Azeotrope Formation between Thiols and Hydrocarbons

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An investigation into the azeotropes formed between the seven C_2, C_3, and C_4 thiols and 28 different hydrocarbons has been carried out. As a result, 55 azeotropes between thiols and paraffins and naphthenes have been determined and their physical properties measured. Benzene formed no azeotropes with any of these thiols. The experimental results have been correlated and shown to fit satisfactorily equations recently put forward by Skolnik to cover azeotropes of benzene with hydrocarbons. In addition, it has been shown that the plot of the boiling point of the pure hydrocarbons against the mole per cent of thiol gives a straight-line relationship for each individual thiol. These correlations have allowed the prediction of 17 azeotropes between these thiols and other hydrocarbons. Furthermore, predictions have been made for azeotropes between paraffins and straight-chain thiols such as methanethiol, 1-pentanethiol, 1-hexanethiol, etc., which have not been used in this work.

IF A sulfur distribution is carried out on a petroleum distillate, the majority of the sulfur-containing fractions appear at boiling points which correspond to no known sulfur compounds. This is an indication that azeotropes are formed between sulfur compounds and hydrocarbons, which is perhaps to be expected, for even the different types of hydrocarbons are known to form azeotropes among themselves (1, 4, 16).

In the past few years a number of articles have appeared in the literature dealing either with the theoretical (3, 5, 7, 14) or the practical (6, 11, 15, 17, 22) side of azeotrope formation. Furthermore, a paper of the utmost practical value is the "Table of Azeotropes and Nonazeotropes" recently published by Horsley (10), which collects all the available information on binary and ternary mixtures known to form maximum or minimum boiling point azeotropes. In addition, it also details systems which have been shown not to form azeotropes.

The azeotropic data for hydrocarbons with sulfur compounds found in petroleum distillates have been abstracted from Horsley's tables and are given in Table I. It is apparent that the information available on the occurrence and properties of these azeotropes is extremely limited, which is surprising because hydrocarbons are found associated with sulfur compounds not only in petroleum products but also in coal tars and shale oils. [A recent paper by Lecat (13) includes three further azeotropes with hydrocarbons and sulfur compounds present in straight-run petroleum naphthas. A few more nonazeotropic systems are also given.]

A program of research has been initiated in these laboratories designed to increase knowledge of the chemical and physical properties of the sulfur compounds present in petroleum distillates. The work, of which the present paper forms a part, is concerned with the separation of sulfur compounds from petroleum by distillation and, consequently, information on the vapor-liquid relationships between the various types of hydrocarbons and sulfur compounds is of both fundamental interest and practical value.

MATERIALS EMPLOYED

The thiols were the first group of sulfur compounds to become available and these were prepared in sufficient quantity for vapor-liquid equilibrium studies to be carried out on mixtures with various classes of hydrocarbons.

All the C_2, C_3, and C_4 thiols, with the exception of 2-methyl-2-propanethiol (tert-butyl mercaptan), were prepared from a bulk quantity of mixed thiols, which had been obtained from the soda-recovery system of a plant used for the caustic soda washing of a naphtha of approximately 120° C. end point. This was first distilled through a 25-plate column and four fractions were prepared, having the boiling ranges 25° to 45°, 45° to 60°, 60° to 70°, and 70° to 110° C. Distillation of the first three fractions in 100-plate columns served to give ethane-, 2-propane-, and 1-propanethiol, respectively. Refractionation of the 70° to 110° C. cut in a 100-plate column served to give 1-butanethiol, 2-methyl-1-propanethiol, and a series of fractions consisting of azeotropes of 2-butanethiol with various hydrocarbons. The 2-butanethiol was prepared from these latter fractions by extractive distillation, using aniline as the washing agent.

2-Methyl-2-propanethiol was synthesized by the action of sulfur on tert-butylmagnesium chloride (19).

The properties of the thiols employed are given in Table II.

Table I. Azeotropes between Hydrocarbons and Sulfur Compounds

(Taken from Horsley's table, 10)

Component	B.P. of Component, ° C.	Properties of Azeotropes	
		B.P., ° C.	Sulfur compound in azeotrope, wt. %
2-Thiapropane	37.2		
2-Methylbutane	27.95	27.3	15
n-Pentane	36.15	33.5	45
Ethanethiol	36.2		
2-Methylbutane	27.95	Nonazeotropic	
n-Pentane	36.15	32	50
1-Propanethiol	67.5		
n-Hexane	68.95	65	55
2-Methyl-1-propanethiol	88		
Benzene	80.20	Nonazeotropic	
3-Thiapentane	92.3		
Benzene	80.2	Nonazeotropic	
Cyclohexane	80.75	Nonazeotropic	
Methylcyclohexane	101.1	Nonazeotropic	
4-Thiaheptane	140.8		
m-Xylene	139.0	137.5	..

Table II. Physical Properties of Thiols

Thiol	B.P., ° C.	Refractive Index, n_D^{20}	Density, d^{20}	F.P., ° C.	Estimated Purity, Mole %
Ethanethiol	35.04	1.4313	0.8375	−147.97	99.9
1-Propanethiol	67.82	1.4380	0.8407	−113.80	99.0
2-Propanethiol	52.60	1.4256	0.8142	−130.63	99.5
1-Butanethiol	98.58	1.4426	0.8408	−116.12	99.1
2-Butanethiol	85.15	1.4367	0.8294	....[a]	..
2-Methyl-1-propanethiol	88.72	1.4386	0.8350	....[a]	..
2-Methyl-2-propanethiol	64.35	1.4230	0.7999	+ 0.82	99.9

[a] Freezing point determination could not be carried out owing to excessive viscosities of these thiols at low temperatures.

The hydrocarbons used in this work were available as a result of syntheses and separations carried out over a period of many years in the research laboratories of the Anglo-Iranian Oil Company. Their properties are given in Table III.
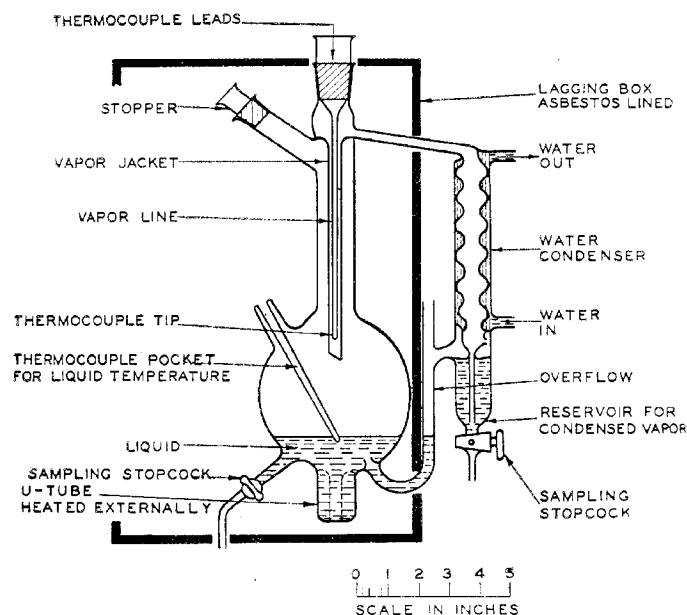
Figure 1. Othmer Still with Lagging Box

DETERMINATION OF PHYSICAL PROPERTIES

BOILING POINT

Thermocouples were used to measure the vapor temperatures in the equilibrium stills. They were of copper-constantan, glass-insulated, and their calibrations were made available by the kindness of M. R. Fenske of Pennsylvania State College. A double junction was used in this work, the temperatures being measured to ±0.05° C.

The boiling points were measured to within 0.05° C. by mercury-in-glass thermometers in a Cottrell-type apparatus (8). Barometric corrections were based on Young's formula (9).

REFRACTIVE INDEXES AND DENSITIES

The refractive indexes were measured for the sodium D line in a Pulfrich refractometer at 20° ± 0.01° C. and are accurate to ±0.0001. Densities, corrected for buoyancy, were measured at 20° ± 0.01° C. in a calibrated 5-ml. pycnometer and are accurate to within 1 unit in the fourth decimal place.

FREEZING POINTS AND PURITIES

The freezing points and purities of the materials used were determined according to the method of Rossini (20).

EQUILIBRIUM STILLS

At the commencement of the work, the vapor-liquid relationships between the propanethiols and a number of hydrocarbons were studied in equilibrium stills. In this way, the nonideality of mixtures of the two classes of compounds was demonstrated.

The first still employed was of the Othmer (18) type, the design of which was modified to include a thermocouple for measurement of the equilibrium temperature. In addition, an electrically heated box made of ¹/₈-inch Sindanyo board (compressed asbestos) lined with asbestos was built to enclose the boiling chamber and vapor lines as shown in Figure 1. This not only prevented reflux formation in the vapor lines, but by excluding draughts contributed materially to the smooth running of the still. The actual heating of the box was done by heating mats attached to the inner walls and also a 15-watt lamp which served to illuminate the interior. The equilibrium chamber and a thermometer suspended inside the box were observed through

a double-glass window, which formed the whole front of the box. The entire apparatus was supported on a specially constructed stand. It was found by experience that the optimum temperature for the air space was about 10° C. below the equilibrium temperature being measured in the still.

A further equilibrium still of the Jones, Schoenborn, and Colburn (12) type was also used. This differs from the Othmer still, inasmuch as the condensed vapor is revaporized before returning to the liquid chamber. The designers claim that this overcomes certain inherent disadvantages of the Othmer still. The Jones-Schoenborn-Colburn still was used in the present work on account of its simplicity of construction, quickness in reaching equilibrium (40 minutes), and the small charge required. A recent paper (2) has described the use of this form of equilibrium still for determining the vapor-liquid relationships of hydrazine hydrate with water.

