Table I. Compressibility Data for 2-Methylpentane and 2,2-Dimethylbutane

Density, Gram Mole/Liter	Pressure, Atmospheres					
	2-Methylpentane					
	230° C.	244° C.	258° C.	272° C.	286° C.	300° C.
1.021	24.90	26.64	28.35	30.01	31.58	33.25
1.317	...	...	...	...	...	40.32
	2,2-Dimethylbutane					
	220° C.	236° C.	252° C.	268° C.	284° C.	300° C.
1.092	26.35	28.67	31.03	33.18	35.31	37.33
1.378	29.94	33.26	36.72	40.07	43.30	45.64

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Boiling Points and Boiling Point Numbers of Alkyl Derivatives of Bivalent S, Se, and Te

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Application of the Kinney equation:

$$\text{b.p. in } ^\circ\text{C.} = 230.14\ (\text{total boiling point number})^{1/3} - 543$$

furnishes adequate results in calculations of normal boiling points of 88 bivalent alkylsulfur compounds (average error, 2.3°), 14 bivalent alkyselenium compounds (average error, 3.2°), and 6 alkyltellurium compounds (average error, 3.1°). This includes use of typical Kinney values such as C, 0.8, H, 1.00, side-chain methyl, 3.05 and 2,2-dimethyl, 5.70. There is a classification according to the number of branched alkyl groups present (none, one, or two). Thus there are eleven values of the boiling point number (b.p.n.) of sulfur in the different bivalent configurations (mercaptan, dithiol, sulfide, and disulfide), six values of b.p.n. for selenium and two values of b.p.n. for tellurium.

SATISFACTORY RESULTS occur through application of the Kinney equation:

$$\text{b.p. in } ^\circ\text{C.} = 230.14\ (\text{total boiling point number})^{1/3} - 543$$

in calculations of the normal boiling points of hydrocarbons (*2*), silanes and organosilicon compounds (*3*), germanes and alkylgermanium compounds (*1*), and boranes and alkylboron compounds (*1*).

However, a related attempt to derive b.p.n. for sulfur and hydrogen from the hydrides H_2S, b.p. −60.3° and H_2S_2, b.p. 70.7°, furnished total b.p.n. of 9.22 and 18.96, respectively. These indicated the unacceptable atomic b.p.n. of 9.74 for sulfur and −0.26 for hydrogen. Thus an entirely different method of deriving the atomic b.p.n. was necessary.

Although textbooks and treatises (*10, 11*) realize that some regularity exists in mercaptans and alkyl sulfides, there is no previous numerical treatment of the boiling points of mercaptans, dithiols, alkyl sulfides and alkyl disulfides, or of related selenium and tellurium compounds.

After separation of bivalent alkylsulfur, alkylselenium, and alkyltellurium compounds into 9 homologous series–RSH, $HSCH_2—CH_2SH$, RSR′, RSSR′, RSeH, RSeR′, RSeSeR, RTeH, and RTeR–there is also separation according to the number of branched alkyl groups present: none, thus linear; one, a single branch such as isopropyl; two, the presence of the same branched group twice, or the presence of two different branched groups. There is use of the following Kinney (*2*) values: C, 0.80; H, 1.00; side-chain methyl, 3.05; 2,2-dimethyl, 5.70; double bond in $RCH{=}CH_2$, 1.5; double bond in $RCH{=}CHR$, 1.9. For example, to find the b.p.n. of Se in C_2H_5SeH, with observed b.p. of 53.5° and thus a total b.p.n. of 17.41, subtract 1.60 for two carbon atoms and 6.00 for six hydrogen atoms to obtain 9.81 for selenium.

In Table I there are eleven values for the b.p.n. of sulfur, six values for the b.p.n. of selenium–two of which involve single compounds only–and two values for the b.p.n. of tellurium. In Table I there are root mean square errors in the individual b.p.n., and the number of examples of each type such as linear RTeH. In Table II the b.p.s. and total b.p.n. of 111 compounds are present.

