

## THERMODYNAMIC TESTING AND CORRELATIONS

The experimental activity coefficient data were found to satisfy Herington's area condition (3). The data are correlated by Wilson's equations (5, 9):

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{12}}{\Lambda_{21}x_1 + x_2} \right] \quad (2)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right] \quad (3)$$

The values of the parameters  $\Lambda_{12}$  and  $\Lambda_{21}$  obtained from a least-squares fit are 0.19644 and 0.42955, respectively. The average deviations of the calculated activity coefficients from the experimental values are expressed by the following equation (6):

$$\omega_1 = \frac{\sum k_1^2 - (\sum k_1)^2 n_1^{1/2}}{n_1 - 1} \quad (4)$$

The small deviations ( $\omega_1 = -0.0602$  and  $\omega_2 = -0.0055$ ) indicate that Wilson's equations correlate the data very well.

### ACKNOWLEDGMENT

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### NOMENCLATURE

$K$  = deviation of calculated  $\ln \gamma$  from experimental  $\ln \gamma$   
 $P^0$  = pure component vapor pressure

$R$  = gas law constant  
 $T$  = absolute temperature  
 $V$  = molal liquid volume  
 $x$  = mole fraction in liquid phase  
 $y$  = mole fraction in vapor phase

### Greek Letters

$\beta$  = second virial coefficient  
 $\gamma$  = liquid activity coefficient  
 $\Lambda$  = Wilson's parameter  
 $\Sigma$  = summation  
 $\pi$  = total pressure  
 $\omega$  = defined deviation of  $k$  from mean value of  $k$

### Subscripts

1, 2 = components 1 and 2  
12, 21 = binary system

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# Vapor Pressure Relations of 36 Sulfur Compounds Present in Petroleum

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**Compilations of vapor pressures measured by static and ebulliometric methods, covering more than five orders of magnitude in pressure, are given for "key" members of classes of alkane thiols, alkane sulfides, alkane disulfides, and cyclic sulfides which were selected for a comprehensive study of their thermodynamic properties. Constants of the Antoine and Cox vapor pressure equations are provided as an aid to interpolating or extrapolating the experimental results.**

SINCE 1948 thermochemical studies of organic sulfur compounds either in or related to petroleum have been in progress at the Bureau of Mines under the sponsorship of the American Petroleum Institute Project 48A. The purpose of this paper is to assemble and summarize the vapor pressure-temperature relationships of 36 of the sulfur compounds selected from the program. Previously, White, Barnard-Smith, and Fidler (33) presented vapor pressure-temperature relationships and Antoine equation constants for 15 alkane sulfides, 8 alkane disulfides, 9 cyclic sulfides, and 3 thiophenes

During the early years of the program, when the pressure and temperature ranges were usually smaller than for the modern equipment now in use, the Antoine equation (1),  $\log p = A - B/(t + C)$ , was capable of representing

the results within experimental error and was adopted generally for correlating purposes. With improvements in apparatus that led to results of greater precision, accuracy, and range, the need for a more accurate equation became apparent. Also, the moderately polar character of sulfur compounds gives a type of behavior in vapor pressure that cannot be correlated accurately with the Antoine equation. Consequently, the Cox equation (4),  $\log(p/760) = A(1 - B.P./T)$  where  $\log A = a + bT + cT^2$ , was adopted because it was more versatile in fitting data. However, for the sake of continuity with previous work on sulfur compounds, the evaluation of Antoine constants was continued, and compounds previously correlated in terms of the Antoine equation were recorelated in terms of the Cox equation. Therefore, constants for both equations were