Only two variations in construction from that described by the inventors were introduced. First, a thermocouple 9 inches long was fitted into the vapor line through a ground-glass joint, and secondly, as with the Othmer still, an electrically heated rectangular box was fitted around the equilibrium chamber and vapor line. The temperature of the lagging box was again maintained about 10° C. below the equilibrium temperature. The operational technique of the stills was substantially identical with that described by their respective designers.

The two-component systems, which were examined in the equilibrium stills, were n-hexane, methylcyclopentane, 2-methylpentane, n-pentane, and cyclohexane with 1-propanethiol and cyclopentane with 2-propanethiol. The vapor-liquid equilibrium data so obtained are given in Tables IV to VI. These tables show the experimentally determined equilibrium temperatures and composition of the liquids and vapors in equilibrium, while the relative volatilities and activity coefficients were calculated by applying the usual formulas. Because, in order to calculate the activity coefficients, it is necessary to know the vapor pressures of the pure components at the equilibrium temperatures, the values for the hydrocarbons were obtained by interpolation from data of Rossini and others (21). The figures for 1-propanethiol were obtained by extrapolation of data of Taylor and Layng (23). As there are no reported vapor pressure-temperature data for 2-propanethiol, the activity coefficient for this component is not presented.

Graphical representation of some of these data is given in Figures 2 to 7. Figures 2, 4, and 6 give the isobaric phase diagrams and also the plot of relative volatility against the molar composition of the liquid. From these, the composition and boiling points of the azeotropes were obtained by interpolation

Table III. Physical Properties of Hydrocarbons Used for Azeotropes

(In order of boiling point)

| Hydrocarbon	B.P. at 760 Mm., ° C.	Refractive Index, n_D^{20}	Density, d^{20}	F.P., ° C.	Estimated Purity, Mole %
2-Methylbutane	27.90	1.3539	0.6196	.....	...
n-Pentane	36.15	1.3576	0.6260	.....	...
Cyclopentane	49.35	1.4063	0.7455	−96.09	98.8
2,2-Dimethylbutane	49.70	1.3688	0.6492	−100.3	99.8
2,3-Dimethylbutane	58.10	1.3749	0.6616	−128.68	99.90
2-Methylpentane	60.40	1.3717	0.6530	.....	...
3-Methylpentane	63.35	1.3768	0.6642	.....	...
n-Hexane	68.75	1.3759	0.6593	−95.56	98.8
Methylcyclopentane	71.85	1.4099	0.7488	−142.945	97.6
2,2-Dimethylpentane	79.20	1.3821	0.6735	.....	...
Benzene	80.10	1.5012	0.8790	+5.494	99.93
2,4-Dimethylpentane	80.55	1.3814	0.6724	−119.314	99.9
Cyclohexane	80.85	1.4262	0.7785	+6.47	99.97
2,2,3-Trimethylbutane	81.05	1.3893	0.6899	−25.13	99.9
1,1-Dimethylcyclopentane	87.90	1.4135	0.7544	−69.91	99.84
2,3-Dimethylpentane	89.90	1.3919	0.6944	.....	...
2-Methylhexane	90.15	1.3849	0.6786	.....	...
trans-1,3-Dimethylcyclopentane	90.80	1.4090	0.7444	−133.97	99.0
3-Methylhexane	91.60	1.3889	0.6871	.....	...
n-Heptane	98.40	1.3876	0.6835	−90.700	99.47
2,2,4-Trimethylpentane	99.30	1.3915	0.6917	−107.417	99.89
cis-1,2-Dimethylcyclopentane	99.60	1.4221	0.7726	−54.02	99.95
Methylcyclohexane	101.05	1.4229	0.7694	−126.34	99.95
Ethylcyclopentane	103.45	1.4200	0.7665	.....	...
2,2-Dimethylhexane	106.85	1.3934	0.6952	−121.56	98.7
2,5-Dimethylhexane	109.15	1.3925	0.6933	−91.204	99.95
Toluene	110.85	1.4968	0.8667	−95.013	99.95
3,3-Dimethylhexane	112.20	1.4002	0.7102	−126.47	98.5
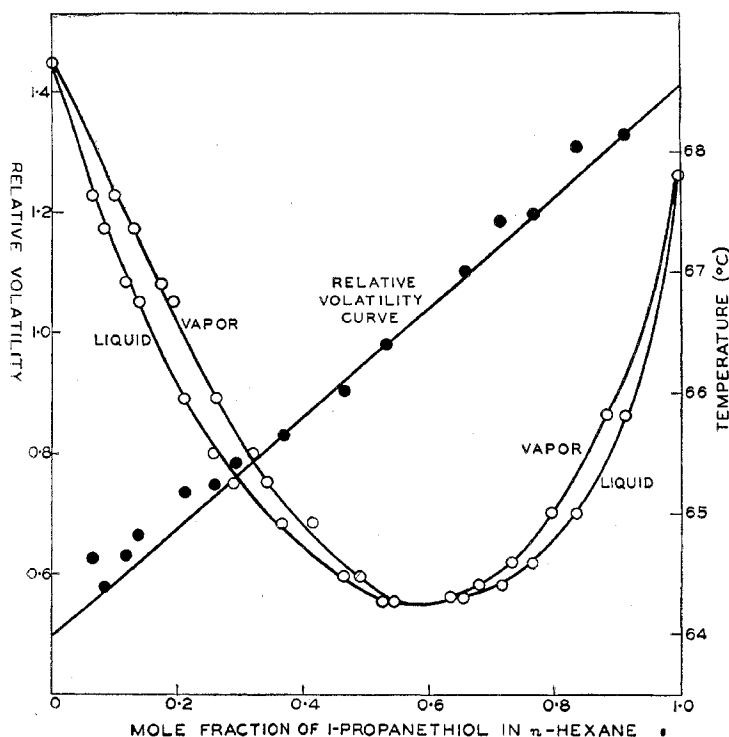
Figure 2. Vapor-Liquid Equilibrium Data for
1-Propanethiol in n-Hexane

Table IV. Vapor-Liquid Equilibrium Data at 760 Mm. Pressure

Temperature, °C.	Mole Fraction of Thiol		Relative Volatility	Log₁₀ Activity Coefficient	
	Vapor	Liquid		Hydrocarbon	Thiol
		1-Propanethiol and n-Hexane			
68.75	0.000	0.000	...	0.000	...
67.64	0.100	0.065	0.625	1̄.998	0.178
67.36	0.135	0.083	0.580	1̄.993	0.210
66.91	0.175	0.118	0.631	1̄.995	0.176
66.76	0.191	0.136	0.667	1̄.990	0.155
65.97	0.265	0.210	0.737	0.006	0.120
65.52	0.317	0.258	0.749	0.008	0.114
65.27	0.342	0.289	0.782	0.014	0.101
64.93	0.417	0.370	0.831	0.018	0.085
64.48	0.490	0.465	0.905	0.038	0.063
64.26	0.542	0.537	0.980	0.057	0.047
64.31	0.633	0.655	1.101	0.087	0.027
64.41	0.680	0.716	1.186	0.111	0.020
64.58	0.731	0.765	1.198	0.115	0.018
65.02	0.797	0.837	1.307	0.146	0.011
65.82	0.887	0.917	1.329	0.163	0.007
67.82	1.000	1.000	...	...	0.000
		1-Propanethiol and Methylcyclopentane			
71.85	0.000	0.000	...	0.000	....
69.74	0.165	0.110	0.625	0.000	0.140
68.02	0.302	0.236	0.714	0.012	0.096
67.65	0.340	0.284	0.770	0.021	0.072
67.30	0.390	0.330	0.770	0.020	0.072
66.85	0.430	0.383	0.822	0.023	0.056
66.76	0.458	0.412	0.829	0.033	0.053
66.60	0.485	0.445	0.851	0.037	0.047
66.37	0.520	0.485	0.869	0.044	0.043
66.24	0.564	0.545	0.927	0.057	0.029
66.21	0.628	0.618	0.958	0.058	0.022
66.20	0.673	0.680	1.023	0.086	0.011
66.20	0.679	0.686	1.033	0.086	0.011
66.19	0.694	0.705	1.054	0.092	0.008
66.34	0.800	0.826	1.187	0.124	1̄.999
66.76	0.873	0.893	1.214	0.143	1̄.997
67.82	1.000	1.000	...	...	0.000
		1-Propanethiol and 2-Methylpentane			
60.40	0.000	0.000	...	0.000	....
59.66	0.103	0.092	1.133	0.008	0.160
59.25	0.240	0.238	1.011	0.012	0.121
59.20	0.305	0.315	0.954	0.026	0.104
59.26	0.335	0.345	0.956	0.020	0.105
59.77	0.443	0.505	0.780	0.058	0.053
59.96	0.477	0.549	0.749	0.076	0.045
61.07	0.580	0.683	0.641	0.124	0.034
67.82	1.000	1.000	...	...	0.000

Table V. Vapor-Liquid Equilibrium Data at 760 Mm. Pressure

Temperature, °C.	Mole % of Thiol		Relative Volatility
	In vapor	In liquid	
	1-Propanethiol and n-Pentane		
36.15	0	0	..
36.13	0.1	0.2	..
36.58	1.0	2.2	..
36.59	1.9	3.8	..
67.82	100	100	..
	1-Propanethiol and Cyclohexane		
80.85	0	0	..
...	56.5	43.0	1.72
...	72.3	67.0	1.29
...	90.7	89.0	1.21
...	91.9	91.7	1.03
...	93.5	93.5	1.00
...	96.2	96.7	0.9
...	87.8	98.0	0.9
67.82	100	100	..

Figures 3, 5, and 7 plot the logarithm of the activity coefficients against the molar composition of the liquid.

