it would seem that n is slightly larger for the deuterides.

The present values of U for LiH and LiD may be compared with those of Kapustinsky, Shamovsky and Bayushkina[17] who measured the ultraviolet absorption spectra of LiH and LiD and, attributing the band to the process

$$\mathrm{LiH(c)} + \mathrm{Li(g)} + \mathrm{H(g)}$$

derived 219.2 and 220.8 kcal./mole for U_{LiH} and U_{LiD}, respectively.

LIVERMORE, CALIF.

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[17] A. F. Kapustinsky, L. M. Shamovsky and K. S. Bayushkina, *Acta Physicochim. U.R.S.S.*, **7**, 799 (1937).

[CONTRIBUTION NO. 74 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

2-Butanethiol: Chemical Thermodynamic Properties between 0 and 1000°K.; Rotational Conformations[1]

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The chemical thermodynamic properties of 2-butanethiol in the ideal gaseous state (0 to 1000°K.) were calculated by use of calorimetric, spectroscopic and molecular structure information. The thermodynamic and spectroscopic results show that 2-butanethiol exists as a mixture of molecules in three distinct rotational conformations—two with about equal energies and a third with about 1.0 kcal. mole^{-1} higher energy. Experimental studies provided the following information: values of heat capacity for the solid (12°K. to the triple point), the liquid (triple point to 307°K.) and the vapor (346 to 453°K.); the triple point temperature; the heat of fusion; thermodynamic functions for the solid and liquid (0 to 310°K.); heat of vaporization (318 to 358°K.); parameters of the equation of state; vapor pressure (38 to 121°); and standard heat of formation at 298.16°K.

Thermodynamic investigations of organic sulfur compounds are made in this Laboratory as part of American Petroleum Institute Research Project 48. Comprehensive studies have been made of all seven isomeric $C_4H_{10}S$ thiols and sulfides to determine accurately the effect of molecular structure on thermodynamic properties as well as to provide useful data for each isomer. Results obtained for six of the isomers have been published.[2] The present paper reports results for the racemic mixture of 2-butanethiol (*sec*-butylmercaptan), the only one of the $C_4H_{10}S$ isomers for which optical isomerism is possible.

The experimental part of this investigation included studies by low temperature calorimetry, vapor flow calorimetry, comparative ebulliometry and combustion calorimetry. The detailed results are given later in the Experimental section. The results needed for calculating thermodynamic properties, as discussed in the next section, are collected in Table I.

Calculation of Thermodynamic Properties

Thermodynamic functions were calculated by standard methods of statistical mechanics and thermodynamics. Most of the parameters needed were obtained from spectroscopic and molecular structure information; the few remaining were chosen so as to obtain agreement with the observed values of entropy and heat capacity in Table I. The calculated thermodynamic functions and the observed value of the heat of formation in Table I were used in calculating the standard heat, standard free energy and equilibrium constant of formation at selected temperatures between 0 and 1000°K.

TABLE I

OBSERVED AND CALCULATED MOLAL THERMODYNAMIC PROPERTIES OF 2-BUTANETHIOL IN THE IDEAL GASEOUS STATE

Entropy, $S°$, cal. deg.$^{-1}$			Heat capacity, $C_p°$, cal. deg.$^{-1}$		
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
298.16	87.67	87.65	346.2	31.83	31.82
318.0	89.57	89.52	368.2	33.29	33.30
328.6	90.54	90.51	403.2	35.56	35.58
336.7	91.27	91.26	453.2	38.68	38.68
358.1	93.22	93.23			

$4\mathrm{C(c, graphite)} + 5\mathrm{H_2(g)} + {}^1/_2\mathrm{S_2(g)} = \mathrm{C_4H_{10}S(g)}$. Heat of formation, $\Delta Hf°_{298.16}$(obsd.) $= -38.39 \pm 0.19$ kcal.

Vibrational Assignment.—Available spectroscopic data for 2-butanethiol are collected in Table II.[3-5] The data of ref. 4 and 5 were obtained with samples of the same highly purified material used in this research.

Three spectroscopically distinguishable rotational conformations of 2-butanethiol are possible, as shown in Fig. 1. The conformation with the ethyl group *gauche* to the thiol group and *trans* to the methyl group is labeled A; that with the ethyl group *trans* to the thiol group and *gauche* to the methyl group is labeled B; and that with the ethyl group *gauche* to both the thiol and methyl groups is labeled C. From considerations of the energy relationships among the rotational conformations of 1-

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[1] This investigation was part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

[2] (a) D. W. Scott, J. P. McCullough, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp, H. L. Finke and Guy Waddington, THIS JOURNAL, **80**, 55 (1958), and earlier publications cited therein; (b) W. N. Hubbard, W. D. Good and Guy Waddington, *J. Phys. Chem.*, **62**, 611 (1958).

[3] K. W. F. Kohlrausch and F. Köppl, *Monatsh.*, **63**, 255 (1933).

[4] American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Raman Spectral Data, Serial No. 229.

[5] Ref. 4, Catalog of Infrared Spectral Data, Serial Nos. 1545 and 1622.

TABLE II

VIBRATIONAL SPECTRA OF 2-BUTANETHIOL, CM.$^{-1}$

Raman, liquid[a] K. & K.	Raman, liquid[a] API[d]	Infrared, liquid[b] API	Interpretation[c]
	90 (vw)		324 − 228 = 96
	143 (2)		377 − 228 = 149
	167 (vw)		620 − 453 = 167
228 (1/2)	228 (2)		CCS bend., A
286 (1)			Impurity
	324 (4)		CCS bend., A
375 (4)	377 (17)		CCC bend., A
	412 (3)		CCC bend., C
456 (2)	453 (7)		CCC bend., A
482 (0)			Impurity
532 (3)	517 (1)	*ca.* 521	CCC bend., C
617 (6)	609 (13)	620 m	C–S str., A, and 228 + 377 = 605
	623 (19)		
	634 (6)		2 × 324 = 648
659 (1/2)	659 (5)	664 w	C–S str., C
683 (2)	683 (12)	683 w	C–S str., B
		ca. 780 w	324 + 453 = 777
788 (1)	790 (6)	797 s	CH_2 rock., A
821 (1/2)		*ca.* 829 w	CH_2 rock., C
842 (2)	839 (11)	843 m	CH_2 rock., B
	863 (3)	873 m	CSH bend., A
954 (1/2)	953 (6)	961 s	CH_3 rock., A
986 (1/2)		978 w	C–C str., A
	996 (4)	1000 s	CH_3 rock., A
1018 (1)	1017 (4)	1017 w	CH_3 rock., A
1064 (1/2)	1070 (6)	1074 m	CH_3 rock., A
	1095 (3)	1098 w	228 + 868 = 1096
1107 (1)	1107 (4)		324 + 794 = 1118
	1123 (4)	1124 w	C–C str., A
1151 (1)	1151 (8)	1156 s	C–C str., A
1228 (1)	1228 (6)	1230 s	CH_2 wag., A
		1285 w	CH_2 twist., A
1294 (1)	1295 (10)	1300 m	CH wag., A
		ca. 1310 vw	324 + 998 = 1322
1346 (0)	1343 (5)	1348 w	CH wag., A
1385 (0)	1383 (4)	1377 s	CH_3 bend., sym., A
1447 (6)	1447 (32)	1451 vs	CH_2 bend., and CH_3 bend., unsym., A
[1500–2500 cm.$^{-1}$ region omitted]			
2568 (8)	2574 (92)	2545 vs	S–H str., A
[2500–5000 cm.$^{-1}$ region omitted]			

