SUMMARY

These thermal data are not entirely comparable in terms of materials and temperature ranges. However, they all bear directly on the problem of heat transfer to carbonaceous briquets containing coal, char, and pitch. The heat capacity data measured for coal and char may be combined with values in the literature for pitch to provide composite values applicable to briquets. The thermal conductivity data were obtained directly on briquet samples. There is no apparent reason why the heat transfer film coefficient, *h*, cannot be applied directly to the heating of carbonaceous shapes of low conductivity.

LITERATURE CITED

(1) Birch, F., Clark, H., *Am. J. Sci.* **238**, 529 (1940).
(2) Burke, S. P., Parry, V. F., *Ind. Eng. Chem.* **19**, 15-20 (1927).
(3) Clendenin, J. D., Barclay, K. M., Donald, H. J., Gillmore, D. W., Wright, C. C., *Trans. Ann. Anthracite Conf. Lehigh Univ.* 1949, Bethlehem, Pa.
(4) Davis, J. D., *Ind. Eng. Chem.* **9, 16,** 726-30 (1924).
(5) Davis, J. D., Place, P. B., *Ibid.*, **16,** 589 (1924).
(6) Davis, J. D., Place, P. B., Edeburn, P., *Fuel* **4,** 286-99 (1925).
(7) Ingersoll, L. R., Zobel, O. J., Ingersoll, A. C., "Heat Conduction." University of Wisconsin Press, Madison, Wisc., 1954.
(8) Millard, D. J., *J. Inst. Fuel* **28,** 345 (1955).
(9) Porter, H. C. and Taylor, G. B., *Ind. Eng. Chem.* **5,** 289-93 (1913).
(10) Schneider, P. J., "Conduction Heat Transfer," Addison-Wesley Press, Cambridge, Mass., 1955.
(11) Terres, E., *Proc. 2nd Intern. Conf. Bituminous Coal* **2,** 657-84 (1928).
(12) Terres, E., Tjia, H. A., Herrman W., Johswich F., Patschek, F., Pfeiffer, H., Schwarzmann, H., *Beiheft Z. Ver. deut. Chem.*, No. 10, *Angew Chem.*, **48,** 17-21 (1935).
(13) Terres, E., Biederbeck, H., *Gas u. Wasserfach* **71,** 265-8, 297-303, 320-5, 338-45 (1928).
(14) Terres, E., Meier, M., *Ibid.*, **71,** 457-61, 490-5, 519-23 (1928).
(15) Terres, E., Voituret, K., *Ibid.*, **74,** 98-101, 122-8, 148-54, 178-82 (1931).
(16) Weyman, G., *J. Soc. Chem. Ind. London* **39,** 168-9 (1920).
(17) Yavorsky, P. M., Batchelor, J. D. Gorin, F., *Ind. Eng. Chem.* **51,** 833 (1959).

RECEIVED for review November 11, 1958. Accepted April 1, 1959. Division of Gas and Fuel Chemistry, 134th meeting, ACS, Chicago, Ill., September 1958.

Isomerization Equilibria

The C_2H_6S, C_3H_8S, and $C_4H_{10}S$ Alkane Thiols and Sulfides and the Methylthiophenes

D. W. SCOTT, G. B. GUTHRIE, J. P. McCULLOUGH, and GUY WADDINGTON
Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla.

Chemical thermodynamic studies of complete groups of isomeric sulfur compounds are included in the program of American Petroleum Institute Research Project 48A in this laboratory. For four groups of compounds, the C_2H_6S, C_3H_8S, and $C_4H_{10}S$ alkane thiols and sulfides and the methylthiophenes, values of free energy of formation for all isomers have been obtained over the temperature range of practical interest. These values have been calculated by statistical thermodynamic methods from spectral and molecular structure data and are based on experimental determinations of the heat capacity, entropy, and heat of formation.

Values of the standard free energy of isomerization and the corresponding equilibrium concentrations are reported here. To illustrate the utility of the results, the isomerization equilibria are discussed in relation to the concentration of sulfur compounds in petroleum. Possible application in future speculation about the origin of petroleum is suggested. Revisions and extensions of previously published tables of chemical thermodynamic properties are included when necessary.

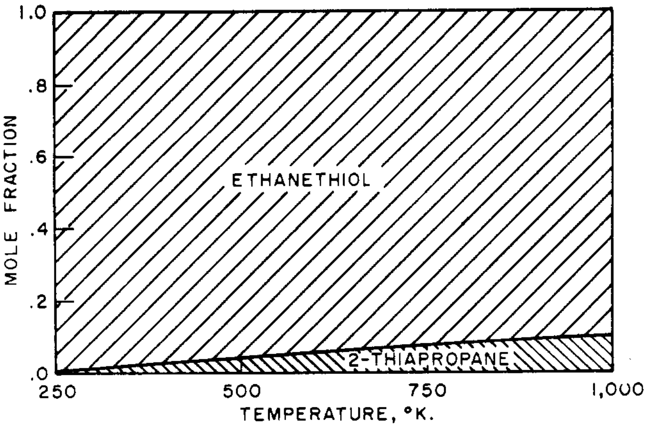


Figure 1. Equilibrium concentrations of C_2H_6S alkane thiols and sulfides

The individual isomers under consideration are:

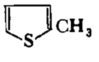
C_2H_6S Compound	
Ethanethiol	CH_3CH_2SH
2-Thiapropane	CH_3SCH_2

C_3H_8S Compounds	
1-Propanethiol	$CH_3CH_2CH_2SH$
2-Propane thiol	$CH_3CH(SH)CH_3$
2-Thiabutane	$CH_3CH_2SCH_3$

