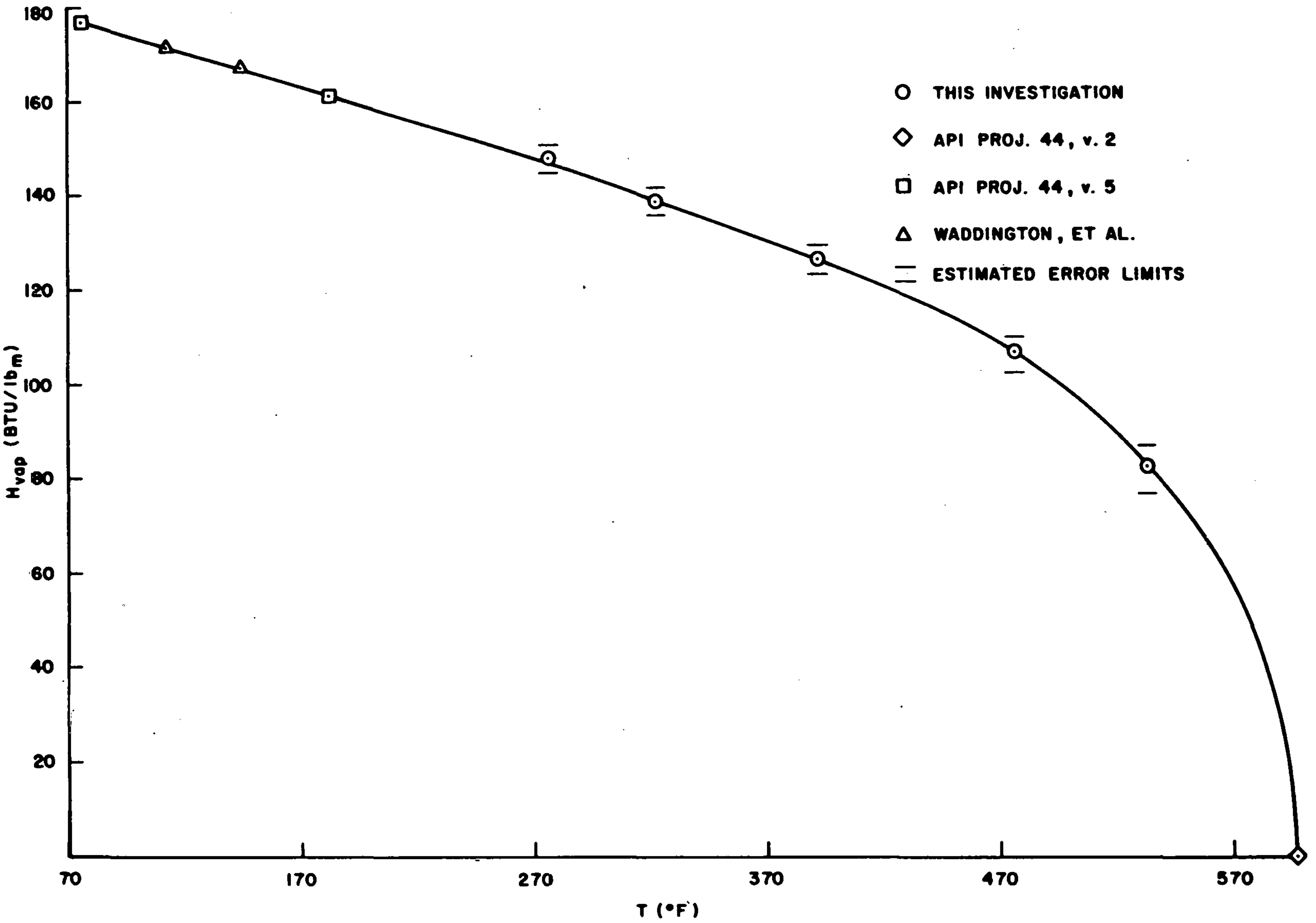


TABLE 14

THIOPHENE VAPOR PHASE ENTHALPY EQUATIONS GENERATED BY LEAST-SQUARES FIT OF EXPERIMENTAL DATA

Pressure psia	Equation T in ^{0}F
50.0	$150.48823 + 0.23961362T + 0.10748985 \times 10^{-3} T^2$
100.0	$143.33750 + 0.25273997T + 0.10044471 \times 10^{-3} T^2$
200.0	$151.12955 + 0.20054828T + 0.15429498 \times 10^{-3} T^2$
400.0*	$150.17810 + 0.17919840T + 0.17285162 \times 10^{-3} T^2$
600.0**	$131.04918 + 0.21652675T + 0.14935554 \times 10^{-3} T^2$

* Runs numbered 164, 165, and 120 were not used to generate the vapor enthalpy curve due to their proximity to the two-phase region.