[a] In parentheses are listed relative intensities. [b] Intensity designated by: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. [c] The rotational conformation to which a fundamental frequency is assigned is denoted by the symbols A, B or C defined in text. [d] Not all of the lines included in ref. 4 are listed because some not reported by other workers can be explained logically as the result of excitation by mercury lines other than that at 4358 Å.

propanethiol,[6] *n*-butane[7] and 2-methylbutane,[8] the A conformation of 2-butanethiol may be predicted to have the lowest energy, the B conformation only slightly greater energy and the C conformation appreciably greater energy than either of the other two. As will be shown later, satisfactory agreement with the calorimetric data was obtained by use of the simplifying assumption that the A and B conformations have equal energies and that the C conformation has 1000 cal. mole^{-1} higher energy. Thus, at room temperature, the calculated concentration of molecules with either the A or the B conformation is 91 mole % and that of molecules with the C conformation is 9 mole %. The large number of frequencies from 200 to 1000 cm.$^{-1}$ in the spectra of 2-butanethiol confirms the obvious conclusion that all three conformations are present in high enough concentration to be detected spectroscopically.

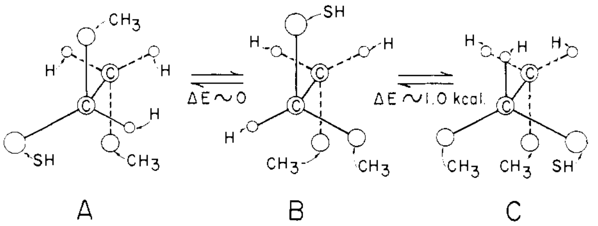

Fig. 1.—The rotational conformations of 2-butanethiol.

For calculating thermodynamic properties, a complete vibrational assignment was needed for only one conformation.[9] The A conformation was chosen for complete analysis because it probably is present in highest concentration at room temperature. To aid in the identification of skeletal bending frequencies, approximate normal coördinate analyses were made as described for the structurally similar molecule, 2-methylbutane,[8] except that interaction force constants were neglected in the present calculations. The results are in Table III. Although the agreement between calculated and observed frequencies is poor, the results support the interpretation given in Table III.

TABLE III

SKELETAL BENDING FREQUENCIES

ν, obsd.	ν, calcd. A[a]	ν, calcd. B[a]	ν, calcd. C[a]
167(vw, bd.)[b]			199
228(2, bd.)	254	218	
324(4)	310		324
377(17)	360	360	
		360	
412(3, d)		442	405
453(7)	477		
517(1)			517

[a] Rotational conformation. [b] See alternative assignment in Table II.

Frequencies of all three conformations also are apparent in the region of C–S stretching frequencies, 600–700 cm.$^{-1}$. In fact, the observation of five frequencies in this region may indicate that spectroscopically distinct rotational conformations are produced by rotation of the thiol group about the C–S bond. However, the Raman doublet at 609–623 cm.$^{-1}$ probably is due to Fermi resonance involving a fundamental at 620 cm.$^{-1}$ and the sum combination, 228 + 377 = 605 cm.$^{-1}$. The frequency at 634 cm.$^{-1}$ can be explained as shown in Table II. The most intense frequency in this region, 620 cm.$^{-1}$, was assigned to the A conformation.

It is possible that C–C stretching frequencies of

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(6) R. E. Pennington, D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **78**, 3266 (1956).

(7) K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944).

(8) D. W. Scott, J. P. McCullough, K. D. Williamson and Guy Waddington, THIS JOURNAL, **73**, 1707 (1951).

(9) K. S. Pitzer, *J. Chem. Phys.*, **14**, 239 (1946).

the three conformations might differ enough to be resolved, but only two frequencies not assigned as fundamentals of the A conformation appear in the expected regions of the spectra. These frequencies, at 1096 and 1107 cm.$^{-1}$, are satisfactorily interpreted as sum combinations of A fundamentals.

Of the carbon–hydrogen deformation vibrations, only the CH_2 rocking mode is likely to depend much upon the rotational conformation of the molecule. The assignments of the CH_2 rocking frequencies at 794, 821 and 841 cm.$^{-1}$ to particular conformations cannot be made unambiguously, except that the weak frequency at 821 cm.$^{-1}$ is logically assigned to the high energy C conformation. However, the CH_2 rocking frequencies of both 2-methylbutane[8,10] and the *gauche* conformation of 1-propanethiol[6] are near 794 cm.$^{-1}$, the frequency assigned to the A conformation of 2-butanethiol.

Assignment of the remaining frequencies in the spectra of 2-butanethiol was made by analogy with 2-methylbutane[8,10] and by use of regularities noted in the spectra of organic sulfur compounds.[11] Because the CH_2 and CH_3 bending frequencies near 1450 cm.$^{-1}$ and the C–H stretching frequencies near 2950 cm.$^{-1}$ were not all resolved, average values were used. The frequencies actually used in calculating thermodynamic functions are, for the A conformation: CCS bending, 228 and 324; CCC bending, 377 and 453; C–S stretching, 620; C–C stretching, 978, 1124, 1156; CH_2 rocking, 794; CSH bending, 868; CH_3 rocking, 957, 998, 1017 and 1072; CH_2 wagging, 1230; CH_2 twisting, 1285; CH wagging, 1300 and 1350; CH_2 and CH_3 bending, 1385(2) and 1450(5); S–H stretching, 2560; and C–H stretching, 2950(9) cm.$^{-1}$.