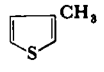
$C_4H_{10}S$ Compounds	
1-Butanethiol	$CH_3CH_2CH_2CH_2SH$
2-Butanethiol	$CH_3CH_2CH(SH)CH_3$
2-Methyl-1-propanethiol	$CH_3CH(CH_3)CH_2SH$
2-Methyl-2-propanethiol	$CH_3C(CH_3)_2SH$
2-Thiapentane	$CH_3CH_2CH_2SCH_3$
3-Thiapentane	$CH_3CH_2SCH_2CH_3$
3-Methyl-2-thiabutane	$CH_3CH(CH_3)SCH_3$

Methylthiophenes

2-Methylthiophene



3-Methylthiophene



RESULTS

The values of ΔFi°, the standard change of free energy for the isomerization reaction,

Reference compound (gas) = isomeric compound (gas)

and Ni, the mole fraction of the given isomer when at equilibrium with all of its other isomers in the gas phase, are listed

Table I. Molal Free Energy of Isomerization and Equilibrium Concentration

	C_2H_6S Compounds				C_3H_8S Compounds						Methylthiophenes			
	Ethanethiol		2-Thiapropane		1-Propanethiol		2-Propanethiol		2-Thiabutane		2-Methylthiophene		3-Methylthiophene	
T, °K.	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni
0	0	1.000	1.90	0.000	0	0.000	- 1.78	1.000	2.02	0.000	0	0.00	- 0.13	1.00
273.16	0	0.99	2.71	0.007	0	0.097	- 1.21	0.90	2.18	0.002	0	0.37	- 0.28	0.63
298.16	0	0.99	2.79	0.009	0	0.13	- 1.13	0.87	2.21	0.003	0	0.39	- 0.27	0.61
300	0	0.99	2.78	0.009	0	0.13	- 1.13	0.87	2.21	0.003	0	0.39	- 0.26	0.61
400	0	0.98	3.02	0.022	0	0.25	- 0.85	0.73	2.28	0.014	0	0.41	- 0.29	0.59
500	0	0.96	3.25	0.037	0	0.35	- 0.58	0.62	2.36	0.033	0	0.43	- 0.29	0.57
600	0	0.95	3.50	0.050	0	0.41	- 0.32	0.54	2.44	0.053	0	0.43	- 0.35	0.57
700	0	0.94	3.76	0.063	0	0.45	- 0.05	0.47	2.54	0.073	0	0.43	- 0.38	0.57
800	0	0.92	3.98	0.076	0	0.48	+ 0.20	0.43	2.62	0.093	0	0.43	- 0.43	0.57
900	0	0.91	4.22	0.086	0	0.50	0.45	0.39	2.73	0.11	0	0.44	- 0.46	0.56
1000	0	0.91	4.50	0.094	0	0.52	0.74	0.36	2.85	0.12	0	0.44	- 0.50	0.56

	$C_4H_{10}S$ Compounds													
	1-Butanethiol		2-Butanethiol		2-Methyl-1-propanethiol		2-Methyl-2-propanethiol		2-Thiapentane		3-Thiapentane		3-Methyl-2-thiabutane	
T, °K.	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni	$\Delta Fi°$ kcal.	Ni
0	0	0.0000	- 1.67	0.00	- 1.69	0.000	- 4.56	1.00	+ 1.64	0.00000	+ 1.38	0.00000	- 0.22	0.0000
273.16	0	0.0057	- 1.55	0.10	- 1.39	0.074	- 2.69	0.82	1.74	0.00023	1.57	0.00032	+ 0.50	0.0023
298.16	0	0.011	- 1.50	0.14	- 1.31	0.10	- 2.47	0.73	1.76	0.00059	1.61	0.00075	0.59	0.0042
300	0	0.012	- 1.50	0.15	- 1.31	0.11	- 2.46	0.73	1.76	0.00062	1.61	0.00079	0.60	0.0043
400	0	0.057	- 1.30	0.29	- 1.02	0.21	- 1.58	0.42	1.85	0.0056	1.78	0.0060	0.98	0.017
500	0	0.11	- 1.10	0.35	- 0.74	0.24	- 0.73	0.24	1.95	0.016	1.97	0.016	1.35	0.029
600	0	0.16	- 0.94	0.36	- 0.47	0.24	+ 0.09	0.15	2.03	0.029	2.15	0.026	1.68	0.039
700	0	0.20	- 0.76	0.34	- 0.19	0.23	0.90	0.10	2.15	0.042	2.34	0.037	2.04	0.046
800	0	0.23	- 0.54	0.32	+ 0.12	0.21	1.73	0.078	2.29	0.055	2.56	0.046	2.41	0.051
900	0	0.26	- 0.30	0.31	0.49	0.20	2.61	0.061	2.44	0.066	2.82	0.054	2.83	0.053
1000	0	0.28	- 0.10	0.29	0.79	0.19	3.43	0.050	2.59	0.075	2.99	0.062	3.18	0.056

in Table I. The equilibrium constant of isomerization,

$$Ki = Ni/Nr$$

(the equilibrium mole fraction of the reference compound is indicated by Nr), is related to $\Delta Fi°$ by the expression,

$$\Delta Fi° = -RT \ln Ki$$

Strictly, the values of equilibrium mole fraction are applicable only in the range from zero pressure up to that pressure at which the ratio of fugacity to pressure still does not differ significantly for the several isomers.