Table I. Boiling Point Numbers of Bivalent S, Se, and Te

Homologous Series	Number of Branched Alkyl Groups: None B.p.n.[a]	No.[b]	One B.p.n.	No.	Two B.p.n.	No.
RSH	8.65 ± 0.34	9	8.08 ± 0.30	11	...	..
sec.-RSH	7.29 ± 0.16	6	...	..	...	..
tert.-RSH	5.90	1	...	..	...	..
$HSCH_2$-CH_2SH	9.76 ± 0.23	9	...	..	...	..
RSR′	7.93 ± 0.33	19	7.48 ± 0.31	16	6.42 ± 0.26	4
RSSR′	7.17 ± 0.20	7	6.77 ± 0.15	5	6.54 ± 0.12	2
RSeH	9.69 ± 0.31	4	9.98 ± 0.26	2	...	..
RSeR′	9.93 ± 0.29	6	...	..	8.69	1
RSeSeR	9.68 ± 0.38	2	...	..	8.86	1
RTeH	13.45 ± 0.49	4	...	..	...	..
RTeR	12.54 ± 0.11	2	...	..	...	..

[a] B.p.n. with root mean square errors. Standard b.p.n.: C, 0.80; H, 100; side chain methyl, 3.05; 2,2-dimethyl, 5.70. [b] No. is number of examples.

LIMITATION

This publication concerns bivalent acyclic alkylsulfur, alkylselenium, and alkyltellurium compounds only. In the heterocyclic compounds such as cyclo—$(CH_2)_5S$ and cyclo—$(CH_2)_6S$, also in related selenium and tellurium compounds (*5, 10, 11, 12*), there are an excessive number of simultaneous variables which typically include the b.p.n. for sulfur, the b.p.n. for the ring and perhaps a b.p.n. for a methyl group attached to the ring in various positions.

Upon study, it proved to be impossible to include halogens, oxygen, phenyl groups, $RSCH_2$—SR′, the group RCH = CH attached to sulfur and two known gem.-dithiols. In $C_2H_5CH(SH)_2$, b.p. 142° and b.p.n. 26.37, the b.p.n. of sulfur is 7.98; in $(CH_3)_2C(SH)_2$, b.p. 114.5° and b.p.n. 23.32, the b.p.n. of sulfur is 6.43, probably because of less association.

A reported b.p. of 230° for *n*-hexyl sulfide (*10*) appears in error. This compound does not appear in Table II, since the use of data in Table I furnishes a total b.p.n. of 43.53 and a calculated normal b.p. of 266.6° for the sulfide.