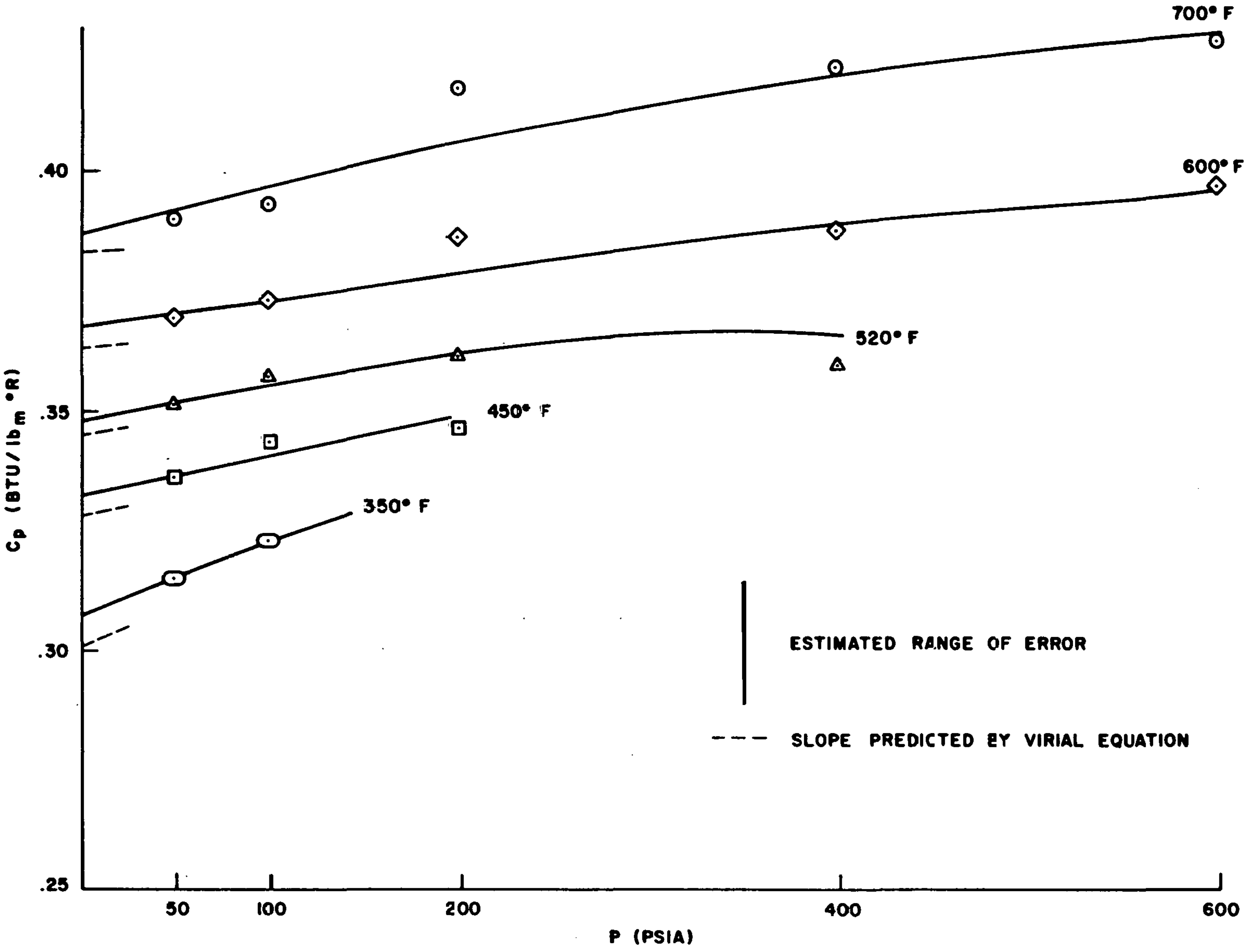
** Runs numbered 126, 113, and 127 were not used to generate the vapor enthalpy curve due to their proximity to the two-phase region.

TABLE 15

THIOPHENE HEAT CAPACITY ESTIMATES FROM SLOPE OF LEAST-SQUARES FIT OF VAPOR ENTHALPY DATA

Temperature °F	Pressure psia	C_P BTU/lb_m °F
350.0	50.0	0.315
	100.0	0.323
450.0	50.0	0.336
	100.0	0.343
	200.0	0.346
520.0	50.0	0.351
	100.0	0.357
	200.0	0.361
	400.0	0.359
600.0	50.0	0.369
	100.0	0.373
	200.0	0.386
	400.0	0.387
	600.0	0.396
700.0	50.0	0.390
	100.0	0.393
	200.0	0.417
	400.0	0.421
	600.0	0.426

FIG. 6 - THIOPHENE HEAT CAPACITY ESTIMATES



As an aid in fitting a curve to this data, the derivative of C_p with respect to pressure at constant temperature was calculated using the virial equation. The values calculated in this manner were used to estimate the initial slope of the lines fitting the data. These lines, as well as the calculated initial slope and ideal gas values from the literature are indicated in Figure 6. Table 16 provides the initial slopes as calculated with the virial equation, as before using both correlations for the virial coefficient. Once more, the specific correlation for thiophene works much better than the general one. The derivation of the virial formula of the slope is provided in Appendix B. The error in the zero-pressure heat capacities extrapolated in Figure 6 should be no less than ±5%, and when these ideal gas heat capacities are compared with the extensive data offered by El-Sabban et al (1970), Hubbard et al (1955), and Waddington et al (1949), and with the equation put forth by Reid et al (1977, p. 629), the data from this study is found to fall within ±2% of the literature values. This is especially good, given the fact that heat capacities were not measured directly in this study. Table 17 and Figure 7 indicate the ideal gas heat capacity data from this study and from the literature.