The mole fraction of each isomer present when at equilibrium with all its other isomers, as given in Table I, is plotted as

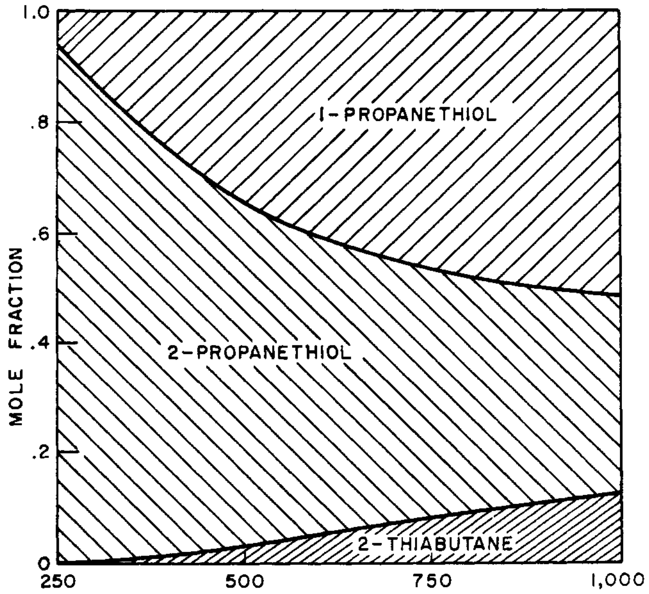
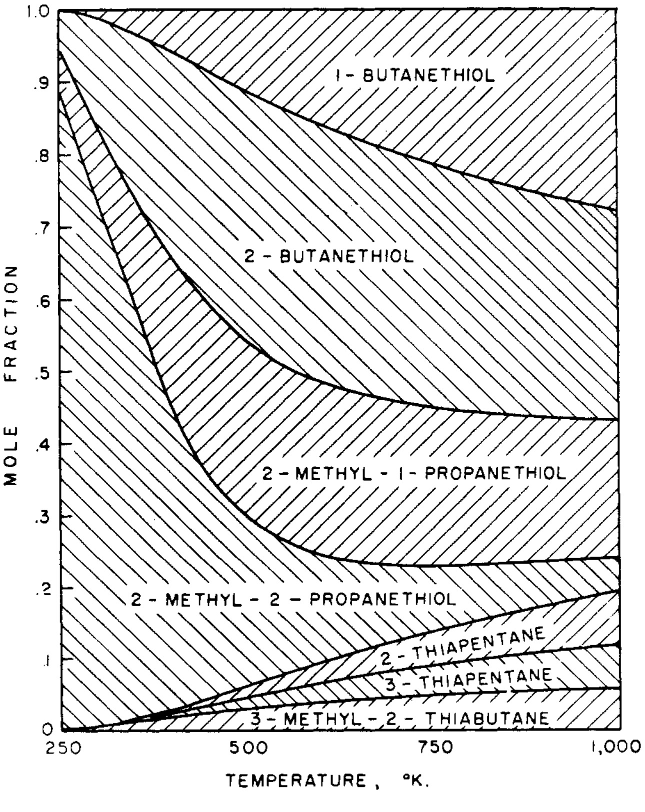


Figure 2. Equilibrium concentrations of C_3H_8S alkane thiols and sulfides



→

Figure 3. Equilibrium concentrations of $C_4H_{10}S$ alkane thiols and sulfides

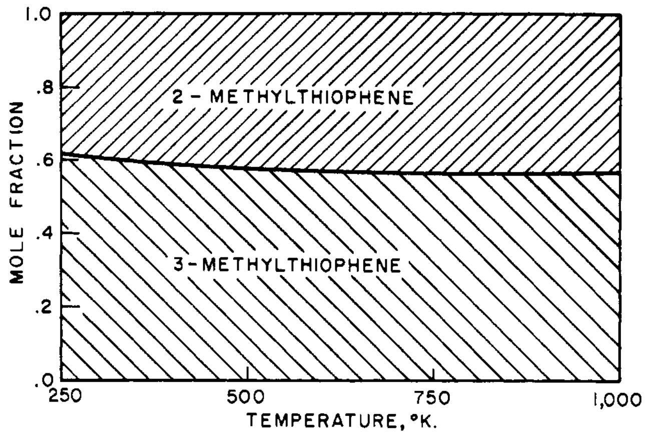


Figure 4. Equilibrium concentrations of methylthiophenes

a function of temperature in Figures 1 to 4. The vertical width of each band gives the mole fraction, and the mole fractions are plotted additively, so that their sum is unity at all temperatures.

Inspection of Figures 1 to 3 shows that the alkane thiols as a class are thermodynamically favored with respect to the isomeric alkane sulfides, particularly at lower temperatures. This behavior reflects the greater strength of a C—C and an S—H bond relative to a C—S and a C—H bond. Within a class the most highly branched compound is the most stable at lower temperatures but decreases in stability with increase in temperature relative to the less highly branched compounds. If the isomers with the same degree of branching are considered together, the equilibrium concentrations vary with temperature in much the same way as do those of the alkanes with the same number of heavy atoms. The comparison in Figure 5 for the $C_4H_{10}S$ thiols and sulfides and the corresponding pentanes illustrates this behavior.