Because of the complex spectra that result from the coexistence of three conformations of 2-butanethiol, the assignment in Table II is schematic at best. However, this vibrational assignment and reasonable values of other molecular structure parameters, discussed later, give excellent agreement between calculated and observed thermodynamic properties. Also, the correlation of fundamental frequencies of six secondary derivatives of butane, in Table IV, supports the assignment for 2-butanethiol. Complete assignments could not be made for the halogen derivatives because only Raman spectra are available. Like 2-butanethiol, the 2-halobutanes appear to exist as mixtures of two or three rotational conformations.

Moments of Inertia, Internal Rotation and Anharmonicity.—The product of principal moments of inertia and the reduced moments of inertia for internal rotation were calculated for the A conformation by the general method of Kilpatrick and Pitzer.[12] Conventional values of bond distances and angles were used: namely, C–C, C–H, C–S and S–H bond distances, 1.54, 1.09, 1.815 and 1.34 Å., respectively; C–S–H bond angle 100°; and all other bond angles tetrahedral. The product of principal moments of inertia is 19.28×10^{-114} g.^{3} cm.^{6}. The reduced moments of inertia, taken as the diagonal elements of the internal rotational kinetic energy matrix, are 5.179×10^{-40}, 2.825×10^{-40} and 31.38×10^{-40} g. cm.^{2} for torsion of either methyl group and of the thiol and ethyl groups, respectively. Interaction of internal rotations makes the neglect of off-diagonal matrix elements a poor approximation. However, uncertainties in some of the other parameters used in the calculations of thermodynamic properties are probably more serious.

TABLE IV

CORRELATION OF VIBRATIONAL FREQUENCIES (IN CM.$^{-1}$) FOR MOLECULES OF THE TYPE $CH_3CH_2CH(X)CH_3$

	X-group					
Descriptive mode	CH_3[8]	OH[a,b]	SH[3-5]	Cl[a,c]	Br[a,d]	I[a]
CCX bend., A	246		228	231	214	196
CCX bend., A	367	347	324	335	292	267
CCX bend., B					$\underline{317}$	$\underline{303}$
CCC bend., A	415	441	377	382	352	332
CCC bend., B			$\underline{412}$			
CCC bend., A	464	467	453	465	457	453
C–X str., A	765	750	620	609	533	490
C–X str., B			$\underline{683}$	$\underline{672}$	$\underline{611}$	$\underline{579}$
C–X str., C			$\underline{634}$	$\underline{629}$	$\underline{581}$	$\underline{548}$
C–C str., A	978	992	978	(Not obsd. in Raman)		
C–C str., A	1150	1147	1124	1109	1106	
C–C str., A	1175	1160	1155	1149	1148	1141
CH_2 rock., A	795	794	794	793	789	784
CH_2 rock., B			$\underline{841}$	$\underline{845}$	$\underline{841}$	$\underline{836}$
CH_2 rock., C			$\underline{821}$		$\underline{816}$	$\underline{817}$
CH_2 wag.	1275	1250	1229	1230	1204	1187
CH_2 twist.	1300	1290	1285	(Not obsd. in Raman)		
CH wag.	1335	1314	1300	1291	1276	1267
CH wag.	1350	1325	1348	1354		
CH_3 bend., sym.	1387	1376	1385	1380	1388	1379
CH_2 bend. and CH_3 bend., unsym.	1465	1455	1450	1450	1445	1440
CH_3 rock.	950	912	957	951	945	953
CH_3 rock.	1020	1012	998		990	988
CH_3 rock.	1040	1031	1017	1016		
CH_3 rock.	1101	1106	1072	1063	1047	1030
CH_3 rock.	910	Only with X = CH_3				
CH_3 rock.	920	Only with X = CH_3				

[a] Raman spectral data from "Ramanspektren" by K. W. F. Kohlrausch, Akademische Verlagsgesellshaft Becker & Erler, Leipzig, 1943, and references cited therein. [b] Ref. 5, Serial Nos. 431 and 750. [c] The assignment of C–Cl stretching frequencies for 2-chlorobutane is the same as that of J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **50**, 1164 (1954). [d] Raman data: W. G. Braun, D. F. Spooner and M. R. Fenske, *Anal. Chem.*, **22**, 1074 (1950).

Simple, threefold cosine-type barriers to internal rotation were assumed for the methyl groups. Values of barrier height selected are: 3100 and 4000 cal. mole^{-1} for the methyl rotations, as in 1-propanethiol[6] and 2-propanethiol[13]; and 1500 cal. mole^{-1} for the thiol rotation, an average value.[6]

A potential function of the following form was assumed for rotation about the central carbon–carbon bond

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[10] To conform with a correlation of the spectra of secondary derivatives of butane, discussed later, the assignments given in ref. 8 for the CH_2 rocking and C–C stretching frequencies of 2-methylbutane (at 765 and 795 cm.$^{-1}$, respectively) have been interchanged.

[11] D. W. Scott and J. P. McCullough, THIS JOURNAL, **80**, 3554 (1958).

[12] J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

[13] J. P. McCullough, H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, R. E. Pennington and Guy Waddington, THIS JOURNAL, **76**, 4796 (1954).

$$V(\phi) = (V_0/2)(1 - \text{Cos } 3\phi),\ 0 < \phi < \pi/3 \text{ and } \pi < \phi < 2\pi$$
$$V(\phi) = (V_0/2)(1 - \text{Cos } 3\phi) + \Delta E,\ \pi/3 < \phi < \pi$$

where V_0 is the barrier height, ϕ is the angle of rotation measured from the A conformation and ΔE is the energy difference between the C conformation and the A and B conformations, the last two assumed of equal energy. The contributions of internal rotation about the central bond to the thermodynamic properties were calculated as those for a simple 3-fold barrier of height 6500 cal. mole^{-1} *plus* those due to "conversion" of molecules in the A and B conformations to those in the C conformation. The latter contributions were calculated by considering the "equilibrium" between rotational conformations.[14] The entropy change for the formation of C from an equimolar mixture of A and B was assumed to be $-R \ln 2$, and the energy change, $\Delta E = 1000$ cal. mole^{-1}, was selected simultaneously with the barrier height (6500 cal. mole^{-1}) to give best agreement between calculated and observed values of $C_p°$.