Analysis of the systems examined in the equilibrium stills was made in every case from reference curves of refractive index against composition. Table VII gives the refractive indexes of the blends used to make these reference curves.

An interesting refractive index–composition curve was obtained with cyclohexane and 1-propanethiol. This shows a minimum refractive index of 1.4259 at 15 mole % thiol.

DISTILLATION STUDIES

After the vapor-liquid equilibrium data had been determined as above, it was decided to prepare the azeotropes by distillation, inasmuch as more accurate and complete determination of their
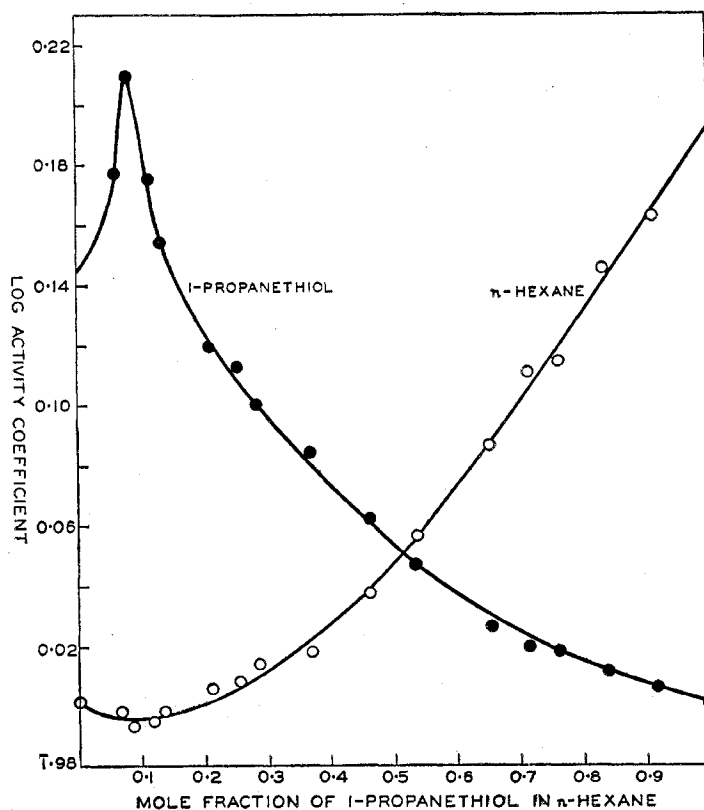

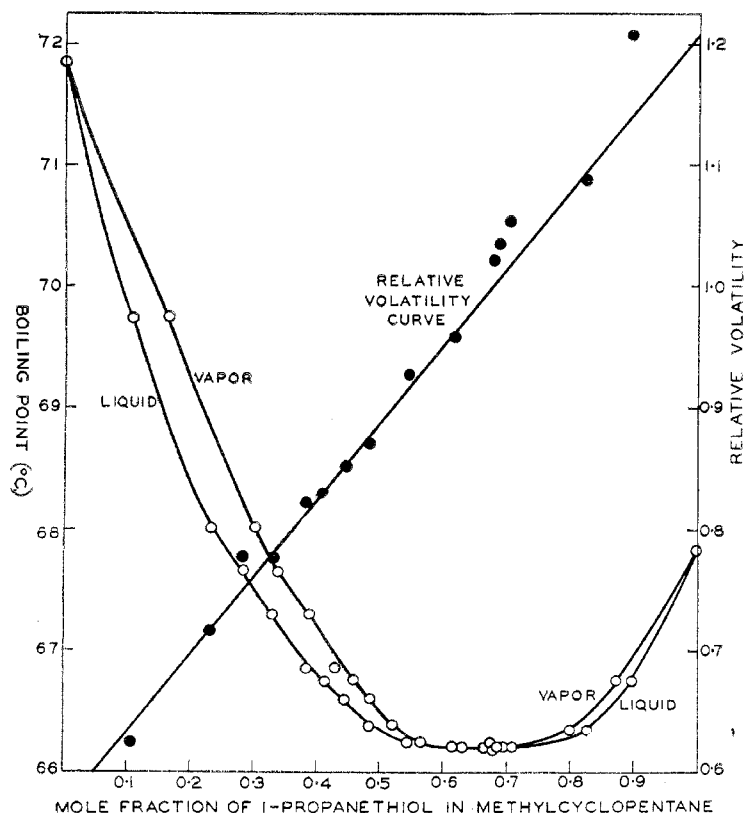Figure 3. Vapor-Liquid Equilibrium Data for
1-Propanethiol in n-Hexane

Figure 4. Vapor-Liquid Equilibrium Data for 1-Propanethiol in Methylcyclopentane

Table VII. Refractive Indexes of Various Thiol-Hydrocarbon Blends

System	Thiol, Mole %	Refractive Index, n_D^{20}
1-Propanethiol and n-hexane	17.36	1.3812
	36.21	1.3899
	52.15	1.3994
	65.16	1.4083
	79.05	1.4187
1-Propanethiol and methyl-cyclopentane	20.44	1.4129
	33.46	1.4157
	47.21	1.4193
	61.54	1.4233
	75.38	1.42805
1-Propanethiol and 2-methyl-pentane	19.50	1.3799
	37.38	1.3832
	51.36	1.3974
	66.49	1.40823
	78.46	1.4180
	90.76	1.42775
1-Propanethiol and cyclo-hexane	5.5	1.4261
	14.81	1.4259
	16.56	1.4260
	32.10	1.4264
	47.06	1.4279
	63.16	1.4302
	75.02	1.4323
	87.57	1.4350
2-Propanethiol and cyclo-pentane	15.33	1.40785
	27.96	1.4097
	43.58	1.4124
	57.82	1.4153
	71.94	1.4186
	85.74	1.4219

straight line, it was possible at this stage to predict approximately the composition of the azeotrope. Accordingly, for each distillation, a charge was prepared to yield separation into the azeotrope and the higher boiling component. Such a choice of charge gave an easier separation and a better identification of the cut point.

As with the systems examined in the equilibrium stills, the compositions of the azeotropes were in most cases determined by measurement of refractive indexes. Complete refractive index-composition curves were not necessary, for in this case it was required only to bracket the azeotropes by preparing synthetic blends on each side of the azeotropes in composition.

physical properties could be obtained if the azeotropes were actually prepared by fractionation of the binary mixtures in efficient columns. On fractionation through a 50-plate column of blends approximating the azeotropes in composition, the latter distilled over as a series of fractions of constant physical properties. Table VIII compares the properties of azeotropes obtained by this procedure with those obtained from vapor-liquid equilibrium data. The two methods give substantially identical results.

A disadvantage of determining azeotropes using equilibrium stills is that their properties are obtained only by graphical interpolation and in no case is the azeotrope actually prepared. The temperatures as read in these stills are only approximate, for no provision is made for the elimination of radiation errors. A further disadvantage is that the equilibrium still procedure is rather long and laborious.

Consequently, from this point onward, all further azeotropic data were obtained as a result of distillations carried out in 50- or 100-plate columns. Because sufficient data had already been obtained to show that the weight per cent of the thiol in the azeotrope plotted against the difference in boiling points of the thiol and hydrocarbon gave an approximately

Table VI. Vapor-Liquid Equilibrium Data for 2-Propanethiol and Cyclopentane at 760-Mm. Pressure

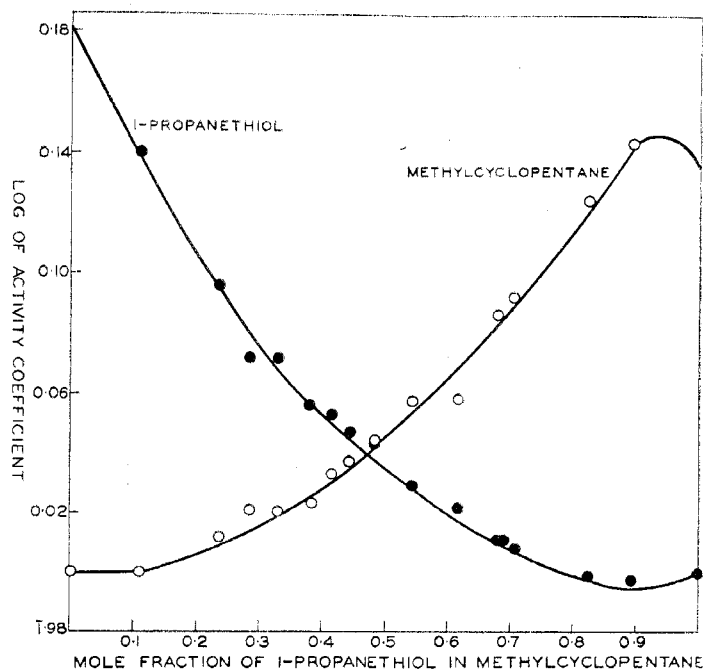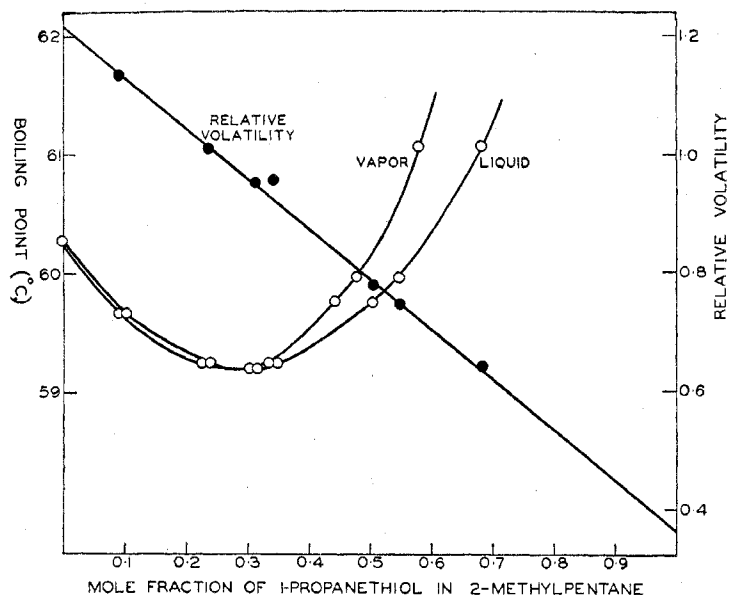| Temperature, °C.	Mole Fraction of Thiol		Relative Volatility	Log₁₀ Activity Coefficient Hydrocarbon
	Vapor	Liquid		
49.35	0.000	0.000	...	0.000
48.94	0.060	0.060	...	0.005
48.05	0.270	0.263	1.036	0.013
47.94	0.324	0.318	1.028	0.015
48.02	0.372	0.383	0.954	0.025
48.15	0.460	0.486	0.895	0.039
49.48	0.660	0.734	0.703	0.103
52.60	1.000	1.000	...	...