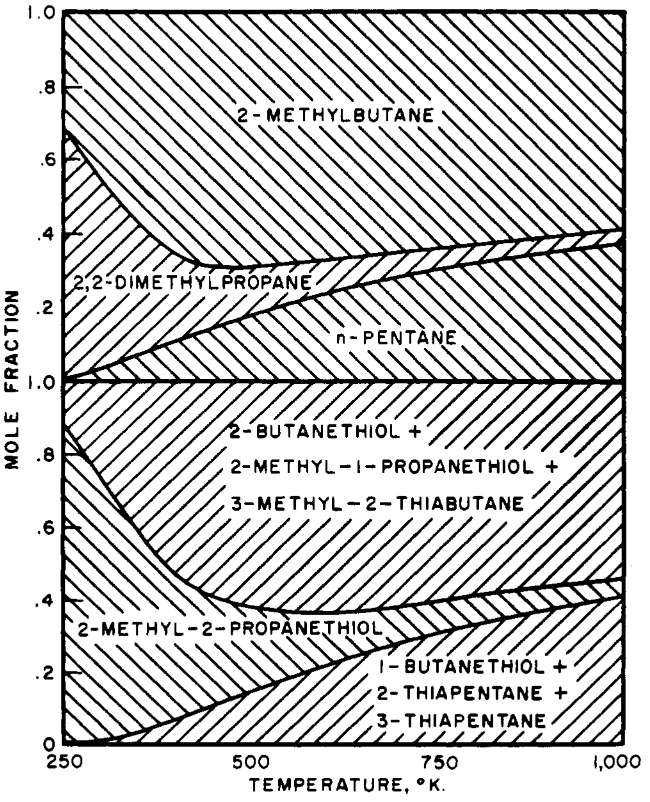


Figure 5. Comparison of equilibrium concentrations of pentane isomers with those for straight-chain, singly branched, and doubly branched $C_4H_{10}S$ alkane thiols and sulfides

Values for the pentanes from (16)

Inspection of Figure 4 shows that the methylthiophenes are of comparable stability, with the 3-isomer slightly favored at all temperatures considered.

The values of free energy of formation used for calculating the isomerization equilibria are discussed below.

COMPARISON WITH CONCENTRATIONS FOUND IN PETROLEUM

The composition studies made by American Petroleum Institute Research Project 48A have provided data on the concentrations of all detectable low-molecular-weight sulfur compounds in Wasson, Tex., crude oil (*23*). Therefore, for the compounds discussed here, it is possible to compare the concentrations actually found in Wasson crude with those that correspond to thermodynamic equilibrium at reasonable temperatures. Such comparisons are made in Figures 6 to 8, in which the equilibrium concentrations are shown for 300° and 1000° K. Because the calculated values are strictly valid only for the ideal gaseous state and because relatively large uncertainties must be assigned to the observed concentrations of these trace components, the comparisons give only a qualitative, but still significant, indication of the degree to which thermodynamic equilibrium is approached in Wasson crude.

The most obvious conclusion to be drawn from Figure 6 is that the concentration of total sulfides in Wasson crude, relative to the isomeric thiols, is much higher than the equilibrium concentration at any reasonable temperature. Evidently, the more reactive thiols either were not formed in equilibrium amounts or have been altered by chemical action after formation.

Figures 7 and 8 show that the members of a particular class (thiol or sulfide) also are not generally present in equilibrium concentrations. The observed concentrations of the C_3H_8S

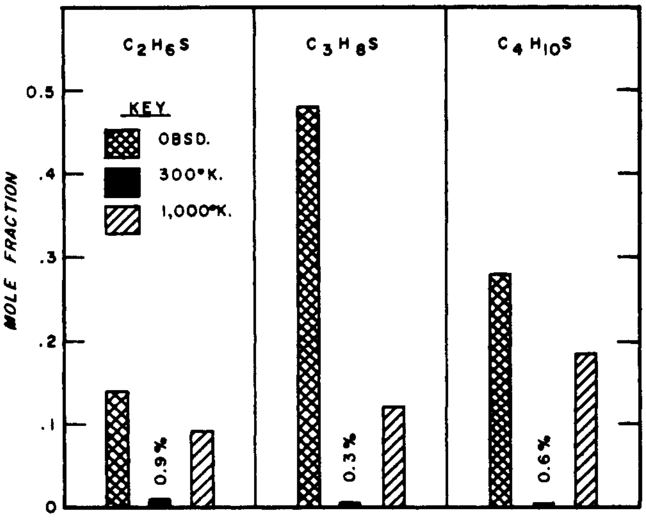


Figure 6. Mole fraction of total sulfides in C_2H_6S, C_3H_8S, and $C_4H_{10}S$ alkane thiols and sulfides

Observed values in Wasson crude oil compared with equilibrium values at 300° and 1000° K.

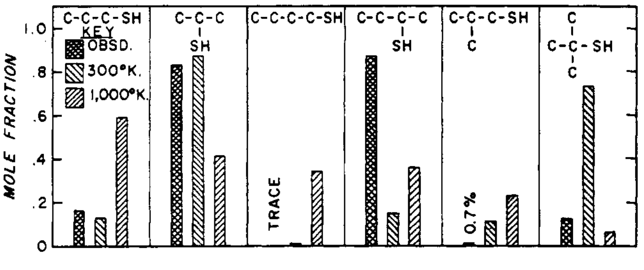


Figure 7. Mole fraction of individual compounds in C_3H_8S and $C_4H_{10}S$ alkane thiols

Observed values in Wasson crude oil compared with equilibrium values at 300° and 1000° K.

thiols do correspond to equilibrium at slightly above room temperature (Figure 7), but this fact probably is not significant, because the $C_4H_{10}S$ thiols definitely are not at equilibrium, as the same figure shows. The high observed concentration of 2-butanethiol is particularly at variance with the equilibrium concentrations. Furthermore, the low observed concentration of 1-butanethiol is consistent with equilibration at low temperatures, but, in contrast, the low concentration of 2-methyl-2-propanethiol is consistent with equilibration at high temperatures.