TABLE 16

EFFECT OF PRESSURE ON THIOPHENE IDEAL GAS HEAT CAPACITIES AT CONSTANT TEMPERATURE

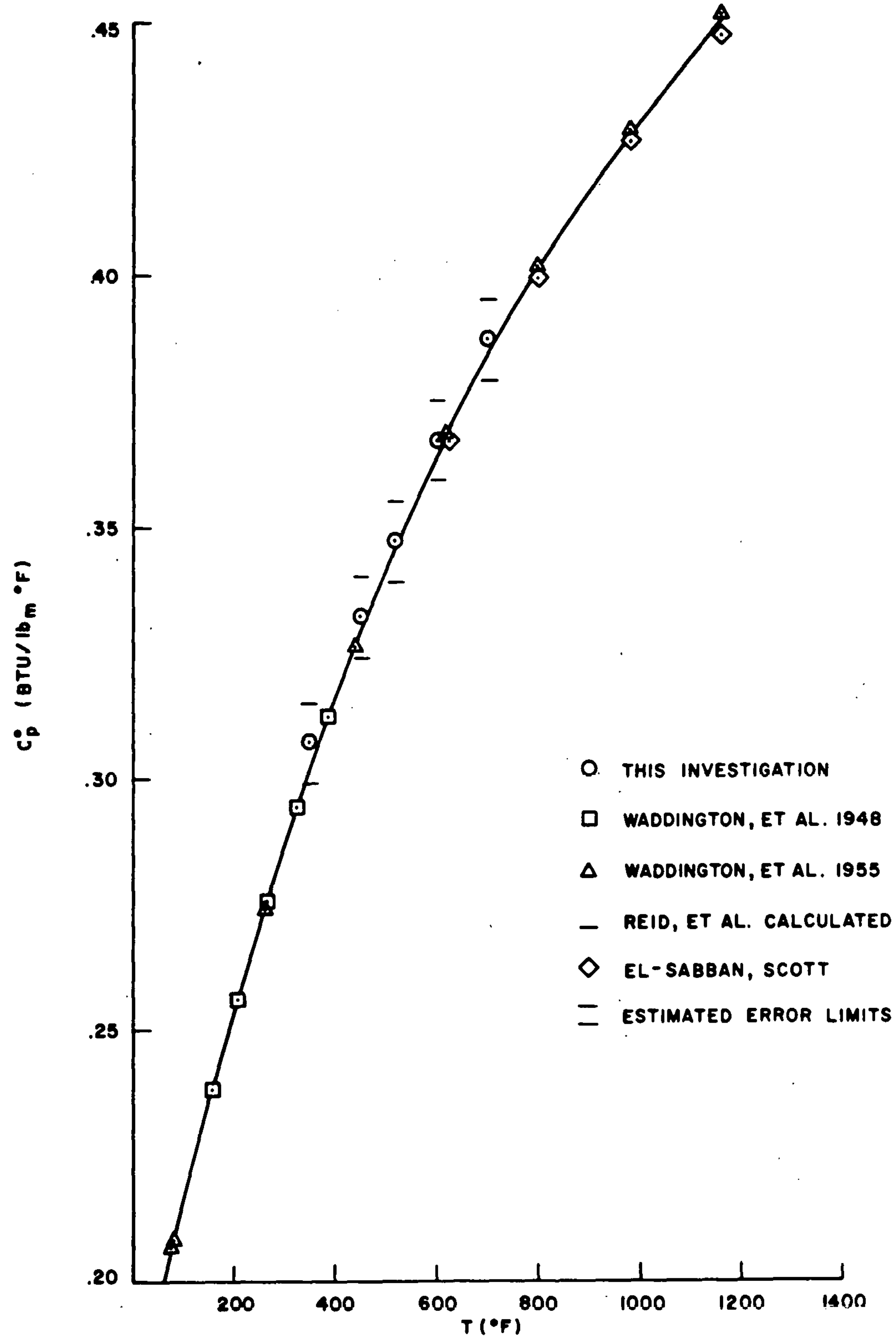
Temperature °F	$\left(\frac{\partial C_p}{\partial P}\right)_T$ $\left(\frac{\text{BTU}}{\text{lb}_m\ ^\circ\text{F psia}}\right)$ Calc. 1	Calc. 2
350.0	7.132×10^{-3}	1.343×10^{-4}
450.0	2.145×10^{-3}	7.435×10^{-5}
520.0	1.107×10^{-3}	5.201×10^{-5}
600.0	5.917×10^{-4}	3.614×10^{-5}
700.0	3.122×10^{-4}	2.421×10^{-5}

TABLE 17

THIOPHENE IDEAL GAS HEAT CAPACITIES

Temperature °F	C_p $\left(\frac{\text{BTU}}{\text{lb}_m\ ^\circ\text{F}}\right)$ This Inv.	El-Sabban	**Hubbard**	Waddington	Reid
350.0	0.307				0.301
450.0	0.332				0.328
520.0	0.347				0.345
600.0	0.367				0.363
700.0	0.391				0.383
32.0		0.189			
76.8		0.207	0.207		0.206
80.4		0.208	0.208		0.208
260.4		0.274	0.274		0.273
440.4		0.326	0.326		0.326
620.4		0.367	0.368		0.368
800.4		0.399	0.401		0.401
980.4		0.426	0.428		0.427
1160.4		0.447	0.451		0.450
1340.4		0.466	0.470		0.470
159.5				0.238	0.238
208.6				0.256	0.256
264.5				0.275	0.275
325.6				0.294	0.294
388.5				0.312	0.312