Table II. Calculations of Boiling Point

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., °C. Calcd.	B.P., °C. Found	Error	Ref.
CH_3SH	13.45	13.57	4.3	6.0	−1.7	(*10*)
C_2H_5SH	16.25	15.82	40.0	34.7	5.3	(*10*)
n-C_3H_7SH	19.05	18.67	71.6	67.5	4.1	(*10*)
n-C_4H_9SH	21.85	21.60	100.4	98.0	2.4	(*10*)
n-$C_5H_{11}SH$	24.65	24.62	126.8	126.5	0.3	(*10*)
n-$C_6H_{13}SH$	27.45	27.48	151.3	151.5	−0.2	(*10*)
n-$C_7H_{15}SH$	30.25	30.52	174.1	176.2	−2.1	(*10*)
n-$C_8H_{17}SH$	33.05	33.52	195.6	199.1	−3.5	(*10*)
n-$C_9H_{19}SH$	35.85	36.45	215.9	220.1	−4.2	(*10*)
$CH_3CH(CH_3)CH_2SH$	20.53	20.61	87.2	88	−0.8	(*10*)
$CH_3CH_2CH(CH_3)SH$	20.53	20.27	87.2	84.5	2.7	(*10*)
$(CH_3)_2CHCH_2CH_2SH$	23.33	23.80	114.6	119	−4.4	(*10*)
$CH_3CH_2CH(CH_3)CH_2SH$	23.33	23.80	114.6	119	−4.4	(*10*)
$CH_3CH_2CH_2CH(CH_3)SH$	23.33	23.15	114.6	112.9	1.7	(*10*)
$(CH_3)_2CHSH$	17.73	17.81	57.1	58	−0.9	(*10*)
n-$C_4H_9CH(CH_3)SH$	26.13	26.01	139.9	138.9	1.0	(*10*)
n-$C_5H_{11}CH(CH_3)SH$	28.93	28.94	163.5	163.6	−0.1	(*10*)
n-$C_6H_{13}CH(CH_3)SH$	31.73	31.83	185.6	186.4	−0.8	(*10*)
n-$C_7H_{15}CH(CH_3)SH$	34.53	34.77	206.4	208.2	−1.8	(*10*)
$CH_3CH_2CH(SH)CH_3$	20.49	20.32	86.8	85	1.8	(*10*)
n-$C_3H_7CH(SH)CH_3$	23.29	23.15	114.2	112.9	1.3	(*10*)
n-$C_4H_9CH(SH)CH_3$	26.09	26.01	139.6	138.9	0.7	(*10*)
n-$C_5H_{11}CH(SH)CH_3$	28.89	28.94	163.2	163.6	−0.4	(*10*)
n-$C_6H_{13}CH(SH)CH_3$	31.69	31.83	185.3	186.4	−1.1	(*10*)
n-$C_7H_{15}CH(SH)CH_3$	34.49	34.77	206.1	208.2	−2.1	(*10*)
$(CH_3)_3CSH$	...	18.35	...	64.0	...[a]	(*10*)
$HS(CH_2)_2SH$	27.13	26.83	148.5	146.0	2.5	(*10*)
$HS(CH_2)_3SH$	29.93	29.73	171.5	170	1.5	(*10*)
$HS(CH_2)_4SH$	32.73	33.05	193.2	195.6	−2.4	(*10*)
$HS(CH_2)_5SH$	35.53	36.05	213.6	217.3	−3.7	(*10*)
$HS(CH_2)_6SH$	38.33	38.94	233.0	237.1	−4.1	(*10*)
$HS(CH_2)_7SH$	41.13	41.25	251.4	252.2	−0.8	(*10*)
$HS(CH_2)_8SH$	43.93	43.97	269.0	269.3	−0.3	(*10*)
$HS(CH_2)_9SH$	46.73	46.40	286.0	284.0	2.0	(*10*)
$HS(CH_2)_{10}SH$	49.53	48.64	302.2	297.1	5.1	(*10*)
$(CH_3)_2S$	15.53	16.03	31.2	37.3	−6.1	(*10*)
$CH_3SC_2H_5$	18.33	18.58	63.8	66.6	−2.8	(*10*)
$(C_2H_5)_2S$	21.13	21.00	93.3	92.0	1.3	(*10*)
CH_3S-*n*-C_3H_7	21.13	21.36	93.3	95.6	−2.3	(*10*)
CH_3S-*n*-C_4H_9	23.93	24.18	120.2	122.5	−2.3	(*10*)
C_2H_5S-*n*-C_3H_7	23.93	23.75	120.2	118.5	1.7	(*10*)
(*n*-$C_3H_7)_2S$	26.73	26.46	145.2	142.8	2.4	(*10*)
CH_3S-*n*-C_5H_{11}	26.73	26.72	145.2	145.0	0.2	(*10*)
C_2H_5S-*n*-C_4H_9	26.73	26.62	145.2	144.2	1.0	(*10*)
CH_3S-*n*-C_6H_{13}	29.53	29.86	168.4	171	−2.6	(*10*)
n-C_3H_7S-*n*-C_4H_9	29.53	29.24	168.4	166	2.4	(*12*)
(*n*-$C_4H_9)_2S$	32.33	32.16	190.2	188.9	1.3	(*12*)
(*n*-$C_5H_{11})_2S$	37.93	37.51	230.3	227.4	2.9	(*10*)

(Continued on page 274)

Table II. Calculations of Boiling Point (*Continued*)