Lack of thermodynamic equilibrium also is shown by results for the methylthiophenes. Thiophene and the methylthiophenes have not been detected in Wasson crude oil. In Wilmington, Calif., crude oil, on the other hand, low-boiling alkane thiols and sulfides are not present in detectable amounts, but thiophene and the methylthiophenes are found (*22*). Again, lack of thermodynamic equilibrium in Wilimington crude is shown by the preponderance of 2-methylthiophene over the thermodynamically favored 3-methylthiophene.

Speculation about the origin of petroleum is always fascinating to those who work with this valuable natural resource. For such speculation, the conclusion that sulfur compounds in crude oils are not in thermodynamic equilibrium is not so idle as it might seem. If the components of crude oils were at equilibrium, composition studies would tell little more about the origin of petroleum than the elemental composition of the substance from which it is derived.

Ultimately, data on the composition of petroleum and on the thermodynamic properties of its constituents should be useful in developing better theories concerning the source and past history of crude oil. Information about trace components, of which sulfur compounds represent a prevalent type, may be especially valuable. Any theory on the origin of petroleum must be consistent with the observations made here. These observations, with others that will become possible with advances in both the chemical thermodynamics and the analytical chemistry of sulfur compounds in petroleum, should provide useful leads to better theories on the origin of petroleum, as well as rigorous tests of proposed theories.

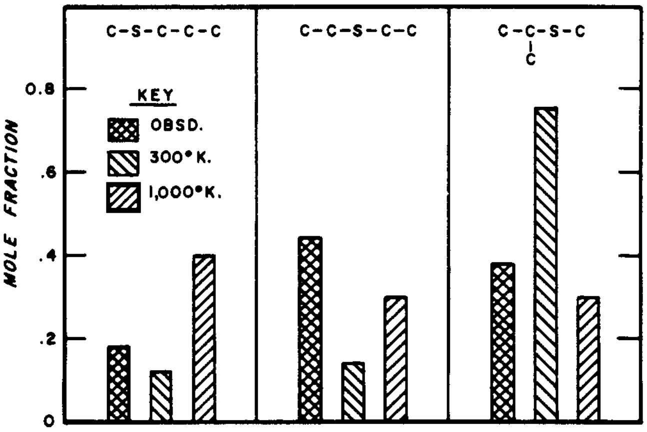


Figure 8. Mole fraction of individual compounds in $C_4H_{10}S$ alkane sulfides

Observed values in Wasson crude oil compared with equilibrium values at 300° and 1000° K.

VALUES OF FREE ENERGY OF FORMATION

C_3H_6S Compounds. Ethanethiol and 2-Thiapropane. Values of free energy of formation for the C_2H_6S compounds are given in a previous publication from this laboratory (*10*), which also reported calculated results for the isomerization equilibrium. The latter are repeated for the sake of completeness.

C_3H_8S Compounds. 1-Propanethiol and 2-Propanethiol. Previous publications (*8*, *15*) reported values of free energy of formation.

2-Thiabutane. A previous publication (*18*) reported calculated values of thermodynamic functions, which, however, did not include corrections for anharmonicity. Later spectroscopic studies (*2*, *21*) have shown that one of the C—S stretching frequencies should have been taken as 653 cm.$^{-1}$ instead of 679 cm.$^{-1}$ The change is not very important thermodynamically and, moreover, would be nearly compensated if other frequencies were increased to the reported gas-phase values. Therefore, the functions of (*18*) were corrected only by inclusion of empirical anharmonicity contributions (*6*, *14*) selected to fit the calorimetric values of $S°$ and $C_p°$. Values used for the parameters of the anharmonicity function were: ν = 1100 cm.$^{-1}$ and Z = 1.00 cal. deg.$^{-1}$ mole^{-1}. The corrected values of the thermodynamic functions are listed in columns 2 to 6 of Table II.

The standard heat of formation of 2-thiabutane in the gaseous state, relative to rhombic sulfur, was reported in a previous publication (*5*). This datum and the thermodynamic functions of Table II were used with appropriate thermodynamic data for C(c, graphite) (*24*), H_2(g) (*24*), and S_2(g) (*1*) to compute values of $\Delta Hf°$, $\Delta Ff°$, and $\log_{10} Kf$ for 2-thiabutane, as given in columns 7 to 9 of Table II.

$C_4H_{10}S$ Compounds. 1-Butanethiol, 2-Butanethiol, 2-Methyl-1-propanethiol, 2-Thiapentane, and 3-Methyl-2-thiabutane. Previous publications (*7*, *9*, *19*, *20*) reported values of free energy of formation.