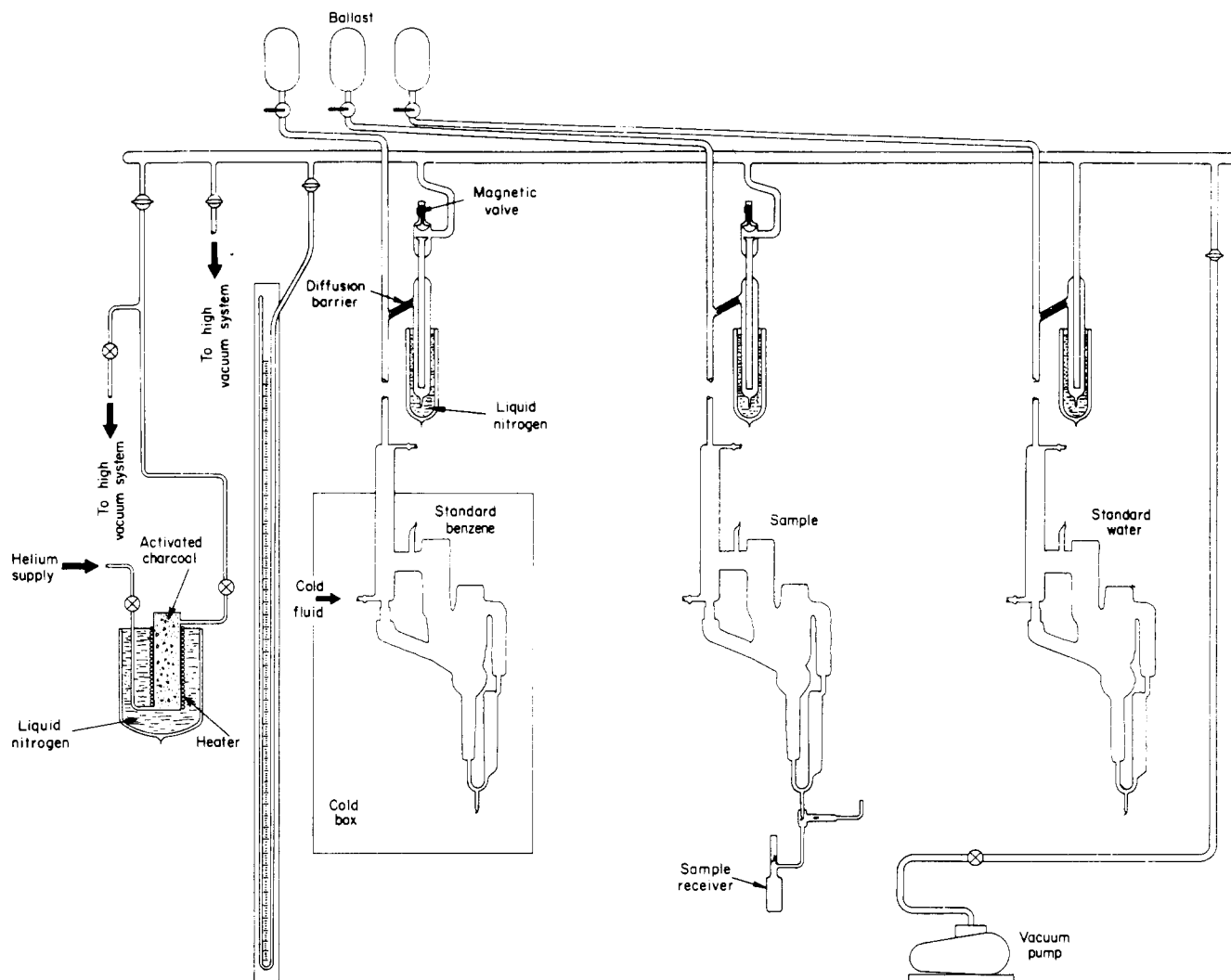


Figure 1. Comparative ebulliometric vapor pressure apparatus

included in the program to provide, for any specific application, a choice between the greater mathematical convenience of the Antoine equation or the greater accuracy of the Cox equation.

Some of the vapor pressure results given here were reported previously in the scientific literature. For those results, derived values of the constants in the correlating equations will appear recalculated in terms of the presently defined International Temperature Scale (30). Consequently, small differences from the constants originally published will appear.

#### MATERIALS

All samples were stock materials prepared and purified for the API Standard Sample Repository (Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.) by the Bureau of Mines Laramie Petroleum Research Center, Laramie, Wyo. Estimated purities of the compounds were determined from freezing temperature *vs.* fraction melted curves observed by the Low-Temperature Calorimetry Group at the Bartlesville Petroleum Research Center.

#### EXPERIMENTAL METHODS

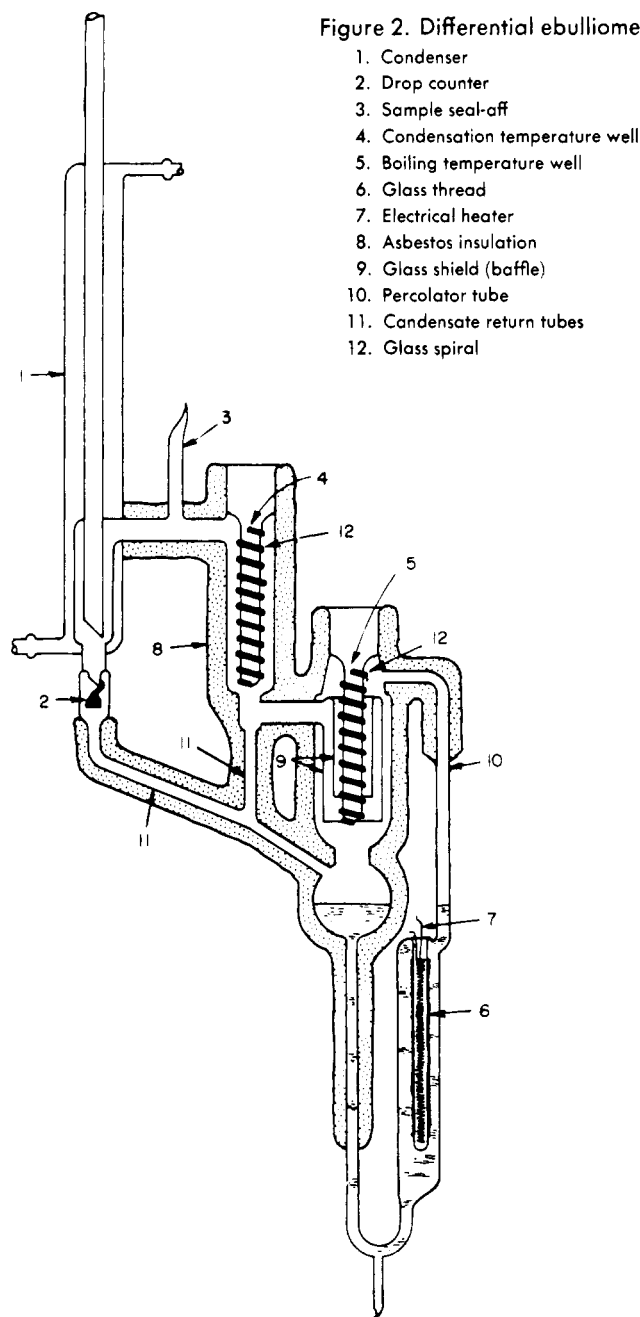
Vapor pressure measurements were made by three different methods. A static method, used to obtain part of the data for 2,3-dithiabutane and 3,4-dithiahexane, was described in an earlier publication (32) from this laboratory.