FIG. 7 - THIOPHENE IDEAL GAS HEAT CAPACITIES



Enthalpy Correlations

The major purpose in studying coal-derived liquids with this apparatus is to evolve a correlation which can predict fairly accurately the enthalpy of such compounds. The two major correlations which seemed most promising before this study were the Kesler and Lee correlation (1975) based on a modified Benedict-Webb-Rubin equation of state, and a correlation utilizing the Soave-Redlich-Kwong equation of state. The Benedict-Webb-Rubin equation is

$$P = \frac{RT}{V} + \frac{B_oRT - A_o - C_o/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6}$$

$$+ \frac{C}{V^3T^2}\left(1 + \frac{\gamma}{V^2}\right) \exp \frac{-\gamma}{V^2}$$

where A_o, B_o, C_o, a, b, c, α, and γ are constants for the fluid of interest. The Soave-Redlich-Kwong equation is

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)}$$

where V is the molar volume and

$$a = a\ (T_c)\ \alpha$$

where

$$a\ (T_c) = 0.42747\ \frac{R^2T_c^2}{P_c}$$

$$\alpha = (1 + m\ (1-T_R)^{0.5})^2$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2$$

$$b = 0.08664\ \frac{RT_c}{P_c}$$

A copy of this second computer-aided method is found in Appendix C. Both methods follow the same procedure: (1) calculation of the enthalpy departure from the real state at the reference state (65°F and 1 atmosphere) to the ideal gas state at 65°F; (2) calculation of the enthalpy change within the ideal gas state from 65°F to the temperature of interest; (3) calculation of the enthalpy departure from the ideal gas state at the temperature of interest to the real state at the temperature and pressure of interest. Step 2 is accomplished in the same manner with both correlations, by utilizing the ideal gas heat capacities. Steps 1 and 3 are accomplished by calculating the enthalpy departure using on one hand the Kesler and Lee correlation based on corresponding states and on the other the Soave-Redlich-Kwong equation of state. The necessary parameters for using these two methods were obtained from Reid et al. (1977): molecular weight, critical temperature, critical pressure, acentric factor, and ideal gas heat capacities.

Enthalpy values were calculated using both methods at intervals of 100°F from 100°F to 700°F for each isobar on which experimental data were taken. The results of these calculations are compared with values obtained from the smooth curves fitted to the experimental data (see Figure 2) in Table 18. Close study of this tabulation yields some distinct patterns.

Both the Soave-Redlich-Kwong and the Kesler and Lee methods give excellent predictions in the liquid phase, predictions falling within ±5% of measured values. Vapor enthalpies fall predominately within ±1% of measured values, with two notable exceptions. First, at the critical pressure and above, both methods begin to fall significantly below measured values: more than 1.5% at 600°F and 825.9 psia to almost 3% at 700°F and 1000 psia. Even so, this is not far beyond the accuracy limits of the data. Second, the enthalpy values close to the two-phase regions are predicted somewhat lower in the liquid phase and somewhat higher in the vapor phase at lower pressures, and just the reverse at higher pressures. This is most likely due to the impurities in the thiophene serving to "round off" the corners of the two-phase regions. Table 19 presents a comparison between vaporization temperatures and heats of vaporization for pressures below the critical as measured in this study and as calculated with the SRK equation. The difference in boiling points is less than 1.8°F in any instance, and the heats of vaporization are within ±4% at pressures of 200 psia and below, and within ±15% at the

TABLE 18

THIOPHENE ENTHALPY CORRELATIONS

Pressure psia	Temperature °F	Phase	H $\left(\frac{BTU}{lb_m}\right)$ This Inv.	SRK	K-L
50.0	100.0	L	11.2	11.6	12.1
	200.0	L	46.7	46.7	48.6
	300.0	V	231.8	232.2	231.7
	400.0	V	262.7	262.8	262.8
	500.0	V	297.9	295.9	296.2
	600.0	V	334.2	331.4	331.9
	700.0	V	371.2	369.0	369.6
100.0	100.0	L	11.2	11.7	12.2
	200.0	L	46.7	46.8	48.7
	300.0	L	89.0	86.4	88.6
	400.0	V	260.1	260.3	259.7
	500.0	V	294.3	293.9	294.0
	600.0	V	331.4	329.8	330.1
	700.0	V	369.1	367.6	368.1
200.0	100.0	L	11.2	11.9	12.4
	200.0	L	46.7	46.9	48.8
	300.0	L	88.3	86.5	88.7
	400.0	V	256.6	254.5	252.6
	500.0	V	288.9	289.5	288.9
	600.0	V	326.9	326.2	326.3
	700.0	V	365.8	364.6	365.1
400.0	100.0	L	11.2	12.4	12.7
	200.0	L	46.7	47.3	49.1
	300.0	L	88.3	86.7	88.9
	400.0	L	129.8	131.5	132.3
	500.0	V	281.7	278.2	275.5
	600.0	V	320.3	318.2	317.7
	700.0	V	359.7	358.3	358.6
600.0	100.0	L	11.2	12.8	13.1
	200.0	L	46.7	47.6	49.4
	300.0	L	88.3	86.8	89.1
	400.0	L	129.8	131.2	132.3
	500.0	L	180.9	184.2	181.9
	600.0	V	313.8	307.8	306.5
	700.0	V	354.7	351.1	351.2