Figure 5. Vapor-Liquid Equilibrium Data for 1-Propanethiol in Methylcyclopentane

Figure 6. Vapor-Liquid Equilibrium Data for 1-Propanethiol in 2-Methylpentane

In cases where the refractive index of the azeotrope was near that of the pure hydrocarbon, the thiol content was determined from the sulfur content.

The properties of the azeotropes formed are given in Table IX together with a list of systems that were found to be nonazeotropic.

DISCUSSION

A rather unexpected result is that benzene and toluene do not appear to form azeotropes with thiols. Benzene, boiling at 80.10° C., would be expected to form azeotropes with 1-propanethiol, 2-butanethiol, and 2-methyl-1-propanethiol, inasmuch as these three thiols form azeotropes with cyclohexane, 2,2-dimethylpentane, 2,4-dimethylpentane, and 2,2,3-trimethylbutane, all boiling at approximately the same temperature as benzene. However, benzene does form azeotropes with paraffins over a 32° C. range (16), which is approximately the same range over which these three thiols also form azeotropes with paraffins (see Table XIII). It thus appears that benzene-paraffin mixtures and thiol-paraffin mixtures depart from ideality to about the same extent.

An interesting point is that the azeotrope-forming properties of the thiols are much less than those of their oxygen analogs, the alcohols. For example, the spread of the boiling points of the hydrocarbons that form azeotropes with 1-propanol is approximately 80° C., whereas the spread with 1-propanethiol is only about 30° C. In general, the greater the boiling point spread, the greater is the azeotrope-forming power of the entrainer.

Dilution of an alcohol with a hydrocarbon reduces the hydrogen-bonding forces between the alcohol molecules, and hence helps to increase the vapor pressure of the mixture. These hydrogen-bonding forces are much less between the thiol molecules, and therefore the contribution from this effect to the vapor pressure of the mixture is much less. Thus, it is probable that the difference in azeotropic power of alcohols and thiols is mainly due to the difference in their hydrogen-bonding effect.

CORRELATION OF DATA

Although the theoretical approach to the formation and properties of azeotropes has received a certain amount of attention, it is probably from the practical application of the data that most of the interest has recently been given. Having obtained a series of experimentally determined results, it is interesting to derive equations that relate the seemingly unconnected facts and put a certain amount of order into the work. Such correlations are extremely valuable, because they allow the prediction of unknown data which are often required and for some reason or other are not easily obtainable.

This aspect of the vapor-liquid relationships of binary systems has been given much consideration of late and three papers on this subject have appeared within 8 months (11, 17, 22). All three are concerned with graphical methods of correlation. One of these—namely, the plot of the boiling point difference of the two components against the weight % of thiol in the azeotrope—has already been mentioned. This was suggested by Horsley (11) and produces a straight-line relationship. A similar plot is that put forward by Meissner and Greenfeld (17), who plot
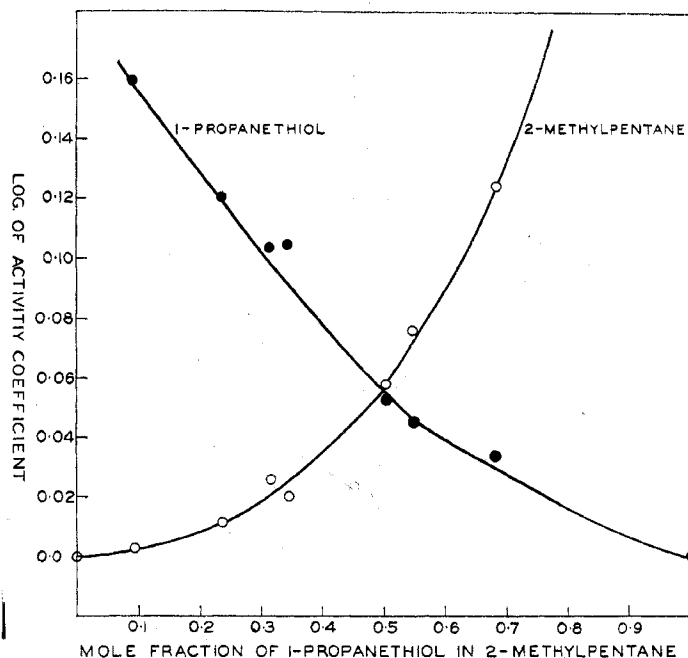

Figure 7. Vapor-Liquid Equilibrium Data for 1-Propanethiol in 2-Methylpentane

Table VIII. Properties of Azeotropes

Components	B.P. of Component, ° C.	Properties of Azeotropes				
		B.P., ° C.	n_D^{20}	d^{20}	Thiol, wt. %	Method[a]
1-Propanethiol	67.82					
n-Hexane	68.75	64.35	1.4016	0.7406	52.6	A
n-Hexane	68.75	64.20	1.4015	....	52.5	B
Methylcyclopentane	71.85	66.45	1.4246	0.8015	64.2	A
Methylcyclopentane	71.85	66.20	1.4245	....	63.8	B
2-Methylpentane	60.40	59.20	1.3835	0.6889	23.9	A
2-Methylpentane	60.40	59.20	1.3833	....	23.7	B
Cyclohexane	80.85	67.77	1.4374	0.8395	97.6	A
Cyclohexane	80.85	67.50	1.4363	....	93.5	B
2-Propanethiol	52.60					
Cyclopentane	49.35	47.75	1.4109	0.7655	35.3	A
Cyclopentane	49.35	47.9	1.4108	....	34.8	B

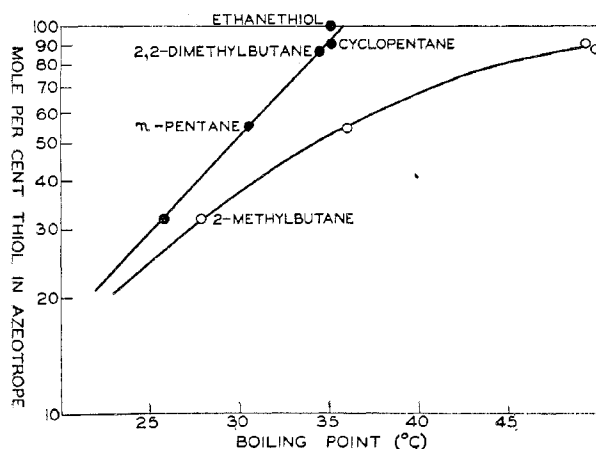[a] A. Fractionation measurements.   B. Vapor-liquid equilibrium measurements.

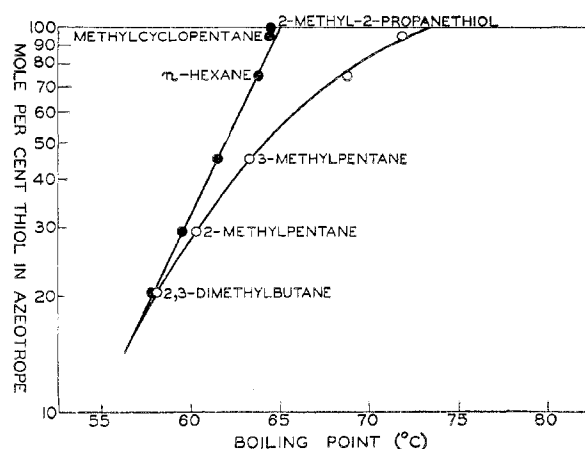Figure 8. Correlation of Azeotropes of Hydrocarbons with Ethanethiol

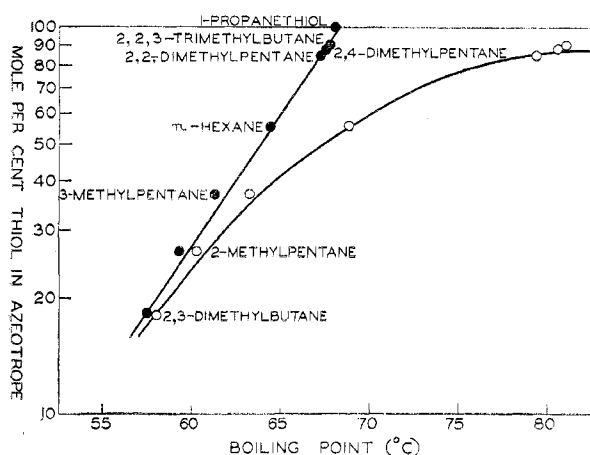Figure 9. Correlation of Azeotropes of Hydrocarbons with 2-Methyl-2-Propanethiol