	B.P.N.		B.P., °C.			
Compound	Calcd.	Found	Calcd.	Found	Error	Ref.
$(n\text{-}C_7H_{15})_2S$	49.13	48.80	300.1	298	2.1	(*10*)
$CH_3SCH_2CH=CH_2$	20.63	21.03	88.2	92.3	−4.1	(*10*)
$C_2H_5SCH_2CH=CH_2$	23.43	23.43	115.5	115.5	0.0	(*10*)
$n\text{-}C_3H_7SCH_2CH=CH_2$	26.23	26.02	140.8	139	1.8	(*10*)
$CH_3SCH_2CH_2CH_2CH=CHCH_3$	29.43	28.81	167.5	162.5	5.0	(*10*)
$n\text{-}C_4H_9SCH_2CH=CHCH_3$	32.23	31.91	189.4	187	2.4	(*10*)
$(CH_3)_2CHSCH_3$	19.93	20.30	81.0	84.8	−3.8	(*10*)
$(CH_3)_2CHSC_2H_5$	22.73	22.56	108.9	107.3	1.6	(*10*)
$(CH_3)_2CHCH_2SCH_3$	22.73	23.11	108.9	112.5	−3.6	(*10*)
$(CH_3)_2CHS\text{-}n\text{-}C_3H_7$	25.53	25.24	134.7	132.1	2.6	(*10*)
$(CH_3)_2CHCH_2SC_2H_5$	25.53	25.48	134.7	134.2	0.5	(*10*)
$CH_3SCH_2CH(CH_3)C_2H_5$	25.53	26.08	134.7	139.5	−4.8	(*10*)
$CH_3SCH_2CH_2CH(CH_3)_2$	25.53	25.79	134.7	137	−2.3	(*10*)
$C_2H_5SCH(CH_3)C_2H_5$	25.53	25.41	134.7	133.6	1.1	(*10*)
$(CH_3)_3CSCH_3$	21.58	21.71	97.7	99	−1.3	(*10*)
$(CH_3)_3CSC_2H_5$	24.38	23.85	124.3	119.5	4.8	(*10*)
$C_2H_5SCH(CH_3)CH(CH_3)_2$	27.58	27.48	152.3	151.5	0.8	(*10*)
$C_2H_5SCH_2CH_2CH(CH_3)_2$	28.33	28.53	158.6	160.2	−1.6	(*10*)
$C_2H_5SCH_2CH(CH_3)C_2H_5$	28.33	28.50	158.6	160	−1.4	(*10*)
$n\text{-}C_3H_7SCH_2CH_2CH(CH_3)_2$	31.13	31.13	181.0	181	0.0	(*10*)
$n\text{-}C_4H_9SCH_2CH(CH_3)_2$	31.13	30.82	181.0	178.5	2.5	(*10*)
$n\text{-}C_5H_{11}SCH(CH_3)_2$	31.13	30.62	181.0	177	4.0	(*10*)
$(\text{iso-}C_3H_7)_2S$	23.72	23.91	118.3	120.0	−1.7	(*12*)
$(CH_3)_2CHSC(CH_3)_3$	25.37	25.01	133.2	130	3.2	(*10*)
$[(CH_3)_2CHCH_2]_2S$	29.32	29.61	166.7	169	−2.3	(*10*)
$[CH_3CH_2CH(CH_3)]_2S$	29.32	29.18	166.7	165.5	1.2	(*10*)
$(CH_3)_2S_2$	21.94	22.82	101.3	109.8	−8.5	(*10*)
$CH_3SSC_2H_5$	24.74	24.97	127.6	129.7	−2.1	(*10*)
$(C_2H_5)_2S_2$	27.54	27.62	152.0	154.0	−2.0	(*12*)