An inclined-piston method, described previously by Douslin and McCullough (5) and Douslin and Osborn (6), was used to obtain low pressure measurements on four compounds: 2,3-dimethyl-2-butanethiol, 2,2-dimethyl-1-propanethiol, 1-heptanethiol, and 1-decanethiol. Comparative ebulliometry was used on all compounds in some part of the reported range. Details of the comparative ebulliometric method and apparatus, an earlier version of which was described by Waddington, *et al.* (32), are given in the next section.

#### EBULLIOMETRIC APPARATUS

Measurements are made by directly comparing the boiling temperature of the sample with the boiling temperature of a suitable reference compound, in a common-pressure manifold system, Figure 1, blanketed with purified helium. From 150 to 2026 mm. of Hg, water served as the reference, and from 72 to 150 mm. of Hg, benzene served as the reference. The upper pressure limit was determined by the strength of the glass ebulliometers, and the lower pressure limit was determined by the boiling characteristics of water and benzene. Also, an upper temperature limit of about 200°C. was imposed by the design of the heating element in the boiler, Figure 2, and a lower temperature limit of about 3°C. was imposed by the capacity of the refrigerant system used to cool the surroundings in which the sample ebulliometer was housed. The reference water was deionized and distilled over potassium permanganate

Figure 2. Differential ebulliometer



to give a conductivity less than 1.0 micro-mho. The benzene was drawn from a central supply that was purified by distillation and certified to be 99.95% pure by freezing point determinations. Thus, the effect on the measured boiling temperatures of any possible impurities in the two reference substances was less than 0.001° C. Standard values of the vapor pressure of water were taken from the International Steam Tables (15) as reported by Osborne, *et al.* (16); values of benzene were taken from the API RP 44 "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds" (19). These standard values of water and benzene, at selected increments, are reproduced in the Appendix.

The differential ebulliometers, Figures 1 and 2, were based on a design described, in principle, by Swietoslawski (31). They consist of boiler and condenser sections provided with re-entrant wells for measurement of boiling and condensing temperatures. Each ebulliometer is connected to a common manifold through a diffusion barrier and is also connected

to a ballast with a volume of about 16.5 liters. Although the ebulliometers were encased in insulation to prevent heat loss, particularly around the thermometer wells, the percolation tube above the boiler heater remained essentially uninsulated so that any superheat created in the boiling liquid would be dissipated during its passage to the thermometer well. To provide the necessary cooling effect in the percolation tube, the surroundings were maintained at least 10° C. cooler than the boiling temperature of the liquid. The boiler section was, therefore, never enclosed in a Dewar or insulated vessel. The electrical heater unit was enclosed in a glass re-entrant well in the boiler with silicone fluid No. 704 for a heat-transmitting medium. To promote steady boiling, the inner surface of the well exposed to the sample was wrapped with glass thread.

Temperatures were measured with a precision of 0.001° on the International Temperature Scale [ $T, ^\circ\text{K.} = t, ^\circ\text{C.} (\text{Int., 1948}) + 273.15$ ] (30), by use of a 25-ohm platinum resistance thermometer that had been calibrated by the National Bureau of Standards and checked at the triple-point temperature of a certified benzoic acid cell. Periodic observations of the ice-point resistance of the thermometer showed no significant change. The ice-point resistance was obtained with the thermometer immersed about 150 mm. into a slush prepared by freezing distilled water with liquid air and decanting the excess water. Corrections (2) were applied to the ice-point resistance for the effects of atmospheric pressure and immersion pressure on the melting point of ice and the specific conductance of the water taken from the ice-point cell at the end of the measurement. The resistance of the thermometer was measured with a precision of  $2 \times 10^{-5}$  ohm on a Mueller G-2 bridge with a high sensitivity galvanometer. Each measuring coil in the bridge was calibrated, by the intercomparison of coils, in terms of a 100-ohm standard resistor certified by the National Bureau of Standards to 0.002%.

According to present procedure, the materials are dried by Molecular Sieve and then introduced directly from the drying section into the boiler through the sample inlet port by low-pressure distillation under a helium blanket. Thus the pure, dry samples are never in contact with air. They are recovered after the measurements in an evacuated break-off tip ampoule connected to the bottom of the boiler section of the sample ebulliometer.

Measurements were made along a series of pressure points that corresponded to preselected boiling temperatures of the reference substances given in the Appendix. At each point the pressure of the helium in the system was first adjusted approximately by mercury manometer; then boiling was started in the sample and reference compound; and finally, the boiling temperature of the reference was brought to the selected reference temperature by adjusting the helium pressure. Small observed differential temperatures of boiler and condenser, usually  $< 0.005^\circ\text{C.}$ , were taken to indicate adequate purity of sample. Any progressive increase in differential temperature at constant pressure would have meant sample deterioration by either decomposition or polymerization. To avoid the effects of small, steady pressure drifts beyond ballast control, it was necessary to take initial and final temperature readings on the reference substance and an intermediate reading on the sample. Then, by interpolating the boiling temperatures of the reference substance with respect to time, the equivalent of simultaneous boiling temperatures on sample and reference could be calculated. As a result of pressure drift the interpolated measurements were seldom at the exact preselected reference points; sometimes they were as much as 0.01° C. from the desired standard boiling point of the reference substance. The measured values were then adjusted exactly to the reference point by applying approximate vapor pressure-temperature relationships between sample and reference substance.

