

data of Knietsch at the higher temperature of 35° C. provide an interesting comparison with the data at 25° C. A qualitative examination shows no significant changes in the thermal expansion from $X(\text{SO}_3) = 0$ to $X(\text{SO}_3) = 0.45$, but as the concentration increases, changes become more apparent. The largest expansion occurs at $X(\text{SO}_3) = 1.0$ and is impressively large.

The conductance measurements presented in Table II and Figure 2 represent the best data available for the concentrations indicated at 25° C.

The curve in Figure 2 rises to a maximum, which constitutes evidence for appreciable ionic dissociation between $X(\text{SO}_3) = 0.1$ and $X(\text{SO}_3) = 0.2$, then falls off sharply as the concentration is increased.

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RECEIVED for review October 7, 1963. Accepted January 6, 1964.

Compressibilities of 2-Methyl Pentane and 2,2-Dimethylbutane

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Compressibility data measured for 2-methyl pentane and 2,2-dimethylbutane were limited both as to temperature and density. The present study extends these data to regions not previously investigated.

COMPRESSIBILITIES of 2-methylpentane and 2,2-dimethylbutane in the superheated vapor phase were previously measured by Kelso and Felsing (5) and Felsing and Watson (3), respectively. The 2-methylpentane data comprised two isotherms at 250° and 275° C. and a density range of 1.5 to 5.5 gram mole/liter. Three isotherms (225°, 250°, 275° C.) were determined for 2,2-dimethylbutane for densities from 1.7 to 6.1 grams mole/liter.

The present study was undertaken to extend the temperature and density ranges previously investigated.

The apparatus used to determine the data on the present study was a modification of the design of Keyes (6) and Beattie (1). A detailed description was published by Cherney, Marchman, and York (2), except for certain changes reported by Li and Canjar (7).

An isometric ($d = 1.021$ gram mole/liter) was measured for 2-methylpentane for temperatures from 230° to 300° C. An additional point at a density of 1.317 gram mole/liter and a temperature of 300° C. was also determined. The 2,2-dimethylbutane data measured in this study consisted of two isometrics (1.092 and 1.378 gram mole/liter). Temperatures for these isometrics varied from 220° C. to 300° C. All experimental data are summarized in Table I.

The data of the present study cannot be directly compared to the data of Kelso and Felsing (5) and Felsing and Watson (3) since the present data are in a density range heretofore not studied.

An indirect comparison was, however, possible by referring to other investigations (4, 5). These studies dealt with compressibilities of *n*-hexane. One set of data (4) were measured with the apparatus of the present study. The other (5) used the same device as the studies of Kelso and Felsing (5) and Felsing and Watson (3). It was felt that a comparison of these *n*-hexane data would give some

insight as to how the data on the present study compared to existing data.

Figure 1 depicts the *n*-hexane data. The two sets of data are seen to disagree somewhat at high densities (greater than 3.5–4.5 gram mole/liter). However, the agreement becomes quite good as density decreases. This behavior indicates that the data of the present work should compare favorably to the previously determined data (3, 5).

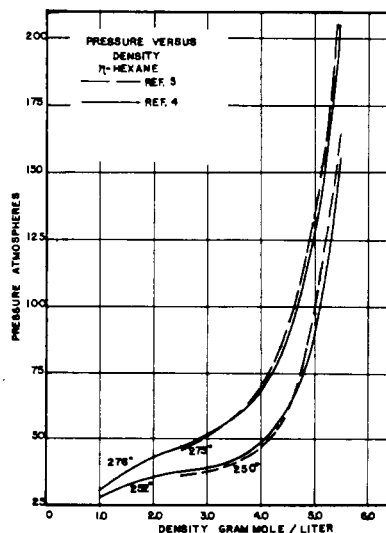


Figure 1. Comparison between data taken with device of present work and that of Felsing and co-workers

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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RECEIVED for review September 17, 1963. Accepted December 23, 1963.

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 alkylselenium 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 H₂S, b.p. -60.3° and H₂Se, 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, HSCH₂-CH₂SH, 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=CH₂, 1.5; double bond in RCH=CHR, 1.9. For example, to find the b.p.n. of Se in C₂H₅SeH, 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.