The parameters, $\nu = 1000$ cm.$^{-1}$ and $Z = -0.50$ cal. deg.$^{-1}$ mole^{-1}, of an empirical anharmonicity function[15] were evaluated from the heat capacity data at higher temperatures. This function is insignificant at 300°K. and increases to -0.58 and -0.26 cal. deg.$^{-1}$ mole^{-1} in $C_p°$ and $S°$ at 1000°K. Although this function has the temperature dependence of an anharmonicity contribution, it also is in part an empirical correction for inadequate treatment of all internal degrees of freedom. The negative values in this instance do not necessarily indicate that negative anharmonicity coefficients are preponderant, because other factors could outweigh the expected positive anharmonicity contribution.

Molal Thermodynamic Properties.—Calculated values of the thermodynamic functions are in columns 2–6 of Table V.[16] Comparison with observed values is made in Table I. Agreement within 0.05% was obtained throughout the range of temperature in which $S°$ and $C_p°$ were measured.

Calculated values of $\Delta Hf°$, $\Delta Ff°$ and log Kf are in columns 7–9 of Table V. These values are based on values of the thermodynamic functions in columns 2–6, the experimental value of $\Delta Hf°_{298.16}$ in Table I and values of the thermodynamic functions of C(c, graphite),[17] H_2(g)[17] and S_2(g).[18]

Conclusion.—The method of calculation just described is adequate for calculation of thermodynamic properties at temperatures inaccessible to calorimetric study, but the quality of the molecular structure information is disappointingly low. Only qualitative significance can be attached to the molecular structure parameters that were determined. For example, the conclusion is valid enough that two of the rotational conformations have about the same energy and that the third has significantly higher energy. Both the calorimetric and the spectroscopic data are consistent with this conclusion. However, a large uncertainty must be assigned to the values of the barrier height to internal rotation about the central C–C bond, 6500 cal. mole^{-1}, and the energy differences between the three conformations, 0 between A and B and 1000 cal. mole^{-1} between C and A or B.

The most important difficulty is in making a complete vibrational assignment for at least one conformation. Low temperature spectroscopic studies of 2-butanethiol or 2-halobutanes would be helpful in making a more reliable vibrational assignment. However, because these substances exist as racemic mixtures of optical isomers and are difficult to crystallize, studies of the crystalline solids might be impossible.

Experimental

The reported thermodynamic property values are based on a molecular weight of 90.186 for 2-butanethiol (1951 International Atomic Weights),[19] the 1951 values of fundamental physical constants[20] and the relations: 0° = 273.16°K. and 1 cal. = 4.1840 abs.j. = 4.1833 int.j. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[21] between 90 and 500°K. and the provisional scale[22] of the National Bureau of Standards between 11 and 90°K. All electrical and mass measurements were referred to standard devices calibrated at the National Bureau of Standards.

The apparatus and methods used in the continuing program of this Laboratory evolve as improvements suggested by experience or modifications required for studies of different substances are made. Not all of the improvements have been described in the literature, but the basic experimental techniques used for 2-butanethiol are presented in published descriptions of apparatus and methods for low temperature calorimetry,[23] vapor-flow calorimetry[24] and comparative ebulliometry.[25]

The Material.—Three samples of 2-butanethiol, prepared at the Laramie, Wyo., Station of the Bureau of Mines, were used. Sample I was used for low temperature calorimetry, and in a calorimetric melting point study the purity was found to be 99.66 mole %. Because this sample did not meet the purity requirements for an API-USBM Standard Sample, the material was repurified. Sample II was part of the repurified material and was designated as API-USBM Standard Sample No. 19.[26] This sample was used for combustion calorimetry and comparative ebulliometry. As discussed in the next paragraph, sample II could not be crystallized, and attempts to make a calorimetric purity determination were unsuccessful. From mass and infrared spectral analyses and the known purity value for sample I, the purity of sample II was estimated conservatively to be 99.9 ± 0.1

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[14] K. S. Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

[15] J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and Guy Waddington, THIS JOURNAL, **76**, 2661 (1954).

[16] The vibrational contributions were computed by use of the tables of H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research, Department of the Navy, Washington, D. C., July, 1949; restricted internal rotation contributions were calculated from the tables of K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942); anharmonicity contributions were computed from the tables of R. E. Pennington and K. A. Kobe, *ibid.*, **22**, 1442 (1954).

[17] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[18] W. H. Evans and D. D. Wagman, *ibid.*, **49**, 141 (1952).

[19] E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

[20] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

[21] H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

[22] H. J. Hoge and F. G. Brickwedde, *ibid.*, **22**, 351 (1939).

[23] H. M. Huffman, *Chem. Revs.*, **40**, 1 (1947); H. M. Huffman, S. S. Todd and G. D. Oliver, THIS JOURNAL, **71**, 584 (1949); D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **74**, 883 (1952).

[24] Guy Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947); J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, *ibid.*, **76**, 4791 (1954).

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

[26] W. E. Haines, R. V. Helm, G. L. Cook and J. S. Ball, *J. Phys. Chem.*, **60**, 549 (1956).

TABLE V

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-BUTANETHIOL[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 Kf[a]
0	0	0	0	0	0	−31.51	−31.51	Infinite
273.16	− 68.28	16.94	4.627	85.22	26.81	−37.94	−10.75	8.60
298.16	− 69.81	17.84	5.319	87.65	28.51	−38.39	− 8.25	6.05
300.00	− 69.91	17.91	5.373	87.82	28.64	−38.42	− 8.06	5.87
400	− 75.56	21.43	8.572	96.99	35.38	−40.08	+ 2.32	− 1.27
500	− 80.69	24.85	12.425	105.54	41.37	−41.41	13.09	− 5.72
600	− 85.52	28.02	16.81	113.54	46.42	−42.46	24.08	− 8.77
700	− 90.07	30.96	21.67	121.03	50.68	−43.23	35.23	−11.00
800	− 94.37	33.67	26.94	128.04	54.29	−43.77	46.49	−12.70
900	− 98.49	36.12	32.51	134.61	57.37	−44.14	57.79	−14.03
1000	−102.40	38.39	38.39	140.79	60.02	−44.31	69.14	−15.11

[a] To retain internal consistency, some values are given to one more decimal place than is justified by the absolute accuracy. [b] For the reaction 4C(c, graphite) + $5H_2(g) + {}^1/_2S_2(g) = C_4H_{10}S(g)$.

mole %. Sample III was used for vapor flow calorimetry. The purity of this sample also was estimated to be 99.9 ± 0.1 mole %, but sample III may have been slightly less pure than Sample II.