Figure 10. Correlation of Azeotropes of Paraffins with 1-Propanethiol
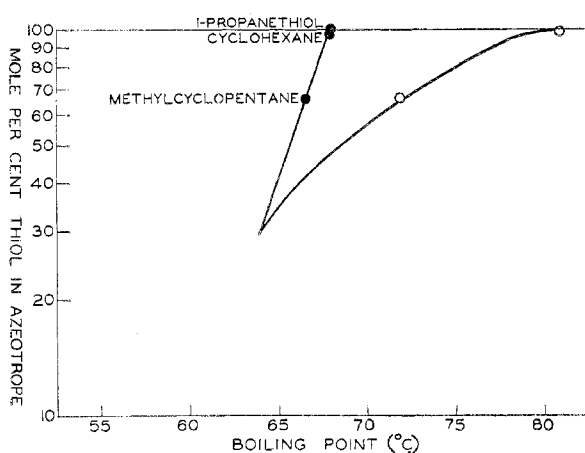

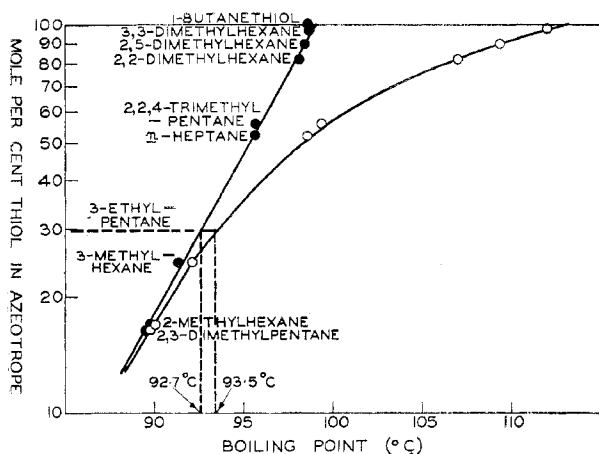Figure 11. Correlation of Azeotropes of Naphthenes with 1-Propanethiol

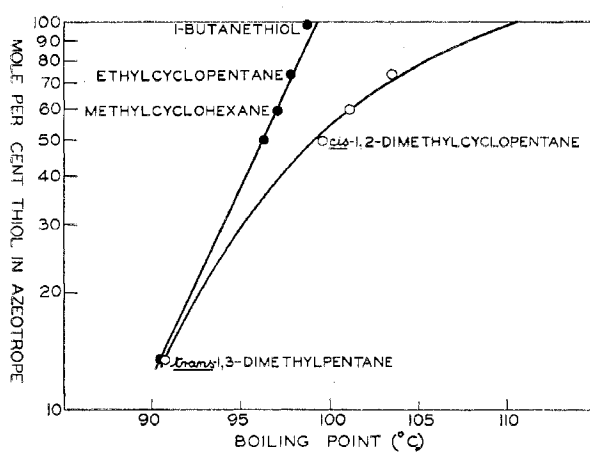Figure 12. Correlation of Azeotropes of Paraffins with 1-Butanethiol

Figure 13. Correlation of Azeotropes of Naphthenes with 1-Butanethiol

the factor $\dfrac{T_M^2(T_H - T_M)}{100,000}$ against the mole per cent of the thiol in the azeotrope, where T_M = boiling point of the thiol, ° K., and T_H = boiling point of the hydrocarbon, ° K. Again, all the points lie approximately on a straight line.

The disadvantage of both these methods lies in the fact that if all the azeotropic data are plotted on one graph, it is difficult to distinguish the slight variations in azeotropic effect on passing from one thiol to another or from paraffins to naphthenes. Be-

cause of these small but definite differences a certain amount of scattering of the points occurs and a band is formed rather than a single line.

A much more satisfactory method of correlation of the properties of azeotropes was recently put forward by Skolnik (22) to cover the azeotropes of benzene with various hydrocarbons—namely, normal paraffins, isoparaffins, and naphthenes. This method allows more accurate predictions of unknown azeotropes and, as the author points out, is more suitable than the procedure

suggested by Rossini and his co-workers (15), because it produces a straight-line relationship rather than a curve.

APPLICATION OF SKOLNIK METHOD OF CORRELATION

For each individual thiol and each hydrocarbon type, the boiling point of the azeotrope has been plotted against the logarithm of the mole per cent of the thiol in the azeotrope and representative curves are given in Figures 8 to 13. As shown by Skolnik, this method of plotting gives a straight line for each of the group of systems investigated. These lines can be represented by equations of the form:

$$\log x = A\,(273.1 + T_{AZ}) + B \quad (1)$$

where x = mole % of the thiol in the azeotrope, T_{AZ} = boiling point of the azeotrope, ° C., and A and B are constants.

The values of A and B have been calculated for all the various binary systems by substituting experimentally determined values in the equation and are given in Table X.

Skolnik used the value of constant A for each system as a measure of the azeotropic effect of the entrainer, and the ratio of A for the system benzene–n-paraffins to A for the system under consideration has been introduced by him as the "relative azeotropic effect." Values of this ratio are given in Table X. It will also be seen that the slopes of the lines represented by Equation 1 are equal to A and hence inversely proportional to the relative azeotropic effect.

It will be seen from Table X that ethanethiol is a more powerful azeotrope former than 1-propanethiol, which in turn is more powerful than 1-butanethiol. Furthermore, in every case where it has been possible to calculate values for both paraffins and naphthenes, the former are more powerful azeotrope formers with any individual thiol than the latter. The general tendency is for secondary thiols (2-propane- and 2-butanethiol) to be slightly more effective for azeotrope formation than the corresponding primary thiols. However, with naphthenes, 2-butanethiol is less effective than 1-butanethiol.

On the same graphs (Figures 8 to 13), the boiling point of the pure hydrocarbon has been plotted against the log of the mole per cent of the thiol in the azeotrope, a relationship that produces a smooth curve. As pointed out by Skolnik, from the two plots on each graph it is possible to predict the properties of undetermined azeotropes between other hydrocarbons and the thiols investigated. For instance, on Figure 12, 3-ethylpentane boils at 93.5° C. and this temperature is read off on the smooth curve giving the boiling point of the pure hydrocarbons. The ordinate now shows the composition of the azeotrope, while the boiling point is found by extrapolating the broken line back to the line relating composition and boiling point of the azeotropes. In this case the composition is 30 mole % and the boiling point 92.7° C. By using this method, the boiling points and composition of 18 azeotropes have been predicted and are given in Table XI.