$C_2H_5SS\text{-}n\text{-}C_3H_7$	30.34	30.20	174.8	173.7	1.1	(*12*)
$C_2H_5SS\text{-}n\text{-}C_4H_9$	33.14	32.71	196.2	193	3.2	(*10*)
$(n\text{-}C_3H_7)_2S_2$	33.14	33.08	196.2	195.8	0.4	(*12*)
$(n\text{-}C_4H_9)_2S_2$	38.74	37.60	235.7	228	7.7	(*10*)
$C_2H_5SSCH(CH_3)_2$	28.79	29.18	162.4	165.5	−3.1	(*12*)
$C_2H_5SSC(CH_3)_3$	30.44	30.45	175.6	175.7	−0.1	(*12*)
$C_2H_5SSCH_2CH(CH_3)_2$	31.59	31.52	184.5	184	0.5	(*10*)
$C_2H_5SSCH(CH_3)C_2H_5$	31.59	31.13	184.5	181	3.5	(*10*)
$n\text{-}C_3H_7SSCH(CH_3)_2$	31.59	31.77	184.5	185.9	−1.4	(*12*)
$(CH_3)_2CHSSCH(CH_3)_2$	30.36	30.64	175.0	177.2	−2.2	(*12*)
$[(CH_3)_2CHCH_2]_2S_2$	35.96	35.73	216.7	215	1.7	(*10*)
CH_3SeH	14.49	14.02	18.1	12.0	6.1	(*10*)
C_2H_5SeH	17.29	17.41	52.1	53.5	−1.4	(*10*)
$n\text{-}C_3H_7SeH$	20.09	20.22	82.7	84.0	−1.3	(*10*)
$n\text{-}C_4H_9SeH$	22.89	23.26	110.5	114.0	−3.5	(*10*)
$CH_3CH(CH_3)CH_2SeH$	22.43	22.17	106.1	103.5	2.6	(*14*)
$C_2H_5C(CH_3)_2SeH$	24.08	24.34	121.6	124	−2.4	(*7*)
$(CH_3)_2Se$	17.53	17.83	54.9	58.2	−3.3	(*10*)
$CH_3SeC_2H_5$	20.33	20.41	85.1	86	−0.9	(*10*)
$(C_2H_5)_2Se$	23.13	22.63	112.7	108	4.7	(*10*)
$CH_3Se\text{-}n\text{-}C_3H_7$	23.13	23.26	112.7	114	−1.3	(*10*)
$CH_3Se\text{-}n\text{-}C_4H_9$	25.93	26.25	138.2	141	−2.8	(*10*)
$(n\text{-}C_3H_7)_2Se$	28.73	28.38	161.9	159	2.9	(*10*)
$[CH_3CH(CH_3)CH_2]_2Se$	...	31.59	...	184.5	...^{a}	(*14*)
$(CH_3)_2Se_2$	26.96	27.66	147.1	153	−5.9	(*8*)
$(C_2H_5)_2Se_2$	32.56	31.78	191.9	186	5.9	(*9*)
$(CH_3)_2CHSeSeCH(CH_3)_2$	...	35.02	...	210	...^{a}	(*6*)
CH_3TeH	18.25	17.72	62.9	57	5.9	(*10*)
C_2H_5TeH	21.05	20.81	92.5	90	2.5	(*10*)
$n\text{-}C_3H_7TeH$	23.85	24.02	119.5	121	−1.5	(*10*)
$n\text{-}C_4H_9TeH$	26.65	27.42	144.4	151	−6.6	(*10*)
$(CH_3)_2Te$	20.14	20.03	83.2	82	1.2	(*13*)
$(C_2H_5)_2Te$	25.74	25.85	136.5	137.5	−1.0	(*4*)