Crystallization of 2-Butanethiol.—At the Laramie Station samples of 2-butanethiol could not be crystallized in a time-temperature freezing-point cell, even if seeded by a wire cooled to liquid air temperatures. The tendency of singly branched hydrocarbons and sulfur compounds to form organic glasses has been noted often.[27] The fact that the racemic mixture of 2-butanethiol probably has a lower melting point than a pure isomer may accentuate the glass-forming tendency. However, sample I (99.66 mole % purity) was crystallized in the low temperature calorimeter. To initiate crystallization a protracted series of cooling and warming cycles in the range 55°K. to just below the melting point (133°K.) was necessary. Once crystallization began, the sample was maintained at a temperature from 5 to 30° below the melting point. The rate of crystallization was extremely slow, and all efforts to accelerate the process were unsuccessful. In all, initiation of crystallization required nearly 2 weeks, and completion of the crystallization process required another 3 weeks.

After sample II was received, an attempt was made to crystallize it in the low temperature calorimeter. Numerous techniques tried over an interval of 6 weeks failed to initiate crystallization. The common notion that pure samples of organic compounds crystallize more readily than do impure samples was not correct in this case. Apparently, a small amount of impurity was needed for nucleation.

Heat Capacity in the Solid and Liquid States.—Low temperature thermal studies were made with 47.150 g. of sample I. The sample was sealed in a platinum calorimeter with helium (3 cm. pressure at room temperature) added to promote thermal equilibration. The observed values of heat capacity C_{satd} are in Table VI. Above 30°K., the accuracy uncertainty is estimated to be no greater than 0.2%, except for possible uncertainty due to the 0.34 mole % impurity in the sample. Measurements of the heat capacity of the liquid were made with sample II, and the results are included in Table VI. There is no systematic difference between the results obtained with the two samples, and the average deviation of *all* values from a smooth curve is 0.03%.

The heat capacity curve for the solid (C_{satd} *vs.* T) has the normal sigmoid shape. The heat capacity of the liquid between 185 and 310°K. may be represented by the empirical equation

$$C_{\text{satd}}(\text{liq.}) = 52.825 - 0.18233T + 0.6076 \times 10^{-3}T^2 - 0.1419 \times 10^{-7}T^3,\ \text{cal. deg.}^{-1}\ \text{mole}^{-1} \quad (1)$$

In the indicated temperature range, eq. 1 represents the values listed in Table VI with average and maximum deviations of 0.03 and 0.05%, respectively.

The Heat of Fusion, Triple Point Temperature, Cryoscopic Constants and Purity of Sample I.—Only one satisfactory determination of the heat of fusion was made, and this experiment yielded the value 1548 cal. mole^{-1}. In a second experiment, the crystallization time was reduced from about 5 to about 3 weeks, and the value obtained for the heat of fusion was 4% lower than the first value, obviously as a result of incomplete crystallization. Unfortunately, the ex-

TABLE VI

THE MOLAL HEAT CAPACITY OF 2-BUTANETHIOL IN CAL. DEG.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]
Crystals		88.79	15.793	122.38	38.318[d]
		90.21	15.983	126.83	38.246[d]
12.44	1.191	92.47	16.274	127.48	38.246[d]
12.83	1.291	94.20	16.493	128.86	38.226
13.47	1.454	95.39	16.658	132.56	38.162[d]
14.14	1.613	97.76	16.947		
14.78	1.805	99.82	17.201	Liquid	
15.28	1.945	100.58	17.314		
16.24	2.213	105.59	17.917	135.50	38.165
17.03	2.433	105.64	17.913	137.58	38.098
17.93	2.695	110.84	18.540	140.16	38.072[d]
19.60	3.189	110.87	18.546	147.82	37.970
19.83	3.261	114.29	18.953	158.03	37.866
21.82	3.845	115.55	19.120	168.21	37.803
22.53	4.053	116.32	19.210	178.35	37.784
23.97	4.476	119.53	19.627	181.50	37.788
25.72	4.960	120.10	19.684	188.46	37.805
26.21	5.111	123.72	20.122	191.27	37.817
28.47	5.715	126.45	20.564[c]	200.97	37.895
28.72	5.776			209.41	37.974[d]
31.78	6.568	Glass and under-cooled liquid		211.11	38.019
34.85	7.286			219.22	38.130[d]
38.33	8.003			221.66	38.169
42.67	8.837	53.24	10.93	232.12	38.428
47.73	9.751	57.95	11.71	242.49	38.704
47.87	9.780	63.55	12.67	248.30	38.880
52.98	10.642	69.15	13.61	255.10	39.110
53.38	10.702	74.71	14.60	257.94	39.213
54.24	10.851	77.13	15.10	267.49	39.571
59.04	11.574	80.26	15.73	269.85	39.670
59.31	11.614	84.36	16.68	276.96	39.980
64.44	12.398	101.63	38.618	282.13	40.198
69.63	13.127	106.16	38.545	292.01	40.638
74.91	13.842	111.10	38.469	297.45	40.869[d]
79.92	14.552	116.02	38.396	301.33	41.076
83.12	15.009	117.78	38.371[d]	306.87	41.367[d]
85.01	15.273	120.36	38.347[d]		
87.42	15.598	121.74	38.314		

[a] T is the mean temperature of each heat capacity measurement. [b] C_{satd} is the heat capacity of the condensed phase. [c] Values below the melting point are *not* corrected for premelting. [d] Values obtained with sample II; all other values obtained with sample I.

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[27] D. R. Douslin and H. M. Huffman, THIS JOURNAL, **68**, 1704 (1946); unpublished results, this Laboratory.

pectation that the one satisfactory value would be confirmed by later studies with sample II was not realized because sample II could not be crystallized. However, it is believed that complete crystallization was obtained in the first experiment with sample I and that the value obtained for the heat of fusion is reliable. The accuracy uncertainty should not be much greater than 0.2%.

The results of a study of melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, are in Table VII. Also in Table VII are the values obtained for the triple-point temperature, $T_{\mathrm{T.P.}}$, the mole fraction of impurity in sample I, N_2^*, and the cryoscopic constants,[28] $A = \Delta H_{\mathrm{fusion}}/RT^2_{\mathrm{T.P.}}$ and $B = 1/T_{\mathrm{T.P.}} - \Delta C_{\mathrm{fusion}}/2\Delta H_{\mathrm{fusion}}$, calculated from the observed values of $T_{\mathrm{T.P.}}$, $\Delta H_{\mathrm{fusion}}$ and $\Delta C_{\mathrm{fusion}}$ (16.93 cal. deg.$^{-1}$ mole^{-1}).