Table I. Experimental Vapor Pressures of Alkane Thiols: Ebulliometric Results<sup>a</sup>

Pressure, Mm. of Hg	Temperature, ° C.								
	Ethane- thiol (13)	1-Propane- thiol (17)	2-Propane- thiol (11)	1-Butane- thiol (26)	2-Butane- thiol (12)	2-Methyl- 1-propane- thiol (29)	2-Methyl- 2-propane- thiol (14)	1-Pentane- thiol (7)	2-Methyl- 1-butane- thiol
71.87	...	...	...	...	...	...	...	...	51.339
81.64	...	...	...	...	...	...	...	...	54.284
92.52	...	...	...	...	...	...	...	...	57.243
104.63	...	...	...	...	...	...	...	...	60.219
118.06	...	...	...	...	...	...	...	...	63.194
132.95	...	...	...	...	...	...	...	...	66.193
149.41	...	24.275	10.697	51.409	38.962	42.207	20.496	76.470	69.207
187.57	0.405	29.563	15.770	57.130	44.549	47.830	25.785	82.569	75.263
233.72	5.236	34.891	20.899	62.897	50.185	53.498	31.127	88.721	81.361
289.13	10.111	40.254	26.071	68.710	55.866	59.211	36.519	94.918	87.510
355.22	15.017	45.663	31.282	74.567	61.597	64.974	41.959	101.167	93.708
433.56	19.954	51.113	36.536	80.472	67.370	70.780	47.446	107.457	99.955
525.86	24.933	56.605	41.833	86.418	73.195	76.641	52.983	113.802	106.253
633.99	29.944	62.139	47.175	92.414	79.063	82.542	58.573	120.193	112.600
760.00	35.000	67.719	52.558	98.454	84.981	88.493	64.217	126.638	118.999
906.06	40.092	73.341	57.985	104.544	90.945	94.493	69.908	133.131	125.446
1074.6	45.221	79.004	63.461	110.682	96.963	100.539	75.654	139.671	131.944
1268.0	50.390	84.710	68.979	116.863	103.020	106.640	81.449	146.255	138.492
1489.1	55.604	90.464	74.540	123.088	109.133	112.785	87.294	152.896	145.089
1740.8	60.838	96.255	80.143	129.362	115.287	118.972	93.188	159.580	151.733
2026.0	66.115	102.088	85.795	135.679	121.489	125.212	99.138	166.314	158.428

Pressure, Mm. of Hg	2-Methyl- 2-butane- thiol (20)	3-Methyl- 2-butane- thiol	Cyclo- pentane- thiol (3)	1-Hexane- thiol	2-Methyl- 2-pentane- thiol	2,3-Di- methyl-2- butanethiol	Cyclo- hexane- thiol	Benzene- thiol (28)	1-Heptane- thiol (6)
	71.87	...	42.969	...	80.694	55.855	55.814	83.740	...
81.64	...	45.876	...	83.837	58.860	58.867	87.006	...	104.908
92.52	...	48.791	...	86.991	61.877	61.931	90.289	...	108.205
104.63	...	51.720	...	90.157	64.907	65.011	93.576	...	111.517
118.06	...	54.658	...	93.334	67.949	68.099	96.881	...	114.840
132.95	...	57.613	...	96.530	71.008	71.208	100.201	...	118.182
149.41	50.888	60.592	80.874	99.733	74.089	74.334	103.549	114.543	121.546
187.57	56.725	66.556	87.107	106.168	80.269	80.613	110.259	121.191	128.269
233.72	62.625	72.575	93.390	112.658	86.502	86.949	117.023	127.897	135.066
289.13	68.578	78.645	99.729	119.198	92.787	93.338	123.843	134.649	141.911
355.22	74.579	84.765	106.113	125.789	99.127	99.783	130.719	141.447	148.807
433.56	80.638	90.936	112.548	132.429	105.521	106.283	137.654	148.294	155.759
525.86	86.749	97.161	119.037	139.121	111.972	112.843	144.647	155.194	162.758
633.99	92.914	103.431	125.577	145.866	118.475	119.458	151.695	162.140	169.812
760.00	99.132	109.760	132.165	152.659	125.032	126.129	158.803	169.137	176.919
906.06	105.401	116.139	138.806	159.507	131.646	132.858	165.968	176.188	184.082
1074.6	111.728	122.571	145.501	166.403	138.314	139.644	173.186	183.278	191.292
1268.0	118.106	129.051	152.245	173.351	145.037	146.492	180.464	190.426	198.551
1489.1	124.537	135.585	159.040	180.349	151.815	153.391	187.801	197.623	...
1740.8	131.021	142.170	165.887	187.397	158.645	160.344	195.196	204.867	...
2026.0	137.559	148.805	172.783	194.494	165.531	167.355	202.645	212.160	...

<sup>a</sup> Results for 2,2-dimethyl-1-propanethiol and 3-methyl-1-butanethiol are in Table VIII.