TABLE 18

(Continued)

			H $\left(\frac{BTU}{lb_m}\right)$		
Pressure psia	Temperature °F	Phase	This Inv.	SRK	K-L
825.9	100.0	L	11.2	13.3	13.5
	200.0	L	46.7	48.0	49.8
	300.0	L	88.3	87.1	89.4
	400.0	L	129.8	131.0	132.3
	500.0	L	180.9	182.2	180.0
	600.0	L	292.9	288.3	285.7
	700.0	L	348.6	341.7	341.5
1000.0	100.0	L	11.2	13.6	13.8
	200.0	L	46.7	48.3	50.1
	300.0	L	88.3	87.2	89.6
	400.0	L	129.8	130.9	132.4
	500.0	L	180.9	181.1	179.5
	600.0	L	258.4	251.0	245.8
	700.0	L	342.9	333.1	332.1
1500.0	100.0	L	11.2	14.7	14.7
	200.0	L	46.7	49.2	50.9
	300.0	L	88.3	87.8	90.2
	400.0	L	129.8	130.8	132.6
	500.0	L	177.8	179.0	178.6
	600.0	L	234.3	235.2	231.9
	700.0	L	312.3	304.6	303.3

TABLE 19

THIOPHENE BOILING POINTS AND HEATS OF VAPORIZATION

	Temperature °F	H_{vapor} BTU/lb_m	H_{liquid} BTU/lb_m	ΔH_{vap} BTU/lb_m
50.0 psia				
This Inv.	266.8	221.8	74.3	147.5
SRK	267.2	222.7	70.5	152.2
100.0 psia				
This Inv.	323.5	235.8	97.2	138.6
SRK	325.3	236.6	95.2	141.4
200.0 psia				
This Inv.	392.8	253.7	127.7	126.0
SRK	394.4	252.4	127.1	125.3
400.0 psia				
This Inv.	477.1	273.8	167.6	106.2
SRK	477.5	268.9	170.4	98.5
600.0 psia				
This Inv.	532.9	280.4	198.7	81.7
SRK	533.9	275.3	205.2	70.1

higher pressures. The greater errors in the predicted values at the higher pressures are not surprising, given the above-illustrated increased error in enthalpy values at higher pressures exhibited by the correlation.

Discussion

In general, little difficulty was encountered in obtaining enthalpy data for thiophene. The only equipment problems which occurred were the previously discussed pump malfunction and occasionally finding coke buildup around the final heater. The pump failure came as no surprise since the check valves had not been replaced in more than one year, and the diaphragms for a much longer period of time. Coke formation around the final heater has troubled all who have worked with this equipment due to the narrow clearance between the heating element and the inner walls of the surrounding tubing. This narrow clearance is necessary, however, to assure even heating of the sample prior to its entrance into the calorimeter.

These problems did not have any negative effect on the data reported in this study. At the first sign of pump irregularities or pressure drop due to coke formation, the system was shut down and the anomaly repaired. In the case of the pump, extensive data were retaken in order to assure that the problem had not gone unnoticed for any period of time.

CONCLUSIONS

The excellent agreement between the quantities measured in this study and those reported in the literature bode well for this system and for the experimental procedure employed. The incredible agreement in the area of vapor pressures between the higher temperature data of this study and the lower temperature measurements available in the literature from several sources in especially gratifying.

Just as significant is the very good agreeement between measured enthalpies and those predicted by the two correlations. So far, these methods have proven quite successful except for compounds which have a high level of association, such as m-cresol. Thus the correlational development is not complete at this point, for if it will not work adequately for certain pure compounds it will probably not be too successful for some coal-derived liquids. It is hoped that the data presented in this study will aid in the development of a correlation which will be successful for predicting the enthalpies of all coal-derived liquids.

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APPENDIX A

DERIVATION OF $\left(\frac{\partial H}{\partial P}\right)_T$

Begin with the complete expression for dH

$$dH = C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right) dP$$

At constant T this becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

We therefore need an expression for V. For this we will use the virial equation:

$$PV = a(1 + B'P + C'P^2 + \ldots)$$

where a = RT. For low pressures, this may be truncated to two terms, and utilizing the compressibility factor Z

$$Z = \frac{PV}{RT} = 1 + B'P$$

Then, substitute the approximation relation $B' = B/RT$

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

Solving for V yields

$$V = \frac{RT}{P} + B$$

Therefore

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{RT}{P} + B - T\frac{\partial}{\partial T}\left(\frac{RT}{P} + B\right)_P$$

Since B is independent of P

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{RT}{P} + B - T\left(\frac{R}{P} + \left(\frac{dB}{dT}\right)\right) = B - T\frac{dB}{dT}$$

Calculation Method 1

Pitzer's correlation in Smith and Van Ness (1975, p 87) represents B as

$$B = \frac{RT_c}{P_c}(B^0 + \omega B^1)$$

and M. M. Abbott expresses B^0 and B' as follows:

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Then

$$\frac{dB}{dT} = \frac{RT_c}{P_c}\left(\frac{dB^0}{dT} + \omega\frac{dB^1}{dT}\right)$$

where

$$\frac{dB^0}{dT} = \frac{d}{dT}\left(\frac{-0.422T_c^{1.6}}{T^{1.6}}\right) = \frac{0.675T_c^{1.6}}{T^{2.6}}$$

$$\frac{dB^1}{dT} = \frac{d}{dT}\left(\frac{-0.172T_c^{4.2}}{T^{4.2}}\right) = \frac{0.722T_c^{4.2}}{T^{5.2}}$$

Therefore

$$\frac{dB}{dT} = \frac{RT_c}{P_c}\left(\frac{0.675T_c^{1.6}}{T^{2.6}} + \frac{0.722\omega T_c^{4.2}}{T^{5.2}}\right)$$

and

$$\left(\frac{\partial H}{\partial P}\right)_T = B - T\frac{dB}{dT}$$

$$= \frac{RT_c}{P_c}(B^0 + \omega B^1) - \frac{TRT_c}{P_c}\left(\frac{0.675T_c^{1.6}}{T^{2.6}} + \frac{0.722\omega T_c^{4.2}}{T^{5.2}}\right)$$

$$= \frac{RT_c}{P_c}\left(0.083 + 0.139\omega - \frac{1.097}{T_r^{1.6}} + \frac{0.550\omega}{T_r^{4.2}}\right)$$

using $R = 1.986 \frac{BTU}{lbmole\ ^\circ R}$

Calculation Method 2

Waddington et al (1949, p.803) correlates the second virial coefficient for thiophene specifically as

$$B = -0.435 - 0.0172\exp\left(\frac{1200}{T}\right)$$

with B expressed in liters/gmole and T in ^{o}K. As above,

$$\left(\frac{\partial H}{\partial P}\right)_T = B - \frac{TdB}{dT}$$

$$= -0.435 - 0.0172\exp\left(\frac{1200}{T}\right) - T\left(-0.0172\left(\frac{-1200}{T^2}\right)\exp\left(\frac{1200}{T}\right)\right)$$

$$= -0.435 - 0.0172\exp\left(\frac{1200}{T}\right)\left(1 + \frac{1200}{T}\right)$$

in liters/gmole. The desired units are $\frac{BTU}{lb_m\ psia}$, so to convert:

$$1\ \frac{liter}{gmole} = 0.03523\ \frac{BTU}{lb_m\ psia}$$

APPENDIX B

DERIVATION OF $\left(\frac{\partial C_P}{P}\right)_T$

Begin with the relation

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\,\frac{\partial^2 V}{\partial T^2}\,_P$$

As in Appendix A

$$V = \frac{RT}{P} + B$$

Calculation Method 1

Since B is independent of P

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT}$$

Then

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{RT_c}{P_c}\left(\frac{0.675T_c^{\,1.6}}{T^{2.6}} + \frac{0.722\omega T_c^{\,4.2}}{T^{5.2}}\right)$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = \frac{RT_c}{P_c}\frac{d}{dT}\left(\frac{0.675T_c^{\,1.6}}{T^{2.6}} + \frac{0.722\omega T_c^{\,4.2}}{T^{5.2}}\right)$$

$$= \frac{RT_c}{P_c}\left(\frac{-1.756T_c^{\,1.6}}{T^{3.6}} - \frac{3.756\omega T_c^{\,4.2}}{T^{6.2}}\right)$$

Therefore

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{RT_c}{P_c}\left(\frac{-1.756T_c^{\,1.6}}{T^{3.6}} - \frac{3.756\omega T_c^{\,4.2}}{T^{6.2}}\right)\right)$$

$$= \frac{RT_c}{P_c}\left(\frac{1.756T_c^{\,1.6}}{T^{2.6}} + \frac{3.756\omega T_c^{\,4.2}}{T^{5.2}}\right)$$

Calculation Method 2

As above

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT}$$

Then

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = \frac{d^2B}{dT^2} = \frac{d^2}{dT^2}\left(-0.435 - 0.0172\exp\left(\frac{1200}{T}\right)\right)$$

$$= \frac{d}{dT}\left(0.0172\left(\frac{1200}{T^2}\right)\exp\left(\frac{1200}{T}\right)\right.$$

$$= \frac{20.64}{T^2}\left(\frac{-1200\exp\left(\frac{1200}{T}\right)}{T^2}\right) + \left(\frac{-41.28}{T^3}\right)\exp\left(\frac{1200}{T}\right)$$

$$= \exp\left(\frac{1200}{T}\right)\left(\frac{-24768}{T^4} - \frac{41.28}{T^3}\right)$$

Thus

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\exp\left(\frac{1200}{T}\right)\left(\frac{-24768}{T^4} - \frac{41.28}{T^3}\right)\right)$$

$$= \exp\left(\frac{1200}{T}\right)\left(\frac{24768}{T^3} + \frac{41.28}{T^2}\right)$$

in liters/gmole °K. Again we must convert to the proper units:

$$1\ \frac{\text{liter}}{\text{gmole }^{\circ}\text{K}} = 0.0196\ \frac{\text{BTU}}{\text{lb}_m\ \text{psia }^{\circ}\text{R}}$$