TABLE VII

2-BUTANETHIOL: MELTING POINT SUMMARY

Triple point temperature, $T_{\mathrm{T.P.}} = 133.02 \pm 0.05$°K., mole fraction of impurity $= N_2^* = AF(T_{\mathrm{T.P.}} - T_{\mathrm{obsd}}) = 0.0034$; cryoscopic constants, $A = 0.04403$ deg.$^{-1}$ and $B = 0.00204$ deg.$^{-1}$

Melted %	$1/F$	T_{obsd}, °K.	T_{graph}, °K.[b]
25.75	3.883	132.8547	132.72
49.64	2.015	132.8913	132.86
75.86	1.318[a]	132.9149[a]	132.9149
92.53	1.081[a]	132.9332[a]	132.9332
100	1.000		132.9395
Pure	0		133.0168

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain $T_{\mathrm{T.P.}}$ [b] Values read from the straight line of footnote *a*.

Thermodynamic Properties in the Solid and Liquid States.—Values of thermodynamic properties for the condensed phases were computed from the calorimetric data for selected temperatures between 10 and 310°K. The results are in Table VIII. The values at 10°K. were computed for a Debye function for 5 degrees of freedom with $\theta = 105.8$; these parameters were evaluated from the heat capacity data between 12 and 23°K. Corrections for the effects of premelting have been applied to the "smoothed" data recorded in Table VIII.

Vapor Pressure.—Observed values of vapor pressure, determined by comparative ebulliometry with water as the reference substance, are in Table IX. The difference between the boiling and condensing temperatures of the sample was less than 0.001° at 1 atm. pressure. The Antoine and Cox equations selected to represent the results are

$$\log p(\mathrm{mm.}) = 6.88698 - 1229.904/(t + 222.021) \quad (2)$$

$$\log P(\mathrm{atm.}) = \mathrm{A}(1 - 358.141/T) \quad (3)$$

where, $\log \mathrm{A} = 0.833740 - 7.1297 \times 10^{-4}T + 7.1068 \times 10^{-7}T^2$. In these equations, t is in °C. and T in °K. Comparisons of observed and calculated vapor pressure for both the Antoine and Cox equation are in Table IX. The normal boiling point, calculated from either equation, is 84.98° (358.14°K.).

Heat of Vaporization, Vapor Heat Capacity and Effects of Gas Imperfection.—The experimental values of heat of vaporization and vapor heat capacity are in Tables X and XI. The estimated accuracy uncertainty of the values of ΔHv and $C_{\mathrm{p}}°$ are 0.1 and 0.2%, respectively. Empirical equations selected to represent the results are

$$\Delta Hv = 12{,}238 - 13.753\ T,\ \mathrm{cal.\ mole^{-1}}\ (318 - 358\text{°K.}) \quad (4)$$

$$C_{\mathrm{p}}° = 5.190 + 0.086883T - 2.8663 \times 10^{-5}T^2,\ \mathrm{cal.\ deg.^{-1}\ mole^{-1}}\ (346\text{–}453\text{°K.}) \quad (5)$$

Equation 4 represents the experimental values of ΔHv within 1 cal. mole^{-1}, and eq. 5 represents the tabulated values of $C_{\mathrm{p}}°$ exactly.

The effects of gas imperfection could *not* be correlated by the method normally used in this Laboratory.[24] Very slight curvature always is observed in plots of C_{p} *vs.* P at constant temperature. Usually, the results can be correlated satisfactorily by the equation of state $PV = RT(1 + B/V)$. However, at low temperatures, there remains a very small but consistent curvature that cannot be accounted for by use of the foregoing equation of state. This curvature is attributed to the effect of the third virial coefficient, but it is usually of borderline significance and can be neglected. For 2-butanethiol the curvature is just large enough that the third virial coefficient must be used if the results are to be correlated without loss of accuracy.

TABLE VIII

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-BUTANETHIOL IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{\mathrm{satd}} - H°_0)/T$ cal. deg.$^{-1}$	$(H_{\mathrm{satd}} - H°_0)/T$ cal. deg.$^{-1}$	$H_{\mathrm{satd}} - H°_0$ cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
			Crystals		
10	0.055	0.162	1.62	0.217	0.641
15	.180	0.516	7.74	0.696	1.862
20	.396	1.030	20.60	1.426	3.304
25	.690	1.632	40.80	2.322	4.762
30	1.043	2.269	68.06	3.312	6.122
35	1.441	2.907	101.75	4.348	7.315
40	1.869	3.523	140.91	5.392	8.325
45	2.319	4.109	184.91	6.428	9.266
50	2.781	4.669	233.46	7.450	10.146
60	3.726	5.717	343.0	9.443	11.722
70	4.681	6.681	467.7	11.362	13.177
80	5.632	7.578	606.3	13.210	14.563
90	6.574	8.432	758.9	15.006	15.954
100	7.505	9.248	924.8	16.753	17.222
110	8.423	10.029	1103.2	18.452	18.442
120	9.328	10.781	1293.7	20.109	19.672
130	10.220	11.511	1496.4	21.731	20.870
133.02	10.486	11.728	1560.0	22.214	21.227
			Liquid		
133.02	10.486	23.365	3108	33.85	38.164
140	11.70	24.101	3374	35.80	38.08
150	13.39	25.028	3754	38.42	37.95
160	15.04	25.832	4133	40.87	37.85
170	16.62	26.538	4511	43.16	37.80
180	18.16	27.163	4889	45.32	37.78
190	19.65	27.722	5267	47.37	37.81
200	21.08	28.228	5646	49.31	37.88
210	22.47	28.690	6025	51.16	38.00
220	23.81	29.117	6406	52.93	38.15
230	25.12	29.514	6788	54.63	38.37
240	26.38	29.889	7173	56.27	38.64
250	27.61	30.24	7561	57.85	38.94
260	28.79	30.59	7952	59.38	39.29
270	29.96	30.91	8347	60.87	39.68
273.16	30.32	31.02	8473	61.34	39.81
280	31.09	31.24	8746	62.33	40.11
290	32.19	31.55	9149	63.74	40.54
298.16	33.07	31.80	9482	64.87	40.92
300	33.26	31.86	9557	65.12	41.01
310	34.32	32.16	9970	66.48	41.51

[a] The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure.