## RESULTS

Observed values of the vapor pressures are summarized for 21 alkane thiols, Tables I, II, and VIII; for 7 alkane sulfides, Table III; for 3 alkane disulfides, Tables IV and V; and for 4 cyclic sulfides, Table VI. The measurements, which were accumulated over a period of years, are reported for four pressure ranges that developed from innovations or improvements in apparatus and method as time progressed. Some of the earliest measurements were obtained on 2,3-dithiabutane and 3,4-dithiahexane by a static, manometric method from 1 to 141 mm. of Hg, and by a comparative ebulliometric method, with water as reference substance, from 150 to 2026 mm. of Hg. Later the ebulliometric range was extended downward to 72 mm. of Hg by using pure benzene as a second reference substance. Finally, development of the inclined-piston gage made possible an extension of the range to still lower pressures, approximately 0.01 to 30 mm. of Hg. However, the vapor pressures of only four compounds, those listed in Tables II and VIII have been measured in the inclined-piston range. For one of these compounds, 2,3-dimethyl-2-butanethiol, the full range of the inclined-piston gage was not used because the measurements were confined to the liquid phase of the

Table II. Experimental Vapor Pressures of Alkane Thiols: Static Inclined-Piston Results

2,3-Dimethyl- 2-butanethiol		1-Heptanethiol (6)		1-Decanethiol (6)	
Pressure, Mm. of Hg	t, ° C.	Pressure, Mm. of Hg	t, ° C.	Pressure, Mm. of Hg	t, ° C.
8.272	12.493	0.211	0.000	0.006	10.000
9.561	15.000	0.247	2.500	0.011	15.000
11.034	17.500	0.317	5.000	0.014	20.000
12.694	19.999	0.384	7.500		
		0.458	10.000		
		0.553	12.500		
		0.663	15.000		
		0.943	20.000		

compound which freezes just below the lowest temperature recorded.

The experimental values, Tables I to VI and VIII, as well as values for 2-thiapropene and 3-methyl-2-thiabutane published by White, Barnard-Smith, and Fidler (33), were correlated by Antoine and Cox equations. Derived values for the constants in these equations were evaluated by a least-mean-square procedure according to the method outlined by Willingham, Taylor, Pignocco, and Rossini (34), with each experimental point assigned unit weight.

Table III. Experimental Data on Alkane Sulfides: Ebulliometric Results

Pressure, Mm. of Hg.	Temperature, ° C.						
	2-Thiabutane (25)	3-Thiapentane (23)	2-Thiahexane (10)	3,3-Dimethyl-2- thiabutane (27)	2,4-Dimethyl- 3-thiapentane	Cyclopentyl- 1-thiaethane	1-Phenyl- 1-thiaethane
71.87	...	...	...	33.713	52.101	82.745	117.146
81.64	...	...	...	36.543	55.052	85.956	120.530
92.52	...	...	...	39.388	58.010	89.177	123.912
104.63	...	...	...	42.242	60.990	92.416	127.321
118.06	...	...	...	45.107	63.980	95.654	130.728
132.95	...	...	...	47.990	66.983	98.917	134.156
149.41	23.435	45.920	73.752	50.890	70.011	102.197	137.606
187.57	28.695	51.536	79.798	56.709	76.075	108.769	144.514
233.72	33.997	57.204	85.888	62.586	82.193	115.396	151.477
289.13	39.339	62.905	92.025	68.507	88.366	122.068	158.487
355.22	44.717	68.659	98.211	74.478	94.588	128.797	165.548
433.56	50.136	74.452	104.442	80.507	100.863	135.575	172.658
525.86	55.600	80.286	110.725	86.585	107.192	142.411	179.821
633.99	61.104	86.169	117.048	92.706	113.574	149.293	187.036
760.00	66.655	92.100	123.423	98.892	120.007	156.230	194.306
906.06	72.241	98.073	129.847	105.128	126.493	163.222	201.622
1074.6	77.870	104.098	136.317	111.420	133.032	170.265	...
1268.0	83.551	110.165	142.839	117.761	139.623	177.364	...
1489.1	89.265	116.279	149.403	124.156	146.269	184.514	...
1740.8	95.020	122.433	156.019	130.595	152.965	191.714	...
2026.0	100.825	...	162.676	137.088	159.712	198.970	...

Table IV. Experimental Data on Alkane Disulfides: Ebulliometric Results

Pressure, Mm. of Hg	Temperature, ° C.		
	2,3-Dithia- butane (21)	3,4-Dithia- hexane (24)	4,5-Dithia- octane (8)
71.87	...	...	117.472
81.64	...	...	120.869
92.52	...	...	124.340
104.63	...	...	127.798
118.06	...	...	131.251
132.95	...	...	134.732
149.41	61.411	100.567	138.207
187.57	67.301	107.079	145.223
233.72	73.234	113.627	152.297
289.13	79.201	120.230	159.426
355.22	85.218	126.884	166.604
433.56	91.283	133.579	173.848
525.86	97.393	140.336	...
633.99	103.540	147.136	...
760.00	109.739	153.986	...
906.06	115.984	160.884	...
1074.6	122.273	...	...
1268.0	128.611	...	...
1489.1	...	...	...
1740.8	...	...	...
2026.0	...	...	...