APPENDIX C

```
C        THE FOLLOWING PROGRAM SOLVES FOR THE VAPOR PRESSURE AND
C        THE ENTHALPY AS A FUNCTION OF TEMPERATURE AT CONSTANT PRE-
C        SSURE OF A CHEMICAL USING THE SOAVE MODIFICATION OF THE
C        REDLICH-KWONG EQUATION OF STATE.
C        THE REQUIRED INPUT DATA IS ARE THE REFERENCE TEMPERATURE,
C        THE PRESSURE OF THE ISOBAR, THE CRITICAL TEMPERATURE, THE
C        THE CRITICAL PRESSURE, THE ACCENTRIC FACTOR, THE MOLECULAR
C        WEIGHT, AND THE COEFFICIENTS OF THE THIRD ORDER POLYNOMIAL
C        FORM OF THE IDEAL GAS HEAT CAPACITY.
       FUGCOF(Z,C2,C1)=EXP(Z-1.-ALOG(Z-C2)-C1/C2*
      $ ALOG((Z+C2)/Z))
 100     FORMAT  (1H1,'ENTHALPY CALCULATION FOR THIOPHENE',///)
 200     FORMAT  (1X,F6.3,3F14.2,3X,E12.5,10X,'V',5X,F10.5,2F15.2,F13.2)
 300     FORMAT  (1X,F6.3,3F14.2,3X,E12.5,10X,'L',5X,F10.5,2F15.2,F13.2)
 400     FORMAT  (1X,'P/BAR',9X,'T/K',8X,'H/J MOL-1',6X,'V,CC/MOL',7X,
      $'ROOT',11X,'PHASE',7X,'FUG COEFF',7X,'P/PSIA',8X,'T/F',7X,'H/BTU L
      $B-1',/)
 500     FORMAT  (4G)
 600     FORMAT  (1X,F10.5,10X,F10.5)
 700     FORMAT  (1H1,'LOCATING THE VAPOR PRESSURE ',///)
 800     FORMAT (1X,'T   TPRIME ',/)
 900     FORMAT (1H0,'WHAT ARE THE VALUES FOR THE COEFFICIENTS ON CP')
1000     FORMAT (1H0,'WHAT ARE THE VALUES FOR PC1,TC1,W1, AND BMW')
1100     FORMAT (1H0,'WHAT IS THE REFERENCE TEMP. AND SYSTEM PRESSURE')
1200     FORMAT (1H0,'T(REF)=',F8.2,8X,'P(SYS)=',F8.3)
1300     FORMAT (1H0,'PC1=',F5.2,5X,'TC1=',F8.2,
      $5X,'W1=',F5.3,5X,'BMW=',F7.3)
1400     FORMAT (1H ,'CP=',G,'+',G,'*T','+',G,'*T**2
      $','+',G,'*T**3',/)
         TYPE 900
       READ  (4,500) A0,B0,C0,D0
         TYPE 1000
       READ  (4,500) PC1,TC1,W1,BMW
         TYPE 1100
         READ (4,500) T,PSYS
       TYPE 700 ; TYPE 800
       R=8.31434
C CALCULATE THE COMMON PARAMETERS FOR BOTH PHASES
         FK1=.480+1.574*W1-.176*W1*W1
       B=.08664*R*TC1/PC1
```

```
C CALCULATE THE RESIDUAL ENTHALPY AT 25C AND 1 BAR.
      P=1.01325
      T1=T
      ID=+1
      CALL TS(B,T,A,C1,C2,TC1,EK1,PC1,P,R)
      CALL VCUB(A,B,P,R,T,V,Z,ID,ROOT)
      CALL ENTDEP(PC1,TC1,R,EK1,T,A,B,Z,C2,HDEP)
      H1=HDEP
      P=PSYS
      EXO=1.0
      T=700.0
C **********************
C **********************
C FROM 20 TO 21. SEARCHING FOR LOCATION OF NEGATIVE "ROOT"
C IF "ROOT" IS GT. 0. THERE IS ONE REAL ROOT(VOLUME)
C IF "ROOT"=0.. THERE ARE THREE REAL ROOTS(VOLUME). AT LEAST
C TWO OF WHICH ARE EQUAL
C IF "ROOT" IS LT. 0. THERE ARE THREE REAL UNEQUAL ROOTS(VOLUME)
C "ROOT" REFERS TO THE VARIABLE DEFINED IN SUBROUTINE VCUB.
C FOR ID=-1 VAPOR REGION  -  FOR ID=1 LIQUID REGION
C **********************
 20   T=T-5.**EXO
      ID=-1
      CALL TS(B,T,A,C1,C2,TC1,EK1,PC1,P,R)
      CALL VCUB(A,B,P,R,T,V,Z,ID,ROOT)
      IF (ROOT.GE.0.0) GOTO 20
      T=T+5.**EXO
      EXO=EXO-1
      IF (EXO.GT.-3.) GOTO 20
C IF THE PROGRAM DOES NOT WORK. THE MOST LIKELY PROBLEM IS
C AN INCORRECT STARTING TEMPERATURE.  ADJUST T AT STATEMENT 21 OR 20
 21   T=T-1.0
C **********************
C FROM 22 TO 5. SEARCHING FOR THE VAPOR PRESSURE
 22   ID=-1