2-Methyl-2-propanethiol. A previous publication (*11*) reported calculated values of the thermodynamic functions, which, however, did not include corrections for anharmonicity. The functions of (*11*) were revised to include empirical anharmonicity contributions (*6*, *14*). Values for the two parameters of the anharmonicity function, ν and Z, and for the height of the potential barrier for rotation about the C—S bond, V_0, were selected to fit the calorimetric values of $S°$ and $C_p°$; the values of all other molecular structure parameters

Table II. Molal Thermodynamic Properties of 2-Thiabutane[a]

T, °K.	$(F° - H°_0)/T$, Cal. Deg.$^{-1}$	$(H° - H°_0)/T$, Cal. Deg.$^{-1}$	$H° - H°_0$, Kcal.	$S°$, Cal. Deg.$^{-1}$	$C_p°$, Cal. Deg.$^{-1}$	$\Delta Hf°$[b], Kcal.	$\Delta Ff°$[b], Kcal.	$\log_{10} Kf$[b]
0	0	0	0	0	0	-24.15	-24.15	Infinite
273.16	-62.92	14.75	4.030	77.68	21.49	-29.11	- 8.56	6.85
298.16	-64.25	15.37	4.584	79.62	22.73	-29.49	- 6.66	4.88
300	-64.34	15.42	4.626	79.76	22.82	-29.52	- 6.52	4.75
400	-69.11	17.89	7.157	87.00	27.81	-30.90	+ 1.36	- 0.74
500	-73.37	20.35	10.17	93.71	32.40	-32.05	9.57	- 4.18
600	-77.30	22.68	13.61	99.98	36.41	-32.97	17.97	- 6.55
700	-80.96	24.90	17.43	105.86	39.89	-33.66	26.52	- 8.28
800.	-84.42	26.95	21.56	111.38	42.93	-34.16	35.15	- 9.60
900	-87.72	28.88	25.99	116.60	45.60	-34.48	43.83	-10.64
1000	-90.85	30.68	30.68	121.53	47.94	-34.61	52.55	-11.48

[a] To retain internal consistency, some values are given to one more decimal place than is justified by absolute accuracy.

[b] Standard heat, standard free energy, and common logarithm of the equilibrium constant for formation of 2-thiabutane by the reaction: 3 C(c, graphite) + 4 H_2(g) + ½S_2(g) = C_3H_8S(g).

Table III. Molal Thermodynamic Properties of 2-Methyl-2-propanethiol[a]

T, °K.	$(F^\circ - H^\circ_0)/T$, Cal. Deg.$^{-1}$	$(H^\circ - H^\circ_0)/T$, Cal. Deg.$^{-1}$	$H^\circ - H^\circ_0$, Kcal.	S°, Cal. Deg.$^{-1}$	C_p°, Cal. Deg.$^{-1}$	$\Delta Hf^{\circ b}$, Kcal.	$\Delta Ff^{\circ b}$, Kcal.	$\log_{10}Kf^b$
0	0	0	0	0	0	-34.40	-34.40	Infinite
273.16	-61.92	16.40	4.480	78.32	27.09	-40.96	-11.89	9.51
298.16	-63.40	17.38	5.182	80.78	28.92	-41.41	- 9.22	6.76
300	-63.51	17.45	5.235	80.96	29.05	-41.44	- 9.02	6.57
400	-69.06	21.24	8.497	90.30	36.08	-43.04	+ 2.04	- 1.11
500	-74.19	24.84	12.42	99.03	42.19	-44.30	13.46	- 5.88
600	-79.01	28.16	16.89	107.17	47.14	-45.26	25.11	- 9.14
700	-83.58	31.18	21.82	114.76	51.12	-45.96	36.89	-11.52
800	-87.92	33.87	27.10	121.79	54.36	-46.49	48.76	-13.32
900	-92.06	36.30	32.67	128.36	57.04	-46.86	60.70	-14.74
1000	-96.00	38.50	38.50	134.49	59.25	-47.08	72.67	-15.88

[a] See footnote *a*, Table II.

[b] Standard heat, standard free energy, and common logarithm of the equilibrium constant for formation of 2-methyl-2-propanethiol by the reaction: $4C(c, graphite) + 5\,H_2(g) + \frac{1}{2}S_2(g) = C_4H_{10}S(g)$.

given in (*11*) were retained. The values selected were: $\nu = 1400$ cm.$^{-1}$, $\zeta = -3.00$ cal. deg.$^{-1}$ mole^{-1}, and $V_0 = 1380$ cal. mole^{-1}. The anharmonicity contribution for 2-methyl-2-propanethiol is negative in sign, as it is for the two other branched-chain $C_4H_{10}S$ thiols, 2-butanethiol (*9*) and 2-methyl-1-propanethiol (*20*). The revised values of the functions are listed in columns 2 to 6 of Table III.

A redetermination of the heat of combustion of 2-methyl-2-propanethiol (*3*) led to the value -25.99 ± 0.21 kcal. mole^{-1} for the standard heat of formation of the vapor at 298.16° K. referred to rhombic sulfur. The foregoing value supersedes the one reported previously (*4*) and used in (*11*). Values of ΔHf°, ΔFf°, and $\log_{10}Kf$, calculated by use of the corrected values for the thermodynamic functions and redetermined value of the heat of formation, are given in columns 7 to 9 of Table III.

3-Thiapentane. A previous publication (*17*) reported calculated values of the thermodynamic functions uncorrected for anharmonicity. Application of empirical corrections for anharmonicity (*6*, *14*) with $\nu = 1200$ cm.$^{-1}$ and $\zeta = 3.00$ cal. deg.$^{-1}$ mole^{-1}, selected to fit the calorimetric values of S° and C_p°, gave the values listed in columns 2 to 6 of Table IV. A redetermination of the heat of combustion of 3-thiapentane (*3*) led to the value -19.77 ± 0.19 kcal. mole^{-1} for the standard heat of formation of the vapor at 298.16° K. referred to rhombic sulfur, a value that supersedes those reported previously (*4*, *17*). Values of ΔHf°, ΔFf°, and $\log_{10}Kf$, calculated by use of the corrected values for the thermodynamic functions and redetermined value of the heat of formation, are given in columns 7 to 9 of Table IV.

Methylthiophenes. 2-Methylthiophene. A previous publication (*13*) reported values of free energy of formation.