Table IX. Physical Properties of Azeotropes of Hydrocarbons with Thiols

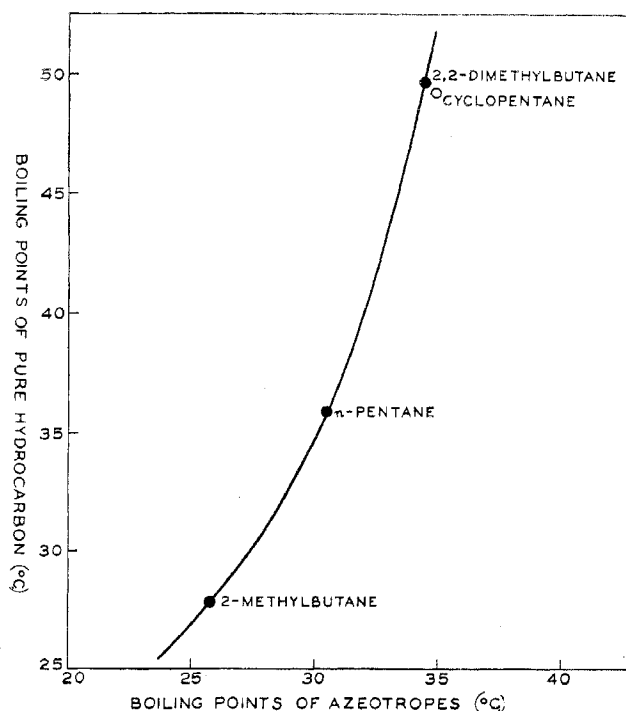| Components	B.P. of Component, ° C.	Properties of Azeotropes				
		B.P., ° C.	Refractive index, n_D^{20}	Density, d^{20}	Thiol in azeotrope, wt. %	Thiol in azeotrope, mole %
Ethanethiol	35.04					
2-Methylbutane	27.90	25.72	1.3703	.....	29	32
n-Pentane	36.15	30.46	1.3864	0.714	51	55
Cyclopentane	49.35	34.95	1.42745	0.8283	89	90
2,2-Dimethylbutane	49.70	34.41	1.4140	0.7911	83	87
1-Propanethiol	67.82					
n-Pentane	36.15		Nonazeotropic			
2,2-Dimethylbutane	49.70		Nonazeotropic			
2,3-Dimethylbutane	58.10	57.54	1.3848	0.6852	16.3	18.1
2-Methylpentane	60.40	59.20	1.3835	0.6889	23.9	26.2
3-Methylpentane	63.35	61.26	1.3921	0.71265	34.2	37.0
n-Hexane	68.75	64.35	1.4016	0.7406	52.6	55.7
Methylcyclopentane	71.85	66.45	1.4246	0.8015	64.2	66.0
2,2-Dimethylpentane	79.20	67.20	1.4242	0.8026	81.3	85.1
Benzene	80.10		Nonazeotropic			
2,4-Dimethylpentane	80.55	67.48	1.4275	0.8119	85.1	88.2
Cyclohexane	80.85	67.77	1.4374	0.8395	97.6	97.8
2,2,3-Trimethylbutane	80.85	67.57	1.4300	0.8177	87.4	90.1
2-Propanethiol	52.60					
n-Pentane	36.15		Nonazeotropic			
Cyclopentane	49.35	47.75	1.4109	0.7655	35.3	33.4
2,2-Dimethylbutane	49.70	47.41	1.3857	0.7016	37.7	40.6
2,3-Dimethylbutane	58.10	51.24	1.4048	0.7547	67.5	70.0
2-Methylpentane	60.40	51.70	1.40795	0.7651	75.9	78.1
3-Methylpentane	63.35	52.40	1.4162	0.7885	87.0	88.3
n-Hexane	68.75		Nonazeotropic			
1-Butanethiol	98.58					
2,3-Dimethylpentane	89.90	89.53	1.3973	0.7116	15.1	16.5
2-Methylhexane	90.15	89.74	1.3914	0.6989	15.4	16.8
trans-1,3-Dimethylcyclopentane	90.80	90.54	1.4121	0.7555	12.7	13.5
3-Methylhexane	91.60	91.20	1.3977	0.7948	22.8	24.5
n-Heptane	98.40	95.45	1.4101	0.7507	49.4	52.0
2,2,4-Trimethylpentane	99.30	95.50	1.4135	0.7568	50.3	56.2
cis-1,2-Dimethylcyclopentane	99.60	96.35	1.4306	0.8048	48.0	50.1
Methylcyclohexane	101.05	97.00	1.4327	0.8083	58.2	60.3
Ethylcyclopentane	103.45	97.76	1.4345	0.8172	72.15	73.8
2,2-Dimethylhexane	106.85	98.01	1.4298	0.8049	78.8	82.5
2,5-Dimethylhexane	109.15	98.22	1.4353	0.8204	88.0	90.3
Toluene	110.85		Nonazeotropic			
3,3-Dimethylhexane	112.20	98.56	1.4414	0.8380	97.6	98.1
2-Butanethiol	85.15					
Methylcyclopentane	71.85		Nonazeotropic			
2,2-Dimethylpentane	79.20	78.60	1.3918	0.7033	23.1	25.0
Benzene	80.10		Nonazeotropic			
2,4-Dimethylpentane	80.55	79.55	1.3937	0.7099	28.1	30.3
Cyclohexane	80.85	79.97	1.4263	0.7879	25.5	24.2
1,1-Dimethylcyclopentane	87.90	83.90	1.4258	0.7976	64.1	66.0
2,3-Dimethylpentane	89.90	84.16	1.4204	0.7835	68.6	70.8
2-Methylhexane	90.15	84.30	1.4189	0.7806	72.1	74.2
trans-1,3-Dimethylcyclopentane	90.80	84.75	1.4290	0.8081	78.1	79.5
3-Methylhexane	91.60	84.70	1.4258	0.7968	80.8	82.4
n-Heptane	98.40		Nonazeotropic			
2-Methyl-1-propanethiol	88.72					
2,2-Dimethylpentane	79.20	79.12	1.3864	0.6867	10.3	11.3
Benzene	80.10		Nonazeotropic			
2,4-Dimethylpentane	80.55	80.28	1.3878	0.69205	14.1	15.4
Cyclohexane	80.85	80.70	1.4263	0.7832	11.7	11.0
2,2,3-Trimethylbutane	81.05	80.60	1.3956	0.7091	16.4	17.9
1,1-Dimethylcyclopentane	87.90	85.69	1.4221	0.7849	44.25	46.4
2,3-Dimethylpentane	89.90	86.26	1.4132	0.7616	54.1	56.7
trans-1,3-Dimethylcyclopentane	90.80	87.02	1.4239	0.7930	58.6	60.7
3-Methylhexane	91.60	87.16	1.4164	0.7720	62.8	65.2
n-Heptane	98.40	88.50	1.4338	0.8197	91.3	92.1
2,2,4-Trimethylpentane	99.30	88.41	1.4325	0.8164	90.0	91.9
cis-1,2-Dimethylcyclopentane	99.60	88.52	1.4383	0.8328	98.6	98.7
Methylcyclohexane	101.05	88.55	1.4384	0.8335	98.9	99.0
Ethylcyclopentane	103.45		Nonazeotropic			
2-Methyl-2-propanethiol	64.35					
2,3-Dimethylbutane	56.10	57.82	1.3815	0.6821	21.1	20.4
2-Methylpentane	60.40	59.55	1.3831	0.6896	30.4	29.5
3-Methylpentane	63.35	61.51	1.3936	0.7178	46.5	45.4
n-Hexane	68.75	63.78	1.4074	0.7583	75.8	75.0
Methylcyclopentane	71.85	64.37	1.4209	0.7967	95.3	95.0

Table X. Values of Constants A and B and Relative Azeotropic Effects for Systems Thiols-Hydrocarbons

Group of Binary Systems	A	B	Relative Azeotropic Effect
Ethanethiol with paraffins	0.049	-13	2.26
1-Propanethiol with paraffins	0.072	-22.4	1.54
1-Propanethiol with naphthenes	0.131	-43	0.85
2-Propanethiol with paraffins	0.066	-19.6	1.68
2-Propanethiol with naphthenes	0.084	-27	1.32
1-Butanethiol with paraffins	0.087	-30	1.27
1-Butanethiol with naphthenes	0.101	-35	1.10
2-Butanethiol with paraffins	0.084	-28	1.32
2-Butanethiol with naphthenes	0.111	-38	1.00
2-Methyl-1-propanethiol with paraffins	0.097	-33	1.14
2-Methyl-1-propanethiol with naphthenes	0.117	-40	0.95
2-Methyl-2-propanethiol with paraffins	0.095	-30	1.17

Table XI. Prediction of Azeotropes between Thiols and Hydrocarbons Using Skolnik's Method

System	B.P.[a] of Component, °C.	Properties of Azeotrope B.P., °C.	Thiol in azeotrope, mole %
1-Butanethiol	98.58		
3,3-Dimethylpentane	86.071	86.1	8.6
1,1-Dimethylcyclopentane	87.84	87.5	7.4
trans-1,2-Dimethylcyclopentane	91.87	91.7	17.5
cis-1,3-Dimethylcyclopentane	91.9	91.7	17.5
3-Ethylpentane	93.468	92.7	30
2,2,3,3-Tetramethylbutane	106.30	97.8	80
2,4-Dimethylhexane	109.432	98.3	90.6
2,2,3-Trimethylpentane	109.844	98.5	92
2-Butanethiol	85.15		
2,2,3-Trimethylbutane	80.871	79.75	31.5
3,3-Dimethylpentane	86.071	82.7	55
trans-1,2-Dimethylcyclopentane	91.87	84.8	83
cis-1,3-Dimethylcyclopentane	91.9	84.8	83
3-Ethylpentane	93.468	85.2	88
2-Methyl-1-propanethiol	88.72		
3,3-Dimethylpentane	86.071	84.6	39
2-Methylhexane	90.05	86.25	57
trans-1,2-Dimethylcyclopentane	91.87	87.3	70
cis-1,3-Dimethylcyclopentane	91.9	87.3	70
3-Ethylpentane	93.468	87.3	72

[a] Boiling points of hydrocarbons given in this table and Table XIV are taken from values given in A.P.I. Research Project 44.

Table XII. Values of Constants D, E, and F in Equation log $(D - T_{AZ}) = E + F (273.1 + T)$ for Thiols and Hydrocarbons

Group of Binary Systems	D	E	F
Ethanethiol and paraffins	37	9.8	-0.029
1-Propanethiol and paraffins	69	13.9	-0.039
2-Propanethiol and paraffins	55	12.0	-0.034
1-Butanethiol and paraffins	100	15.9	-0.041
1-Butanethiol and naphthenes	101	15.7	-0.040
2-Butanethiol and paraffins	88	13.5	-0.036
2-Butanethiol and naphthenes	87	18.3	-0.049
2-Methyl-1-propanethiol and paraffins	90	17.0	-0.045
2-Methyl-1-propanethiol and naphthenes	92	13.7	-0.036
2-Methyl-2-propanethiol and paraffins	67	15.0	-0.042

A further relationship that has been plotted is the boiling point of the azeotropes against the boiling point of the pure hydrocarbons. This has been done for each individual thiol with both paraffins and naphthenes. A series of curves has been produced (Figures 14 to 17) and these have been fitted to equations of the form:

$$\log (D - T_{AZ}) = E + F (273.1 + T) \qquad (2)$$

where D represents one asymptote of the curve, T = boiling point of the azeotrope in ° C., and E and F are constants.

Where sufficient data allow the plotting of curves for both paraffins and naphthenes (Figures 16 and 17), the curve for the latter lies slightly to the right of the curve for paraffins. This means that if two hydrocarbons, one a paraffin and one a naphthene, having the same boiling point are distilled with the same thiol, the azeotrope with the naphthene will boil at a higher temperature than the one with the paraffin (cf. 15).

The constants D, E, and F for the various groups of binary systems have been calculated by substituting experimentally determined values in the equation (Table XII).