Table V. Experimental Data on Alkane Disulfides: Static Manometric Results

t, ° C.	Pressure, Mm. of Hg	
	2,3-Dithia- butane <sup>a</sup> (21)	3,4-Dithia- hexane <sup>a</sup> (24)
0.00	6.78	0.76
15	16.73	2.22
20	22.02	3.10
25	28.69	4.23
30	36.98	5.74
35	47.26	7.66
40	59.82	10.14
45	75.06	13.32
50	93.37	17.28
55	115.20	22.18
60	141.11	28.20
65	...	35.56
70	...	44.47
75	...	55.16
80	...	67.96

<sup>a</sup> Average of two determinations.

Table VI. Experimental Data on Cyclic Sulfides: Ebulliometric Results

Pressure, Mm. of Hg	Temperature, ° C.			
	Thiacyclo- butane (22)	Thiacyclo- pentane (9)	2-Methyl- thiacyclo- pentane	3-Methyl- thiacyclo- pentane
71.87	...	...	62.633	67.540
81.64	...	...	65.683	70.633
92.52	...	...	68.744	73.733
104.63	...	...	71.813	76.849
118.06	...	...	74.898	79.973
132.95	...	...	77.997	83.112
149.41	48.357	71.182	81.114	86.270
187.57	54.044	77.278	87.359	92.606
233.72	59.771	83.405	93.661	98.990
289.13	65.534	89.580	100.004	105.423
355.22	71.341	95.803	106.398	111.905
433.56	77.187	102.056	112.840	118.436
525.86	83.073	108.365	119.336	125.019
633.99	88.998	114.716	125.877	131.648
760.00	94.968	121.114	132.471	138.330
906.06	100.977	127.558	139.114	145.062
1074.6	107.027	134.046	145.809	151.846
1268.0	113.118	140.574	152.555	158.679
1489.1	119.249	147.163	159.352	165.561
1740.8	125.421	153.775	166.197	172.495
2026.0	131.639	160.451	173.090	179.476

Alternatively, a least-mean-square evaluation of the constants in the Cox equation could not be approached directly as for the Antoine equation. However, a Cox equation that is very close to a formal least-mean-square solution of the experimental results was derived by adjusting its constants while keeping the deviations between calculated and observed values always less than the deviations given by the least-mean-square Antoine equation for the same set of points. This method of deriving Cox constants seemed to work quite well even in special cases—for example, 2,2-dimethyl-1-propanethiol and 2,3-dimethyl-2-butanethiol—where least-mean-square Antoine equations that would represent the observed results with acceptable accuracy could not be derived. By proceeding as described, Cox equations were obtained which represented, in nearly every case, the experimental data more accurately over a wider temperature range than did the corresponding Antoine equation. Detailed results for two compounds, Table VIII, demonstrate the usual performance of each equation.

Tables of boiling temperatures at even pressures based on the Cox equations will be made available to any interested person by request addressed to the Bureau of