3-Methylthiophene. A previous publication (*12*) reported

Table IV. Molal Thermodynamic Properties of 3-Thiapentane[a]

T, °K.	$(F^\circ - H^\circ_0)/T$, Cal. Deg.$^{-1}$	$(H^\circ - H^\circ_0)/T$, Cal. Deg.$^{-1}$	H° - H°_0, Kcal.	S°, Cal. Deg.$^{-1}$	C_p°, Cal. Deg.$^{-1}$	$\Delta Hf^{\circ b}$, Kcal.	$\Delta Ff^{\circ b}$, Kcal.	$\log_{10}Kf^b$
0	0	0	0	0	0	-28.46	-28.46	Infinite
273.16	- 68.05	17.52	4.787	85.57	26.35	-34.72	- 7.63	6.11
298.16	- 69.62	18.34	5.467	87.96	27.97	-35.19	- 5.14	3.77
300	- 69.74	18.39	5.519	88.13	28.09	-35.22	- 4.95	3.61
400	- 75.48	21.63	8.652	97.11	34.65	-36.95	+ 5.40	- 2.95
500	- 80.66	24.85	12.43	105.51	40.75	-38.36	16.16	- 7.06
600	- 85.46	27.97	16.78	113.43	46.11	-39.43	27.17	- 9.90
700	- 90.01	30.89	21.62	120.90	50.81	-40.23	38.33	-11.97
800	- 94.31	33.63	26.90	127.94	54.91	-40.75	49.59	-13.55
900	- 98.41	36.22	32.60	134.63	58.56	-41.00	60.91	-14.79
1000	-102.37	38.60	38.60	140.97	61.79	-41.04	72.23	-15.79

[a] See footnote *a*, Table II.

[b] Standard heat, standard free energy, and common logarithm of the equilibrium constant for the formation of 3-thiapentane by the reaction: $4C(c, graphite) + 5\,H_2(g) + \frac{1}{2}S_2(g) = C_4H_{10}S\,(g)$.

Table V. Molal Thermodynamic Properties of 3-Methylthiophene[a]

T, °K.	$(F^\circ - H^\circ_0)/T$, Cal. Deg.$^{-1}$	$(H^\circ - H^\circ_0)/T$, Cal. Deg.$^{-1}$	$H^\circ - H^\circ_0$, Kcal.	S°, Cal. Deg.$^{-1}$	C_p°, Cal. Deg.$^{-1}$	$\Delta Hf^{\circ b}$, Kcal.	$\Delta Ff^{\circ b}$, Kcal.	$\log_{10}Kf^b$
0	0	0	0	0	0	8.80	8.80	$-\infty$
273.16	-61.75	13.18	3.599	74.93	21.00	4.85	18.45	-14.76
298.16	-62.94	13.90	4.145	76.84	22.81	4.54	19.70	-14.44
300	-63.02	13.96	4.187	76.98	22.94	4.52	19.80	-14.42
400	-67.47	17.06	6.823	84.53	29.61	3.44	25.06	-13.69
500	-71.60	20.16	10.08	91.76	35.20	2.59	30.57	-13.36
600	-75.53	23.06	13.83	98.59	39.73	1.94	36.23	-13.20
700	-79.29	25.70	17.99	104.99	43.41	1.44	41.99	-13.11
800	-82.88	28.12	22.50	111.00	46.49	1.09	47.80	-13.06
900	-86.33	30.30	27.27	116.63	49.08	0.86	53.65	-13.03
1000	-89.62	32.30	32.30	121.92	51.27	0.77	59.53	-13.01

[a] See footnote *a*, Table II.

[b] Standard heat, standard free energy, and common logarithm of equilibrium constant for the formation of 3-methylthiophene by the reaction: $5C(c, graphite) + 3\,H_2(g) + \frac{1}{2}S_2(g) = C_5H_6S\,(g)$.

values of thermodynamic properties uncorrected for anharmonicity. The functions of (*12*) were corrected by inclusion of empirical anharmonicity contributions (*6, 14*) selected to fit the calorimetric values of S° and C_p°. Values used for the parameters of the anharmonicity function were: $\nu = 400$ cm.$^{-1}$ and $Z = 0.198$ cal. deg.$^{-1}$ mole^{-1}. The corrected values of the thermodynamic properties are listed in Table V.

PHYSICAL CONSTANTS

The reported values are based on the 1951 values of fundamental constants for physical chemistry, the 1951 international atomic weights, and the relation 0° C. = 273.16° K.