Figure 14. Relation of Boiling Points of Hydrocarbons and Their Azeotropes with Ethanethiol
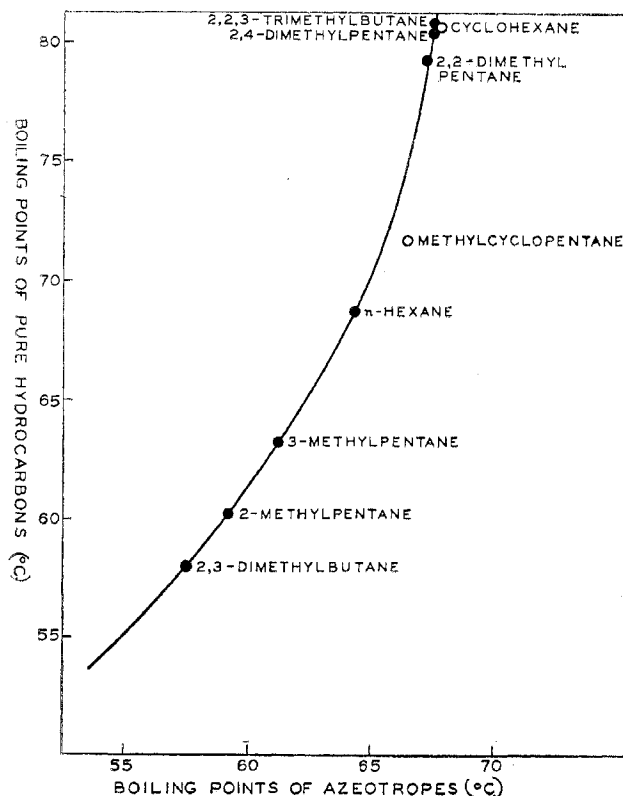
Figure 15. Relation of Boiling Points of Hydrocarbons and Their Azeotropes with 1-Propanethiol
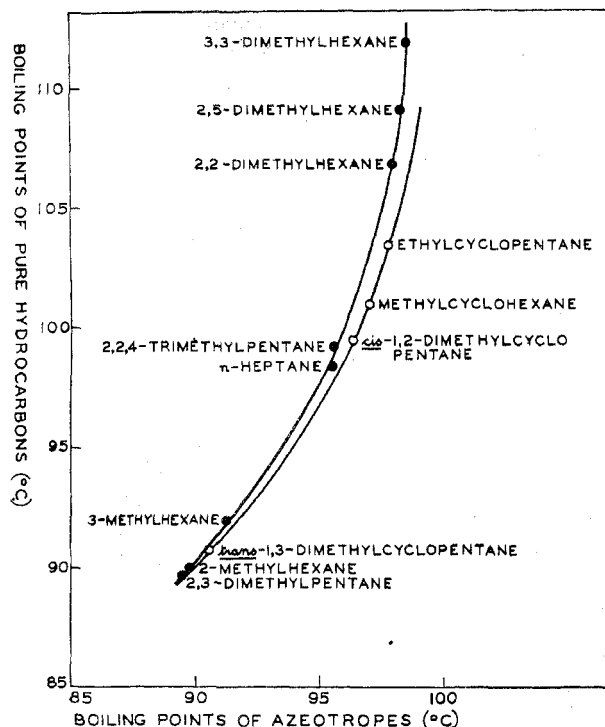
Figure 16. Relation of Boiling Points of Hydrocarbons and Their Azeotropes with 1-Butanethiol

Figure 17. Relation of Boiling Points of Hydrocarbons and Their Azeotropes with 2-Butanethiol

Equation 2 may be used to find the maximum boiling point for a hydrocarbon which will form an azeotrope with a particular thiol. This temperature is given by T when the boiling point of the pure thiol is substituted for T_{Az} in Equation 2. These maximum temperatures are given in Table XIII. In no case has a hydrocarbon of boiling point above the maximum temperature as given by this method been found to form an azeotrope with the thiol to which it refers.

The minimum boiling point of the hydrocarbon for azeotrope formation can theoretically be calculated by substituting the same value for T_{Az} and T until both sides of the equation are equal. However, the minimum temperatures obtained by this procedure were not at all definite and consequently are not quoted in the table.

PROPOSED METHOD OF CORRELATION

A disadvantage of the Skolnik methods of correlation and prediction of azeotropes is that no straight-line plot is obtained involving the boiling points of the pure hydrocarbons. The curves (Figures 8 to 13) can be reasonably well constructed if sufficient experimental data are available, but if only one or two azeotropes are known, it is necessary to make use of the straight-line relationship between the boiling point of pure hydrocarbons and the logarithm of (D — boiling point of the azeotrope) as demonstrated in his paper (22). However, it can be shown that if the boiling points of the pure hydrocarbons are plotted against the mole per cent of the thiol in the azeotropes, a series of straight lines is obtained, each one corresponding to a particular thiol (Figure 18). [A similar plot of boiling point of hydrocarbon against composition was made by Marschner and Cropper (16) for systems of paraffins with benzene and ethanol.] This is a simple but important relationship and such a graph shows at once whether a hydrocarbon does or does not form an azeotrope with any thiol; if it does, the composition of the azeotrope can
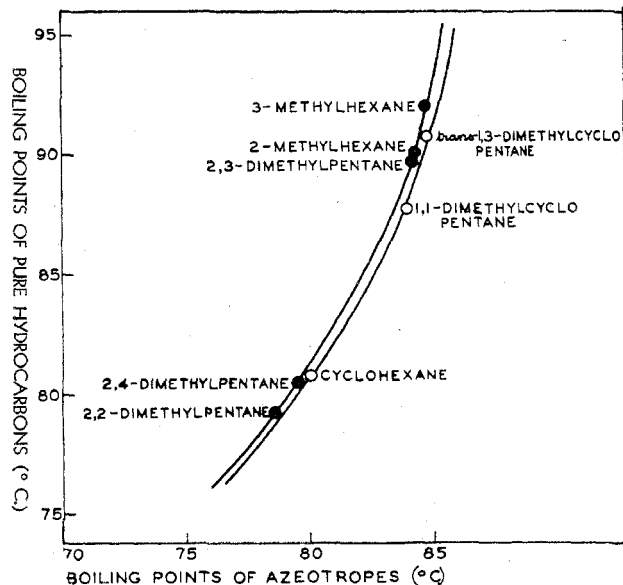
be read directly. The slopes of the lines for the azeotropes of naphthenes with thiols are slightly less than the corresponding slopes for the azeotropes of paraffins with thiols, but in order to avoid confusion the naphthene lines have not been drawn in. A point of interest is that in every case the boiling points of the pure thiols intercept these lines at 51.5 mole % thiol. The usefulness of this fact will be apparent later.

The intercepts of the lines at 0 and 100% thiol give the maxi-
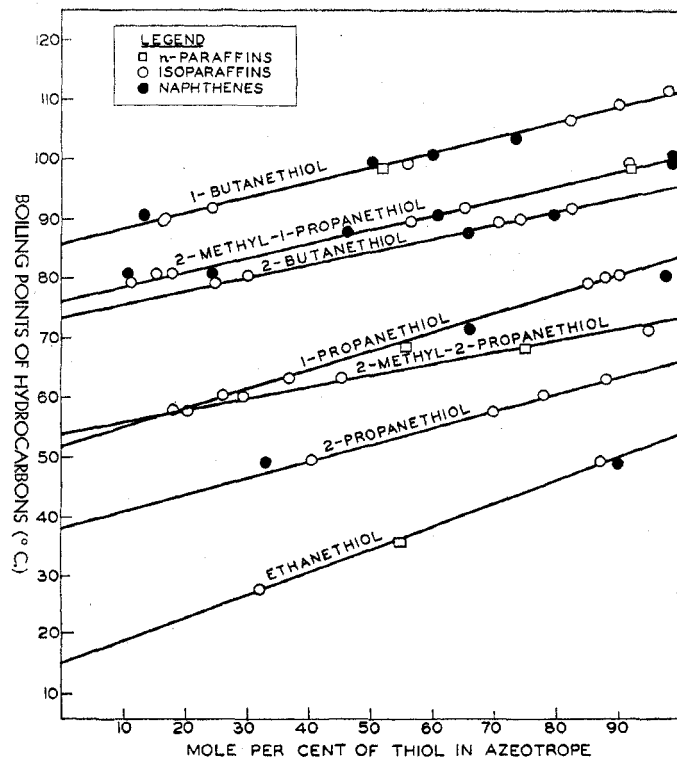
Figure 18. Boiling Points of Hydrocarbon vs. Mole Per Cent of Thiol in Azeotropes
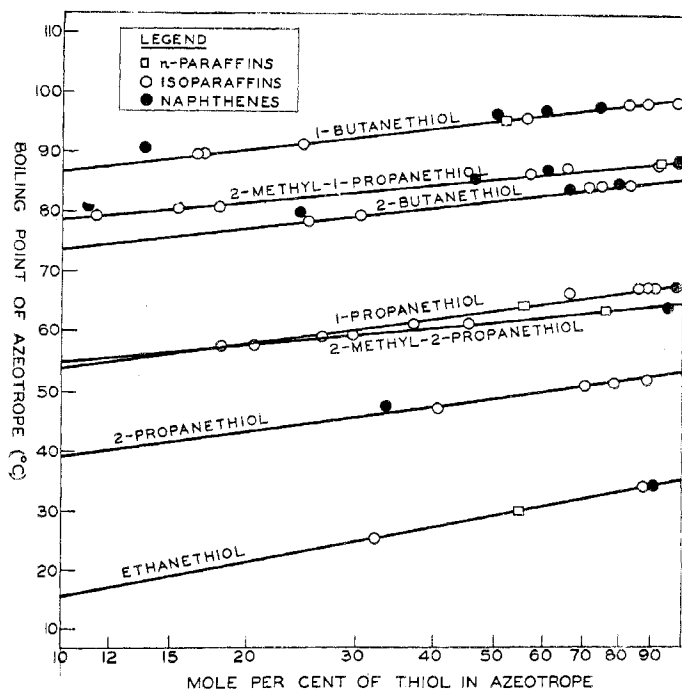
Figure 19. Boiling Point of Azeotrope vs. Log of Mole Per Cent Thiol in Azeotropes

mum and minimum boiling points of the hydrocarbons for azeotrope formation, while the difference in these values gives the boiling point range over which azeotrope formation is possible. These values are shown in Table XIII, where the maximum temperatures are compared with those previously obtained from the Skolnik plot (Equation 2). The agreement between the two sets of maximum temperatures is reasonably good.