      CALL TS(B,T,A,C1,C2,TC1,EK1,PC1,P,R)
      CALL VCUB(A,B,P,R,T,V,Z,ID,ROOT)
      P1V=FUGCOF(Z,C2,C1)
      ZV=Z
      VV=V
      ID=+1
      CALL VCUB(A,B,P,R,T,V,Z,ID,ROOT)
      P1L=FUGCOF(Z,C2,C1)
      ZL=Z
      VL=V
```

```
      TPRIME= ((P/83.1434)*(VL-VV))/(ALOG(P1V/P1L)+(ZL-ZV))
      IF (ABS(T-TPRIME).LT.0.001) GOTO 5
      TYPE 600,T,TPRIME
      DELT=T-TPRIME
      T=T-(DELT/10.)
      GOTO 22
5     TSATV=T
      TSATL=TSATV
C ********************
         TYPE 1200,T1,PSYS
         TYPE 1300,PC1,TC1,W1,BMW
         TYPE 1400,A0,B0,C0,D0
         TYPE 100
         TYPE 400
       K=1
      T=700.0
50    CALL IB(B,T,A,C1,C2,TC1,FK1,PC1,P,R)
      IF (T.GT.TSATV) ID=-1
      IF (T.EQ.(TSATV-5.0).AND.ID.EQ.-1) ID=1
      IF (T.LT.TSATV.AND.ID.EQ.-1) TOLD=T
      IF (T.LT.TSATV.AND.ID.EQ.-1) T=TSATV
        IF (K.EQ.-1) T=TOLD
      IF (T.EQ.(TSATV-5.0).AND.ID.EQ.1) T=TSATL
      CALL VCUB(A,B,P,R,T,V,Z,ID,ROOT)
      CALL ENTDEP(PC1,TC1,R,FK1,T,A,B,Z,C2,HDEP)
      H3=-HDEP
C CALCULATE THE IDEAL GAS DELTA H
      H2=(A0*(T-T1)+(B0/2.)*(T**2.-T1**2.)+(C0/3.)*(T**3.-
     *T1**3.)+(D0/4.)*(T**4.-T1**4.))*4.1840
      H=(H1 + H2 + H3)
      P1=FUGCOF(Z,C2,C1)
C P1 IS THE FUGACITY COEFFICIENT
      PSIA=14.50377*P
      TF=(T*1.8)-459.67
      HBTU=(H*453.59)/(1055.0*BMW)
      IF (ID.EQ.-1) TYPE 200,P,T,H,V,ROOT,P1,PSIA,TF,HBTU
      IF (ID.EQ.1) TYPE 300,P,T,H,V,ROOT,P1,PSIA,TF,HBTU
      IF (T.LT.100.0) STOP
       IF (T.EQ.TSATL.AND.ID.EQ.1) K=-1
       IF (T.EQ.TOLD) K=1
      T=T-5.
      GOTO 50
      END
      SUBROUTINE ENTDEP(PC1,TC1,R,FK1,T,A,B,Z,C2,HDEP)
      APRIME=.42747/PC1*(R*TC1)**2*2.*(1.+FK1-FK1*SQRT(T/TC1))*
     * (-FK1)*.5*(T/TC1)**(-.5)/TC1
      HDEP=R*T*(1.-Z)+(T*APRIME-A)/B*ALOG(Z/
     * (Z+C2))
      RETURN
      END
```

```
      SUBROUTINE VCUB(A,B,P,R,T,V,Z,ID,ROOT)
C SOLVE THE CUBIC EQUATION IN VOLUME FORM   (V**3+DV**2+EV+F=0)
      D=-R*T/P
      E=-(B*B+R*T*B/P-A/P)
      F=-A*B/P
      G=(3.*E-D*D)/3.
      H=-(9.*D*E-27.*F-2.*D*D*D)/27.
      ROOT=(G**3./27.+H*H/4.)
      IF (ROOT.LE.0.) GOTO 10
      S=(ABS(-H/2.+SQRT(G**3./27.+H*H/4.)))**(1./3.)
      IF ((-H/2.+SQRT(G**3./27.+H*H/4.)).LT.0.0) S=-1.*S
      TT=(ABS(-H/2.-SQRT(G**3./27.+H*H/4.)))**(1./3.)
      IF ((-H/2.-SQRT(G**3./27.+H*H/4.)).LT.0.0) TT=-1.*TT
C SINGLE REAL ROOT
      V=S+TT-D/3.
      GOTO 40
C THERE ARE THREE REAL ROOTS
 10   THETA = (ACOS(-.5*H/SQRT(-G**3./27.)))/3.
      V1=2.*SQRT(-G/3.)*COS(THETA)
      V2=2.*SQRT(-G/3.)*COS(THETA+2.0944)
      V3=2.*SQRT(-G/3.)*COS(THETA+4.1888)
C IF ID=-1 TAKE THE LARGEST V FOR THE VAPOR VOLUME.
C IF ID=1 TAKE THE SMALLEST V FOR THE LIQUID VOLUME.
      V=AMAX1(V1,V2,V3)-D/3.
      IF (ID.EQ.1) V=AMIN1(V1,V2,V3)-D/3
 40   Z=P*V/(R*T)
      V=V*10.
C ADJUST V BY 10 BECAUSE WE ARE USING R=8.31434
      RETURN
      END
      SUBROUTINE TR(B,T,A,C1,C2,TC1,FK1,PC1,P,R)
      TR1=T/TC1
      AL1=(1.+FK1*(1.-SQRT(TR1)))
      A=.42747*(R*TC1*AL1)**2/PC1
      C1=A*P/(R*R*T*T)
      C2=B*P/(R*T)
      RETURN
      END
```

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