Table VII. Constants of the Antoine and Cox Vapor Pressure Equation

Compound	Purity, Mole %	Constants of Antoine Equation			Standard Deviation, Mm. of Hg	Constants of the Cox Equation			Standard Deviation, Mm. of Hg
		A	B	C		a	b × 10 <sup>-4</sup>	c × 10 <sup>-7</sup>	
Ethanthiol	99.978	6.95206	1084.531	231.385	0.17	0.818329	-7.18956	8.02409	0.15
1-Propanethiol	99.985	6.92846	1183.307	224.624	0.08	0.832530	-7.16756	7.37109	0.03
2-Propanethiol	99.989	6.87734	1113.895	226.157	0.06	0.830445	-7.61346	8.18602	0.04
1-Butanethiol	99.990	6.92754	1281.018	218.100	0.10	0.843563	-6.91825	6.53302	0.05
2-Butanethiol	99.9 <sup>c</sup>	6.89698	1229.904	222.021	0.10	0.833712	-7.12952	7.10737	0.03
2-Methyl-1-propanethiol	99.99	6.88746	1237.282	220.313	0.11	0.840128	-7.25874	7.16173	0.05
2-Methyl-2-propanethiol	99.989	6.87871	1115.565	221.314	0.10	0.843650	-8.28280	8.78380	0.05
1-Pentanethiol	99.944	6.93311	1369.479	211.314	0.11	0.863844	-7.16655	7.29159	0.04
2,2-Dimethyl-1-propanethiol <sup>b,c</sup>		6.84006	1274.353	218.187	0.09	0.844496	-7.48718	6.45783	0.04
2-Methyl-1-butane <sup>b</sup>		6.91385	1347.317	215.072	0.09	0.851295	-7.04489	7.29159	0.04
3-Methyl-1-butane <sup>b</sup>		6.91491	1342.509	214.446	0.05	0.850516	-7.04489	6.50881	0.03
2-Methyl-2-butane <sup>b</sup>	99.89	6.82837	1254.885	218.759	0.13	0.842972	-6.91250	6.28310	0.03
3-Methyl-2-butane <sup>b</sup>	99.996	6.87521	1307.162	217.488	0.09	0.838139	-7.56801	7.46880	0.05
Cyclopentanethiol	99.99	6.91375	1387.803	211.952	0.07	0.850756	-6.84930	6.39177	0.02
1-Hexanethiol	99.97	6.94664	1454.004	204.954	0.07	0.877159	-6.66744	5.85098	0.01
2-Methyl-2-pentanethiol <sup>b</sup>		6.85849	1343.804	212.803	0.07	0.850841	-7.06393	5.98143	0.01
2,3-Dimethyl-2-butanethiol <sup>b,c</sup>		6.83943	1354.154	215.947	0.09	0.835466	-6.71995	6.39145	0.03
Cyclohexanethiol	99.978	6.88709	1476.958	209.857	0.06	0.846929	-6.38262	5.36868	0.05
Benzenethiol	99.98	6.99019	1529.454	203.048	0.07	0.872514	-6.44146	5.16493	0.04
1-Heptanethiol <sup>f</sup>	99.97	6.95249	1525.311	197.696	0.04	0.897168	-7.29517	5.95229	0.02
SULFIDES									
2-Thiopropane	99.95	6.94879	1090.755	230.799	0.10	0.833669	-7.20206	7.44489	0.09
2-Thiabutane	99.998	6.93849	1182.562	224.784	0.08	0.839793	-6.77471	6.37205	0.05
3-Thiopentane	99.995	6.92836	1257.833	218.662	0.08	0.857733	-6.86510	6.11472	0.04
2-Thiathane	99.96	6.94583	1363.808	212.074	0.08				
3-Methyl-2-thiabutane	99.8	6.90196	1232.170	221.670	0.11				
3,3-Dimethyl-2-thiabutane	99.98	6.84709	1259.648	218.692	0.12	0.836063	-7.04177	6.71654	0.09
2,4-Dimethyl-3-thiapentane	99.992	6.87487	1328.942	212.722	0.07	0.860511	-7.47503	6.92767	0.04
Cyclopentyl-1-thiathane	99.986	6.94462	1483.379	208.784	0.11	0.849172	-6.07268	4.93503	0.04
1-Phenyl-1-thiathane	99.97	7.01149	1603.887	193.984	0.06	0.904411	-6.97893	5.40851	0.03
DISULFIDES									
2,3-Dithiabutane	99.97	6.97792	1346.342	218.863	0.12	0.844338	-6.69483	6.17889	0.04
3,4-Dithiathane	99.92	6.97507	1485.970	208.958	0.05	0.885753	-7.79157	7.11901	0.02
4,5-Dithiooctane	99.97	6.97529	1603.793	195.848	0.06	0.918895	-8.06535	6.82511	0.05
CYCLIC SULFIDES									
Thiacyclobutane	99.988	7.01667	1321.331	224.513	0.04	0.819904	-5.86488	5.52129	0.04
Thiacyclopentane	99.987	6.99540	1401.939	219.607	0.10	0.822304	-5.57266	4.83166	0.10
2-Methylthiacyclopentane	99.76	6.94412	1409.503	214.408	0.10	0.838967	-6.13330	5.26227	0.03
3-Methylthiacyclopentane	99.95	6.95111	1433.157	213.766	0.06	0.840672	-6.12052	5.22293	0.02

<sup>a</sup> Purity estimated from mass and infrared spectral analyses. <sup>b</sup> Purity not determined. However, small observed differences between boiling and condensing temperatures indicated that the sample was of high purity. <sup>c</sup> Antoine equation fitted to the ebulliometric results.

Table VIII. Comparison of Observed and Calculated Values

Observed		$p(\text{Obsd.}), \text{Mm.} - p(\text{Calcd.}), \text{Mm.}$	
Pressure, Mm. of Hg	$t, ^\circ\text{C.}$	Antoine Eq. <sup>a</sup>	Cox Eq. <sup>a</sup>
3-METHYL-1-BUTANETHIOL			
71.87	50.952	+0.02	-0.01
81.64	53.895	0.00	-0.02
92.52	56.838	+0.01	0.00
104.63	59.800	0.00	+0.01
118.06	62.770	0.00	+0.02
132.95	65.757	-0.01	+0.01
149.41	68.760	-0.05	-0.03
187.57	74.786	-0.05	-0.03
233.72	80.862	-0.04	-0.03
289.13	86.984	-0.01	-0.02
355.22	93.155	+0.03	0.00
433.56	99.378	+0.05	-0.01
525.86	105.648	+0.08	+0.01
633.99	111.970	+0.08	-0.01
760.00	118.341	+0.07	0.00
906.06	124.762	+0.05	0.00
1074.6	131.234	0.0	0.0
1268.0	137.754	0.0	+0.1
1489.1	144.327	-0.1	0.0
1740.8	150.949	-0.1	0.0
2026.0	157.618	0.0	0.0
2,2-DIMETHYL-1-PROPANETHIOL			
0.073 <sup>b</sup>	-60.069	+0.013	0.000
0.125 <sup>b</sup>	-55.419	+0.022	+0.005
0.195 <sup>b</sup>	-50.619	+0.023	-0.001
0.316 <sup>b</sup>	-45.768	+0.035	+0.004
0.495 <sup>b</sup>	-40.925	+0.047	+0.008
0.748 <sup>b</sup>	-36.027	+0.049	+0.001
1.213 <sup>b</sup>	-30.184	+0.060	+0.001
1.764 <sup>b</sup>	-25.344	+0.059	-0.009
2.552 <sup>b</sup>	-20.453	+0.067	-0.008
3.634 <sup>b</sup>	-15.551	+0.076	-0.005
5.079 <sup>b</sup>	-10.664	+0.075	-0.009
7.014 <sup>b</sup>	-5.753	+0.076	-0.009
9.898 <sup>b</sup>	-0.266	+0.074	-0.006
13.447 <sup>b</sup>	+4.851	+0.067	-0.005
18.062 <sup>b</sup>	10.004	+0.054	-0.006
23.767 <sup>b</sup>	15.001	+0.045	+0.001
30.918 <sup>b</sup>	19.998	+0.030	+0.003
71.87	37.527	0.00	+0.04
81.64	40.395	+0.01	+0.06
92.52	43.282	0.00	+0.05
104.63	46.180	0.00	+0.05
118.06	49.086	+0.01	+0.06
132.95	52.009	+0.01	+0.06
149.41	54.953	-0.04	+0.01
187.57	60.860	-0.04	0.00
233.72	66.819	-0.02	-0.01
289.13	72.829	+0.01	0.00
355.22	78.892	+0.04	0.00
433.56	85.009	+0.06	0.00
525.86	91.179	+0.06	-0.01
633.99	97.401	+0.07	+0.02
760.00	103.680	+0.01	0.00
906.06	110.010	-0.03	+0.03
1074.6	116.396	-0.1	+0.1
1268.0	122.831	-0.1	+0.1
1489.1	129.325	-0.2	0.0
1740.8	135.869	-0.1	+0.1
2026.0	142.464	+0.3	0.0