The relatively large curvature in the plots of C_{p} *vs.* P for 2-butanethiol is believed to be real. Also, the unusual linear variation of ΔHv with T(eq. 4) apparently is real. Repeat measurements of both C_{p} and ΔHv made at the end of the investigation indicated that the *precision* of the results was 0.05% or better. Measurements of the heat of vaporization and vapor heat capacity of benzene made immediately after the study of 2-butanethiol agreed within 0.1% with previous results obtained in this Laboratory over a period of years.

Additional evidence that the curvature in plots of C_{p} *vs.* P is real is provided by the fact that the observed curvature

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[28] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

TABLE IX

THE VAPOR PRESSURE OF 2-BUTANETHIOL

Boiling point, °C. Water	Boiling point, °C. 2-Butanethiol	p(obsd.),[a] mm.	p(obsd.) − p(calcd.), mm. Eq. 2	p(obsd.) − p(calcd.), mm. Eq. 3
60.000	38.962	149.41	−0.01	−0.01
65	44.549	187.57	.00	.00
70	50.185	233.72	.00	.00
75	55.866	289.13	+ .02	+ .01
80	61.597	355.22	.00	− .02
85	67.370	433.56	.04	+ .01
90	73.195	525.86	.01	− .04
95	79.063	633.99	.03	.00
100	84.981	760.00	.02	.00
105	90.945	906.06	.01	+ .04
110	96.963	1074.6	− .1	.0
115	103.020	1268.0	− .1	.1
120	109.133	1489.1	− .2	− .1
125	115.287	1740.8	.0	.0
130	121.489	2026.0	+ .3	.0

[a] From the vapor pressure data for water given by N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

TABLE X

THE MOLAL HEAT OF VAPORIZATION AND GAS IMPERFECTION OF 2-BUTANETHIOL

T, °K.	P, atm.	ΔHv, cal.	$V - RT/P$, cc. Obsd.	$V - RT/P$, cc. Calcd.[a]
318.03	0.250	7864 ± 3[b]	−1540	−1537
328.64	.375	7717 ± 1	−1485	−1452
336.68	.500	7608 ± 3	−1410	−1391
358.14	1.000	7312 ± 3	−1211	−1226

[a] Calculated from eq. 6–8. [b] Maximum deviation from the mean of 4 determinations at 318.03, 336.68 and 358.14°K. and 2 determinations at 328.64°K.

TABLE XI

THE MOLAL HEAT CAPACITY OF 2-BUTANETHIOL IN CAL. DEG.$^{-1}$

T, °K.	346.20	368.20	403.20	453.20
C_p (1.000 atm.)		34.050	36.000	38.905
C_p (0.500 atm.)	32.282	33.586	35.743	38.777
C_p (0.375 atm.)	32.147			
C_p (0.250 atm.)	32.057	33.425	35.656	38.700
$C_p°$ (obsd.)	31.83	33.29	35.56	38.68
$C_p^1 - C_p°$, obsd.		0.76	0.44	0.22
$C_p^1 - C_p°$, calcd.[a]		0.75	0.43	0.22

[a] Calculated from eq. 9.

decreases regularly with increasing temperature. The plot of results at 453.20°K. is linear within the precision of the data. Any systematic error in the results would yield plots with pronounced curvature at every temperature.

The effects of gas imperfection were correlated by aid of the equation of state previously used for water vapor[29]

$$PV = RT + BP + CP^2/RT \qquad (6)$$

where

$$B = -760 - 16.6 \exp(1200/T), \text{ cc. mole}^{-1} \qquad (7)$$

$$C = 11.6 \times 10^6 - 3.98 \times 10^5 \exp(1200/T), \text{ cc.}^2 \text{ mole}^{-2} \qquad (8)$$

The constants in eq. 5, 7 and 8 were evaluated by an iterative process similar to that described for water vapor. In terms of these equations, the heat capacity of 2-butanethiol vapor is represented as a function of P and T by the equation

$$C_p = C_p° + XP + YP^2 \qquad (9)$$

where $C_p°$ is represented by eq. 5 and

$$X = [1/T^2][2 + 1200/T][483 \exp(1200/T)]$$

$$Y = [1/T^2][(1200/T)(4 + 1200/T) + 2 - 58.2/\exp(1200/T)][58.8 \exp(1200/T)]$$

These equations represent the observed values in Table XI with average and maximum deviations of 0.03% and 0.07%, respectively. Also, as shown in Table X, observed and calculated values of $V - RT/P = B + CP/RT$ agree within 0.05% of the molal volume. (Observed values of $V - RT/P$ were calculated with the Clapeyron equation from observed values of the heat of vaporization and vapor pressure.)

Because the correlation used is not sensitive enough to determine individual values of B and C accurately, the equation of state (eq. 6–8) should be considered merely as a satisfactory empirical expression. The individual values of B and C are not accurate values of the true virial coefficients, but the *sum*, $B + CP/RT$, is an accurate representation of the corresponding sum for the true coefficients.

It should be emphasized that the effect of the third virial coefficient on the pressure dependence of the heat capacity of 2-butanethiol is only slightly greater than that previously noted for related compounds. In fact, the effect is just large enough to justify its consideration. Fortunately, the particular method of correlation used has only a small effect on the values obtained for $C_p°$. Even if the equation of state $PV = RT(1 + B/V)$ had been used, only the value of $C_p°$ at 368.20°K. would have differed by as much as 0.2% from the value in Table XI.

The Entropy in the Ideal Gaseous State.—The entropy in the ideal gaseous state was calculated as shown in Table XII. The indicated accuracy uncertainty for values of $S°$ pertains to observational uncertainties only. Possible errors due to impurity and/or incomplete crystallization cannot be estimated but are believed to be small enough to be included in the conservatively estimated uncertainty interval given in Table XII.

TABLE XII

THE MOLAL ENTROPY OF 2-BUTANETHIOL IN CAL. DEG.$^{-1}$

T, °K.	298.16	318.03	328.64	336.69	358.14
S_{satd}(liq.)	64.87	67.54[a]	68.93[a]	69.96[a]	72.65[a]
$\Delta Hv/T$	27.22[b]	24.73	23.48	22.60	20.42
S(ideal) − S(real)[c]	0.03	0.06	0.08	0.09	0.15
$R \ln P$[d]	−4.45	−2.76	−1.95	−1.38	.00
$S°$(obsd.) (±0.20[e])	87.67	89.57	90.54	91.27	93.22

[a] Calculated from the value at 310°K. and increments computed by visual extrapolation of the heat capacity data. [b] Calculated from eq. 3, 6, 7 and 8 and the Clapeyron equation. [c] Calculated from eq. 6–8. [d] Calculated from eq. 3. [e] See text.