LITERATURE CITED

(1) Evans, W. H., Wagman, D. D., *J. Research Natl. Bur. Standards* **49**, 141 (1952).
(2) Hayashi, M., Shimanouchi, T., Mizushima, S., *J. Chem. Phys.* **26**, 608 (1957).
(3) Hubbard, W. N., Good, W. D., Waddington, G., *J. Phys. Chem.* **62**, 614 (1958).
(4) Hubbard, W. N., Katz, C., Waddington, G., *Ibid.*, **58**, 142 (1954).
(5) Hubbard, W. N., Waddington, G., *Rec. trav. chim.* **73**, 910 (1954).
(6) McCullough, J. P., Finke, H. L., Hubbard, W. N., Good, W. D., Pennington, R. E., Messerly, J. F., Waddington, G., *J. Am. Chem. Soc.* **76**, 2661 (1954).
(7) McCullough, J. P., Finke, H. L., Messerly, J. F., Pennington, R. E., Hossenlopp, I. A., Waddington, G., *Ibid.*, **77**, 6119 (1955).
(8) McCullough, J. P., Finke, H. L., Scott, D. W., Gross, M. E., Messerly, J. F., Pennington, R. E., Waddington, G., *Ibid.*, **76**, 4796 (1954).
(9) McCullough, J. P., Finke, H. L., Scott, D. W. Pennington, R. E., Gross, M. E., Messerly, J. F., Waddington, G., *Ibid.*, **80**, 4786 (1958).
(10) McCullough, J. P., Hubbard, W. N., Frow, F. R., Hossenlopp, I. A., Waddington, G., *Ibid.*, **79**, 561 (1957).
(11) McCullough, J. P., Scott, D. W., Finke, H. L., Hubbard, W. N., Gross, M. E., Katz, C., Pennington, R. E., Messerly, J. F., Waddington, G., *Ibid.*, **75**, 1818 (1953).
(12) McCullough, J. P., Sunner, S., Finke, H. L., Hubbard, W. N., Gross, M. E., Pennington, R. E., Messerly, J. F., Good, W. D., Waddington, G., *Ibid.*, **75**, 5075 (1953).
(13) Pennington, R. E., Finke, H. L., Hubbard, W. N., Messerly, J. F., Frow, F. R., Hossenlopp, I. A., Waddington, G., *Ibid.*, **78**, 2055 (1956).
(14) Pennington, R. E., Kobe, K. A., *J. Chem. Phys.* **22**, 1442 (1954).
(15) Pennington, R. E., Scott, D. W., Finke, H. L., McCullough, J. P., Messerly, J. F., Hossenlopp, I. A., Waddington, G., *J. Am. Chem. Soc.* **78**, 3266 (1956).
(16) Rossini, F. D., Prosen, E. J. R., Pitzer, K. S., *J. Research Natl. Bur. Standards* **27**, 529 (1941).
(17) Scott, D. W., Finke, H. L., Hubbard, W. N., McCullough, J. P., Oliver, G. D., Gross, M. E., Katz, C., Williamson, K. D., Waddington, G., Huffman, H. M., *J. Am. Chem. Soc.* **74**, 4656 (1952).
(18) Scott, D. W., Finke, H. L., McCullough, J. P., Gross, M. E., Williamson, K. D., Waddington, G., Huffman, H. M., *Ibid.*, **73**, 261 (1951).
(19) Scott, D. W., Finke, H. L., McCullough, J. P., Messerly, J. F., Pennington, R. E., Hossenlopp, I. A., Waddington, G., *Ibid.*, **79**, 1062 (1957).
(20) Scott, D. W., McCullough, J. P., Messerly, J. F., Pennington, R. E., Hossenlopp, I. A., Finke, H. L., Waddington, G., *Ibid.*, **80**, 55 (1958).
(21) Sheppard, N., unpublished investigation, University of Cambridge.
(22) Thompson, C. J., Coleman, H. J., Mikkelsen, L., Yee, D., Ward, C. C., Rall, H. T., *Anal. Chem.* **28**, 1384 (1956).
(23) Thompson, C. J., Coleman, H. J., Rall, H. T., Smith, H. M., *Ibid.*, **27**, 175 (1955).
(24) Wagman, D. D., Kilpatrick, J. E., Taylor, W. J., Pitzer, K. S., Rossini, F. D., *J. Research Natl. Bur. Standards* **34**, 143 (1945).

RECEIVED for review June 23, 1958. Accepted October 2, 1958. Division of Petroleum Chemistry, 134th Meeting, ACS, Chicago, Ill., September 1958. Contribution No. 75 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines, U. S. Department of the Interior. Part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

Heat of Solution of Ammonia in Ethyl Alcohol at 25° C.

JOHN R. MORTON, III
U. S. Army Chemical Warfare Laboratories, Army Chemical Center, Md.[1]

Certain thermochemical studies at these laboratories recently required some knowledge of the heat of solution of anhydrous ammonia in ethyl alcohol. An exhaustive search of the literature revealed that a rise in temperature had been observed during measurement of the solubility of ammonia in ethyl alcohol (*1*); unfortunately, the energy equivalent of that system had not been measured to permit a molar heat of solution to be computed. This work was done to supply that information.

The reagents used were absolute ethyl alcohol and anhydrous ammonia. No additional purification was attempted with either compound.

Temperatures within the calorimeter were measured and graphed by an automatic temperature recorder using a thermistor for a sensing element (*2*).

For each run, approximately 300 ml. of ethyl alcohol were placed in the calorimeter. After thermal equilibrium was attained, 1800 ml. of ammonia were introduced by mercury displacement from a gas buret (760 mm., 25° C.). When thermal equilibrium was again attained, the energy equivalent was determined by electrical heating. The temperature rises were determined graphically from the time-temperature plot on the recorder chart.

The quantity of ammonia in solution was determined by cold titration with hydrochloric acid. The final solution contained ammonia in a mole ratio of 0.014, approximately one sixth the quantity needed for saturation (*1*).

The average integral heat of solution for ammonia in ethyl alcohol at 25° C. was 6.27 ± 0.03 kcal. per mole exothermic.

ACKNOWLEDGMENT

The author gratefully acknowledges the helpful suggestions of P. B. Coulter in this work.

LITERATURE CITED

(1) Hatem, S., *Bull. soc. chim. France* 337 (1949).
(2) Zeffert, B. M., Witherspoon, R. R., *Anal. Chem.* **28**, 1701 (1956).

RECEIVED for review July 22, 1958. Accepted January 5, 1959.

---

[1] Present address, University of California Radiation Laboratory, Berkeley 4, Calif.