<sup>a</sup>Pressure differences calculated using Antoine and Cox vapor pressure constants given in Table VII. <sup>b</sup>Inclined-piston data.

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#### APPENDIX

Standard vapor pressure values for water, based on the International Steam Tables (IST), and standard values for

#### Appendix

Water Reference Substance		Benzene Reference Substance	
Boiling Temperature, $^\circ\text{C.}$	Pressure, Mm. of Hg	Boiling Temperature, $^\circ\text{C.}$	Pressure, Mm. of Hg
60	149.41	19.061	71.87
65	187.57	21.720	81.64
70	233.72	24.388	92.52
75	289.13	27.068	104.63
80	355.22	29.757	118.06
85	433.56	32.460	132.95
90	525.86	35.174	149.41
95	633.99		
100	760.00		
105	906.06		
110	1074.6		
115	1268.0		
120	1489.1		
125	1740.8		
130	2026.0		

benzene, based on the American Petroleum Institute Research Project 44 (API RP 44) Tables, are slightly inconsistent with each other below a water temperature of 100 $^\circ\text{C.}$  At the juncture of the two reference scales, 149.41 mm. of Hg, the observed vapor pressures of the samples being studied would consequently be about 0.05 mm. of Hg higher on the benzene scale than on the water scale. The difference in the two scales originated with the "Stimson and Cragoe" corrections which Rossini, *et al.* (18), applied to the IST water values and, thus, through the use of water as a calibration substance, introduced into the benzene vapor pressure values. In the present vapor pressure work the "Stimson and Cragoe" corrections were not applied to the standard water values; however, this correction is inherently present in the benzene standard values. Since the "Stimson and Cragoe" corrections to the IST values are small and have not appeared in the scientific literature, they were ignored in the present work with the water scale and also in the correlating equations. Should the IST water values or the API RP 44 benzene values be adjusted at some future time, pertinent small changes in the standard values could, if needed, be applied to the comparative ebulliometric vapor pressure results.

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## Heat Capacities of the Liquid Phase in the System $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$

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Measurements were made of the heat capacities at 25°, 50°, and 80° C. of solutions in the system  $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ , and the measured specific heats were converted to partial molal heat capacities of the calcium phosphates  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{CaHPO}_4$ .

Thermal data on the solid and liquid phases in the system  $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$  are useful in interpretation of the reactions involved in fertilizer manufacturing processes and in the behavior of fertilizers in the soil. Measurements were made of the specific heats of liquid phases in the system at 25°, 50°, and 80° C., and the partial molal quantities were derived from the results. The specific heats, with the heats of solution at the same composition (2), may be used to determine the temperature dependence of other physical properties of the solutions, such as vapor pressure and electrochemical potentials. The specific heats of the solution are of direct value in engineering calculations involving calcium phosphate solutions.

The measured specific heats of the solutions were converted to partial molal heat capacities of the calcium phosphates  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{CaHPO}_4$ , and  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ . For these conversions, the solution compositions were recalculated to represent each of the four ternary systems comprising a single calcium phosphate, phosphoric acid, and water.

### MATERIALS AND APPARATUS

**Phosphoric Acid.** Phosphoric acid hemihydrate,  $2\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ , was twice recrystallized from reagent phosphoric acid (3). The drained, unwashed crystals were melted to form a stock solution (90%  $\text{H}_3\text{PO}_4$ ), the exact composition of which was established by its density (1).

**Dicalcium Phosphate.** A solution (5) containing 5%  $\text{CaO}$ , 21%  $\text{P}_2\text{O}_5$ , and 74%  $\text{H}_2\text{O}$  was prepared from reagent dicalcium phosphate and the stock phosphoric acid. The solution was filtered, then heated to crystallize anhydrous dicalcium phosphate.

**Preparation of Solutions.** The compositions of the solutions used in the measurements were intersections of "water rays" (9) of constant ratios  $\text{P}_2\text{O}_5:\text{CaO}$  with tielines between  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and 0.5, 1, 1.5, 2, 3, 4, 6, 8, and 10 molal phosphoric acid solutions. The weight ratios  $\text{P}_2\text{O}_5:\text{CaO}$  selected for the water rays were 39.180, 19.081, 12.706, 9.514, 7.596, 6.314, 5.396, 4.705, and 4.161. The most concentrated solution on each water ray was prepared by