The Heat of Formation and Related Properties.—The heat of formation was determined by a rotating-bomb method of combustion calorimetry.[30] A detailed description of the experiments has been published.[2b] The standard heat of formation of the liquid was found to be $\Delta Hf°_{298.16} = -31.10 \pm 0.18$ kcal. mole^{-1} for the reaction

$$4\text{C(c, graphite)} + 5\text{H}_2\text{(g)} + \text{S(c, rhombic)} = \text{C}_4\text{H}_{10}\text{S(liq.)}$$

From this result and thermodynamic data for C(c, graphite),[17] H_2(g)[17] and S(c, rhombic)[18], the following values of standard entropy, standard free energy and logarithm of the equilibrium constant of formation were calculated:

$\Delta Sf°_{298.16} = -104.25$ cal. deg.$^{-1}$ mole^{-1}; $\Delta Ff°_{298.16} = -0.02$ kcal. mole^{-1}; and $\log_{10} Kf = 0.01$.

The standard heat of vaporization at 298.16°K. was calculated to be 8.13 kcal. mole^{-1} by use of eq. 3, 6, 7 and 8 and the relationship $\Delta Hv° = \Delta Hv + \int_0^P [V - T(\partial V/\partial T)_P]\,dP$. This value was used to obtain the standard heat of formation of the vapor, $\Delta Hf°_{298.16} = -22.97 \pm 0.19$ kcal. mole^{-1}, for the reaction

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(29) J. P. McCullough, R. E. Pennington and Guy Waddington, THIS JOURNAL, **74**, 4439 (1952).

(30) W. N. Hubbard, C. Katz and Guy Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

$$4C(c, \text{graphite}) + 5H_2(g) + S(c, \text{rhombic}) = C_4H_{10}S(g)$$

The following values of related properties were calculated as before: $\Delta Sf°_{298.16} = -81.47$ cal. deg.$^{-1}$ mole^{-1}; $\Delta Ff°_{298.16} = +1.32$ kcal. mole^{-1}; and $\log_{10}Kf = -0.97$.

Finally, the heat of formation of $S_2(g)$ from rhombic sulfur[18] was used to compute the standard heat of formation of 2-butanethiol vapor from $S_2(g)$, $\Delta Hf°_{298.16} = -38.39 \pm 0.19$ kcal.mole^{-1}, for the reaction

$$4C(c, \text{graphite}) + 5H_2(g) + {}^1/_2S_2(g) = C_4H_{10}S(g)$$

This value is listed in Table I.

BARTLESVILLE, OKLA.

[CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Volumetric and Thermodynamic Properties of Fluids. V. Two Component Solutions

BY KENNETH S. PITZER AND GLEN O. HULTGREN

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The acentric factor theory of volumetric behavior of pure fluids is applied to mixed gases. The pseudo-critical temperature and pressure and the acentric factor are evaluated for twelve binary systems each at several compositions. It is found that a linear equation in the mole fraction and the properties of the components is adequate for the acentric factor in all cases and for the pseudo-critical constants in some systems. In other systems small quadratic terms are required for the pseudo-critical temperature and pressure. The relationship of these quadratic terms to the intermolecular forces is considered. It is believed that useful predictions of fugacities as well as of volumetric data can be made on the basis of these results.

Corresponding states theory has been extensively used in the treatment of solutions. Particularly notable contributions were the introduction of the pseudo-critical concept by Kay[1] and of the method of conformal solutions by Longuet-Higgins.[2] Recent important work includes that of Prigogine and collaborators[3] and of Scott.[4] Salsburg[5] and Prigogine[6] have presented excellent reviews which give further references.

One limitation on all corresponding states theories of solutions is the fact that the pure components seldom follow the law of corresponding states strictly. Brown[7] showed that the deviations of the CO–CH_4 system from solution theory of this type differed substantially depending on the choice of CO or CH_4 as the reference substance. In this paper we apply to solutions the extended theory based upon the acentric factor which has been applied to pure fluids in a recent series of papers.[8]

This removes the contradiction which is inherent in a corresponding states treatment of a solution of two components which do not themselves follow the principle of corresponding states. The acentric factor theory is not exact either, but it was found to reduce the magnitude of deviation in pure substances by about a factor of ten from that of simple corresponding states theory. At the present level of accuracy of solution studies, this residual uncertainty in treatment of pure substance properties is unimportant.

In this investigation the volumetric properties of several solution systems in the single phase region are compared with the functions for pure substances. Best values of the pseudo-critical temperature and pressure and of the acentric factor are obtained as well as an estimate of the accuracy of agreement throughout the region of available data. Then the pseudo-critical constants and acentric factors for the solutions are compared with those for the pure components and methods of relating one with the other are discussed. Possible thermodynamic applications are illustrated by fugacity calculations.

Determination of Pseudo-critical Constants.—In the acentric factor theory the compressibility factor is given by the equation

$$(PV/RT) = z = z^{(0)} + \omega z^{(1)} \qquad (1)$$

where $z^{(0)}$ and $z^{(1)}$ are functions of the reduced temperature T_r and the reduced pressure P_r which are tabulated in Paper II.[8] The acentric factor ω is defined by the equation

$$\omega = -\log (P/P_c)_{sat} - 1.000 \text{ at } T_r = 0.700 \qquad (2)$$

where $(P/P_c)_{sat}$ is the reduced vapor pressure at $T_r = 0.700$. It was explained in earlier papers that the acentric factor may be determined from vapor pressure data at any temperature well removed from the critical point.

In our present work, we seek to determine an acentric factor and pseudo-critical constants for a solution such that its volumetric behavior is given by eq. 1. Since solutions cannot be expected to conform exactly with even the acentric factor extension of the corresponding states theory for pure substances, there is necessarily some arbitrariness in the selection of pseudo-critical constants. The most characteristic and sensitive single phase region is that just above the critical point in both temperature and pressure. The two phase region is expanded for solutions, as compared to pure substances, consequently the range available for comparison of single phase properties begins somewhat above the point $T_r = 1$, $P_r = 1$. For

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