Table XIII. Maximum and Minimum Boiling Points of Hydrocarbons That Form Azeotropes with Individual Thiols

|	From Figure 18, °C.			From Equation 2,
Group of Binary Systems	Range	Min. b.p.	Max. b.p.	Max. B.P.,°C.
Ethanethiol and paraffins	39	15	54	55
1-Propanethiol and paraffins	32	52	84	83.5
2-Propanethiol and paraffins	28.5	38	66.5	63.5
1-Butanethiol and paraffins	27	85	112	112
1-Butanethiol and naphthenes	23	87	110	109
2-Butanethiol and paraffins	22.5	73.5	96	93.5
2-Butanethiol and naphthenes	18.5	75	93.5	92.5
2-Methyl-1-propanethiol and paraffins	24.5	76	100.5	100
2-Methyl-1-propanethiol and naphthenes	21	78	99	99
2-Methyl-2-propanethiol and paraffins	20	54	74	71

The boiling range is usually regarded as a measure of the azeotrope-forming power of a given entrainer, and, actually, the order given by this method appears to be more reasonable than that using the values of the "relative azeotropic effect" obtained from the constants A in Equation 1. The same general tendencies can be observed—i.e., the azeotropic power decreases with carbon chain length of the thiol, and paraffins are stronger azeotrope formers than naphthenes with a given thiol. However, it appears also that primary thiols are stronger azeotrope formers than secondary thiols, which in turn are stronger than the tertiary. This latter relationship is not obvious from a consideration of the relative azeotropic effects.

In the same way that a composite graph has been drawn for the correlation of the boiling point of the pure hydrocarbon with the azeotrope composition, so Figure 19 gives a similar series of straight lines relating the boiling points of the azeotropes with

the logarithm of the azeotrope compositions. This graph, in effect, contains all the straight lines that have been given on Figures 8 to 13. Predictions of the properties of unknown azeotropes for paraffins and naphthenes with thiols can now be simply made by using only Figures 18 and 19. From the boiling point of the hydrocarbon, the composition of the azeotrope can be found directly from Figure 18 and this can then be used on Figure 19 to give the boiling point of the azeotrope. In this way, predictions for the same 18 unknown azeotropes have been made (Table XIV), to compare with the values already obtained by the Skolnik procedure (Table XI).

The agreement between these values and the previous ones is good, except in the case of 3,3-dimethylpentane and 1,1-dimethylcyclopentane with 1-butanethiol. It is probable that the values of mole per cent thiol given in Table XIV are more correct than the 8.6 and 7.4 mole % given in Table XI, because at this part of the range the Skolnik method is liable to error owing to the degree of extrapolation required in the logarithmic plot. (A recent examination of a mixture of 1,1-dimethylcyclopentane and 1-butanethiol showed the existence of an azeotrope containing approximately 4 mole % thiol.)

PREDICTIONS FOR OTHER THIOLS

When the logarithms of the boiling ranges and the "relative azeotropic effects" for the straight-chain thiols with paraffins (as given in Tables X and XIII) are plotted against the boiling point of the thiol, each group of three points—i.e., for ethane, 1-propane-, and 1-butanethiol—lies on a straight line (Figure 20). Assuming that this relationship holds for other members of the series, extrapolation gives the boiling point ranges and the relative azeotropic effects for methanethiol, 1-pentanethiol, 1-hexanethiol, 1-heptanethiol, etc., and possibly for hydrogen sulfide, if this can be regarded as the simplest thiol (Table XV).

Using these extrapolated values, full predictions for the azeotrope-forming properties of these thiols with paraffins can be obtained in the following manner:
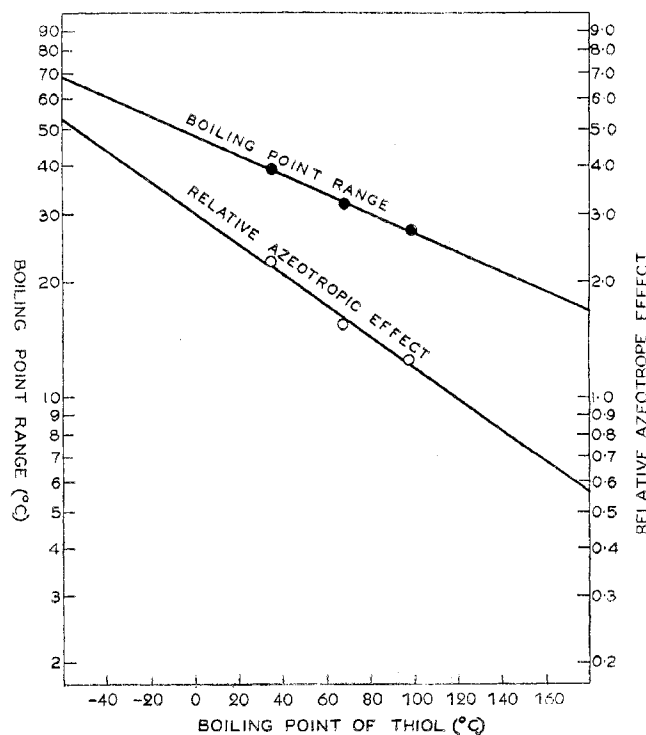

Figure 20. Azeotropic Constants of Straight-Chain Thiols

Table XIV. Predictions of Azeotropes between Thiols and Hydrocarbons Using Figures 18 and 19

System	B.P. of Component, °C.[a]	Properties of Azeotropes	
		B.P., °C.	Thiol in azeotrope, mole %
1-Butanethiol	98.58		
3,3-Dimethylpentane	86.071	. . .	2
1,1-Dimethylcyclopentane	87.84	. . .	2
trans-1,2-Dimethylcyclopentane	91.87	91.7	18
cis-1,3-Dimethylcyclopentane	91.9	91.7	18
3-Ethylpentane	93.468	92.8	31
2,2,3,3-Tetramethylbutane	106.30	97.8	80.5
2,4-Dimethylhexane	109.432	98.5	92
2,2,3-Trimethylpentane	109.844	98.55	93.4
2-Butanethiol	85.15		
2,2,3-Trimethylbutane	80.871	79.9	32.3
3,3-Dimethylpentane	86.071	82.7	55
trans-1,2-Dimethylcyclopentane	91.87	84.9	86
cis-1,3-Dimethylcyclopentane	91.9	84.9	86
3-Ethylpentane	93.468	85.2	88
2-Methyl-1-propanethiol	88.72		
3,3-Dimethylpentane	86.071	84.6	40
2-Methylhexane	90.05	86.25	56.5
trans-1,2-Dimethylcyclopentane	91.87	87.2	66
cis-1,3-Dimethylcyclopentane	91.9	87.2	66
3-Ethylpentane	93.468	87.3	70.5

[a] Boiling points taken from A.P.I. Research Project 44.

Table XV. Predictions of Azeotropic Constants of Straight-Chain Thiols with Paraffins

Entrainer	B.P. of Entrainer, °C.	Maximum B.P. of Hydrocarbon, °C.	Minimum B.P. of Hydrocarbon, °C.	Boiling Range, °C.	Relative Azeotropic Effect
Hydrogen sulfide	−60.3	−26.3	−95.3	69	5.3
Methanethiol	6.5	28.8	−17.2	46	2.8
1-Pentanethiol	126	137.0	114.0	23	0.93
1-Hexanethiol	150	159.7	139.7	20	0.74
1-Heptanethiol	176	184.4	167.2	17	0.58

Table XVI. Predicted Azeotropes between Paraffins and Methanethiol

Components	B.P. of Component, °C.	Properties of Azeotropes	
		B.P., °C.	Thiol in azeotrope, mole %
Methanethiol	6.5		
2-Methylpropane	−11.73	−16.5	12.5
n-Butane	−0.50	−4	37.0
2,2-Dimethylpropane	9.503	0.6	58.0
2-Methylbutane	27.854	6.3	97.0

The straight-line relationship for each thiol can be drawn on Figure 18 from a knowledge of the boiling range—i.e., the slope—and the fact that a hydrocarbon with the same boiling point as the thiol forms an azeotrope having a composition of 51.5 mole % thiol. Similarly, the line on Figure 19 that can be drawn for its slope is equal to the relative azeotropic effect divided by the value of constant A for benzene-n-paraffins—i.e., 0.1108—while its exact position is fixed because it passes through the boiling point of the thiol at 100% composition. From these two lines, predictions can now be made of the properties of azeotropes with paraffins of suitable boiling point. This has been done for methanethiol (Table XVI).

Future experimental work will serve to show how far these predictions are true and whether the suggested procedure for obtaining them is a sound one.

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Thermodynamic Properties of Some Sulfur Compounds

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THE purpose of this paper is to present the available thermochemical data on sulfur compounds of petroleum interest. Some values are taken directly from the literature; others are calculated by statistical methods where the necessary molecular data are available. Methods of estimation are given for the changes in these values on substitution of larger organic radicals. Binder (2) very recently has published some thermodynamic functions for methyl mercaptan and dimethyl sulfide which agree fairly well with those presented here.

The molecular data necessary for the accurate calculation of the thermodynamic properties of methyl mercaptan (methanethiol) and dimethyl sulfide are available. The fundamental vibrations for these two compounds are given by Thompson and Skerrett (17, 18). The moments of inertia and the barrier to internal rotation, 1460 calories per mole, for methyl mercaptan were taken from Russell, Osborne, and Yost (12).

The moments of inertia of dimethyl sulfide were calculated from the structural parameters as measured by electron diffraction (3). The barrier to internal rotation of the methyl groups has been determined to be 2000 calories per mole (9). Using these barriers the contribution of internal rotation was obtained from the tables of Pitzer and Gwinn (11).

The thermodynamic functions for these compounds are presented in Tables I to IV.

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