^{a}These three compounds are the only examples of the exact configuration; the calculated total b.p.n. and the calculated b.p. are the same as those found.

Table II, produced chiefly from information gathered by Reid (*10*) and without use of a computer, depends upon experimental value, or selecting the average or most representative value from a number of normal b.p.s, or by taking the center of a b.p. range of 3.0° or less.

DISCUSSION OF RESULTS

In Table II there are calculated normal boiling points with the following average errors: 2.3° for 88 alkylsulfur compounds, 3.2° for 14 alkylselenium compounds and 3.1°

for six alkyltellurium compounds. These averages exclude three single occurrences: one tertiary mercaptan, one double branched alkyl selenide and one double branched alkyl diselenide. In eleven of 108 compounds errors in calculated b.p.s exceed 5.0°, namely: C_2H_5SH, 5.3°; $CH_3CH_2CH(CH_3)SH$, 5.6°, $HS(CH_2)_{10}SH$, 5.1°; $(CH_3)_2S$, 6.1°; $(CH_3)_2S_2$, 8.5°; $(n\text{-}C_4H_9)_2S$, 7.7°; CH_3SeH, 6.1°; $(C_2H_5)_2Se_2$, 5.9° $(CH_3)_2Se_2$, 5.9°; CH_3TeH, 5.9°; $n\text{-}C_4H_9TeH$, 6.6°.

Slight association through hydrogen bonding is the probable cause of a higher b.p.n. for sulfur in mercaptans and dithiols than in sulfides and disulfides.

With one exception, in single branched selenols, the greater the branching of the alkyl group or groups, the less the value of b.p.n. for sulfur, selenium, or tellurium. Selenium shows a relative constancy of b.p.n.; upon omission of the two lone occurrences, the b.p.n. 9.84 ± 0.33 fits the 14 alkylselenium compounds fairly well. In selenium there is less displacement of valence electrons than in tellurium, and also less association through hydrogen bonding than in sulfur. The tellurols, RTeH, have no association through hydrogen bonding, but have some slight displacement of valence electrons.

In the two comparable series of compounds RMH and RMR–in which M is sulfur, selenium or tellurium–the b.p.n. increases from sulfur to selenium to tellurium. Oxygen (*2*) varies too much for comparison.

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Specific Volumes of *n*-Alkanes

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A table of the specific volumes of eight pure *n*-alkanes from seven to forty carbons in chain length is presented. The values are listed at seven even temperatures from ambient to 300° C., and at eleven even pressures from ambient to 5000 bars. These values are believed to be accurate to within 0.2% for 97% of the specific volumes listed.

In 1954-58, Simon and Cornish of Arthur D. Little, Inc., under contract to Union Carbide Corporation, made some very accurate measurements on eight pure *n*-alkanes over broad ranges of temperature and pressure. A sampling of these data was published in 1960 (*1*-*3*). The experimental method chosen by Simon and Cornish did not provide means for the direct calculation of the specific volumes from the measurements taken. Computer time was required in order to convert these measurements into specific volumes—thus, the delay in presenting these data for publication.

With the cooperation of S.S. Kurtz, Jr., of the Sun Oil Company, these calculations have now been completed and a table has been compiled (Table I) giving the specific volumes of eight pure *n*-alkanes from seven to forty carbons in chain length at seven even temperatures from ambient to 300° C., and at eleven even pressures from ambient to 5000 bars. Although the precision of the measurements is at least 0.02%, the overall accuracy for 97% of the specific volumes reported is believed to be of the order of 0.2%.

The method of measurement chosen by Simon and Cornish was selected because it provided a very accurate direct measurement of the length of the column in the piezometer. With this method, however, the mass of the sample contained in the piezometer could be measured with only one-tenth of this accuracy. It is not necessary to know the weight of the sample in order to compute the specific volumes—hence the limitation of the experimental method chosen lies only in the amount of machine time required to make these calculations.

Essentially, it is not necessary to know the weight of the sample in the piezometer because the computations described below deal with compressions which are dimensionless ratios entirely independent of the quantity of sample involved. Compressions are the ratios of the measured volumes to the hypothetical volume of the sample at the same temperature but at zero pressure. These ratios would be the same for any sample weight.

It has been explained in a prior publication (*2*) that the Hudleston equation:

$$\ln \frac{P\,v^{2/3}}{(v^{\circ})^{1/3} - (v)^{1/3}} = A + B[(v^{\circ})^{1/3} - (v)^{1/3}] \qquad (1)$$

may be used as a tool to extrapolate highly accurate