Boiling Points and Boiling Point Numbers of Organogermanium Compounds

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APPLICATION of the Kinney equation (*20, 23*) b.p. in ° C. = 230.14 (total boiling point number)$^{1/3}$ − 543 to the normal boiling points of GeH_4, Ge_2H_6 and Ge_3H_8 furnished the boiling point number (b.p.n.) 7.413 for germanium and 0.085 for a hydrogen atom attached to germanium. Thereupon, standard procedures in exact estimations of b.p.n. for the various configurations of alkyl groups, halogens or isocyanate occur through a least squares fit to a standard linear regression model, with the use of an IBM 650 computer.

Programming for the computer requires preliminary substraction of the portion of the total b.p.n. due to germanium and to any hydrogen attached to germanium. It is necessary to assume simultaneous variation of the individual b.p.n. for the alkyl groups, halogen atoms, and isocyanate groups in the compounds. The computer then obtains the best fit to the data. Individual b.p.n. for 38 configurations are in Table I. Four b.p.n. for values of values of X and GeX_4—such as Cl in $GeCl_4$—are definite and do not require the computer; the best available boiling do not require the computer; the best available boiling points (*2, 4, 15*) are used. However, the computer failed to perform a later estimation including compounds with n-C_4H_9 in the RGe≡ in the $R_2Ge=$ configurations. Therefore, these two b.p.n. result from personal selection at a later date. Twenty-eight b.p.n. were determined by the computer. Table II shows observed normal and calculated boiling points for 84 germanium compounds and also the total b.p.n. for each compound, the individual errors in calculation of boiling point, and the reference numbers.

SAMPLE CALCULATION OF $(n\text{-}C_3H_7)_2GeCl_2$

Total b.p.n.

$2n$-C_3H_7 groups in $R_2Ge=$,	2×8.30, = 16.60
2 Cl atoms in R_2GeX_2,	2×5.67, = 11.34
1 Ge atom	= 7.41
	Total b.p.n. = 35.35

Boiling Point, ° C.

$$\begin{aligned} \text{Calcd.} &= 230.14\,(35.35)^{1/3} - 543 \qquad (2)\\ &= 212.3°\\ \text{Observed} &= 209.5°\ (5)\\ \text{Error} &= 2.8° \end{aligned}$$

The method of assignment of configuration used for organogermanium compounds is the same as that reported for organosilicon compounds (*23*). Thus in $R_cR'_{4-c}Ge$ there are "c" R groups of configuration R_4Ge and "4 − c" R′ groups of configuration R'_4Ge; similarly, $R_2R'GeH$ contains R_3Ge- and R'_3Ge-configurations. Both $RGeH_2X$ and R_2GeHX have the same X as R_3GeX.

LIMITATION

This method of calculating boiling points through the use of b.p.n. is not applicable to GeH_3Cl, GeH_2Br_2 or $GeFCl_3$; not applicable to organogermanium isothiocyanates or to $(C_2H_5)_3GeOCOCH_3$, the latter a typical ester or carboxylate. Three configurations occur only once each: namely, as fluorine in $C_2H_5GeF_3$, as isocyanate in $C_2H_5Ge(NCO)_3$, or as isopropyl in i-$C_3H_7GeCl_3$. Efforts to prepare $(i\text{-}C_3H_7)_4Ge$ are unsuccessful (*6*), while decomposition obscures the true boiling point of GeI_4. Many organogermanium compounds have normal boiling points listed to the closest centigrade degree only; unfortunately, many authors list boiling points under diminished pressure exclusively. The most reliable normal boiling points available are in Table II.

Table I. Boiling Point Numbers of Atoms and Groups

(Ge, 7.413; Germane H, 0.085)

Group	RGe≡	$R_2Ge=$	R_3Ge-	R_4Ge
	Configuration of Alkyl Groups			
CH_3	2.59	2.80	2.88	2.29
C_2H_5	6.72	5.94	5.63	5.41
n-C_3H_7	8.45	8.30	7.96	7.46
i-C_3H_7	8.83	7.64	7.67	...
n-C_4H_9	12.27	10.88	10.01	9.50
	Configuration of Halogen or Isocyanate			
Halogen	$RGeX_3$	R_2GeX_2	R_3GeX	GeX_4
F	2.99	3.73	2.79	0.81
Cl	4.27	5.67	6.54	3.20
Br	6.51	7.50	7.96	6.09
I	10.12	10.91	11.08	...
NCO	7.70	8.65	9.10	6.70

DISCUSSION OF RESULTS

The Kinney equation (Equation 1) serves in the derivation of b.p.n. for germanium and for hydrogen bonded to germanium, using the boiling points of GeH_4, Ge_2H_6, and Ge_3H_8, but rejecting the less accurate extrapolated boiling points of Ge_4H_{10} and Ge_5H_{12}. Three configurations occur only once each in substituted compounds, such as fluorine in $C_2H_5GeF_3$.

There is an over-all average error of 3.6° in calculating boiling points of 84 compounds in Table II. The optimum fit in calculated boiling points, occurring at moderate chain length, consists of an average error of 2.5° for 17 ethylgermanium compounds and an average error of 2.5° for 24 n-propylgermanium and i-propylgermanium compounds. Greater chain length increases the average error to 3.9° for 21 n-butylgermanium compounds. The shortest chain length accompanies the highest average error, 8.3°, for 12 methylgermanium compounds.

Errors in calculation of boiling point equal or exceed 10° only with 4 compounds: CH_3GeH_3, $(CH_3)_2GeF_2$, $(CH_3)_3GeH$, and $(C_2H_5)_3(n\text{-}C_4H_9)Ge$; the last compound appears to have a boiling point somewhat low for its structure.

The numerical contribution of the central atom toward the total b.p.n. in the compound becomes progressively more important and the numerical contribution of the hydrogen atom becomes progressively less important as the size of the central atom increases in going from carbon (*20*) (b.p.n. of C, 0.8; H, 1.0) to silicon (*23*) (Si, 4.20; H, 0.60) to germanium (Ge, 7.413; H, 0.085) in the Kinney equation (Equation 1).

Other equations fit the boiling points of the germanium hydrides less satisfactorily. English and Nicholls (*11*) calculate the boiling point of Ge_2H_6 and Ge_3H_8 fairly well and the boiling point of GeH_4 poorly (−71.0°), with the equation

$$\text{B.p. in } ^\circ\text{K.} = (446.1)(2.303)(\log n + 3.0) - 416.31 \quad (3)$$

wherein n is the number of germanium atoms in the molecule. This method now allows calculation of the boiling points of 181° for Ge_4H_{10} and 241° for Ge_5H_{12}, with an average error of 5.5°. A method satisfactory for calculating boiling points of organic ethers (*33*) uses the equation

$$\text{B.p. in } ^\circ\text{K.} = a\,(\text{molecular weight})^b \quad (4)$$

which is unsatisfactory for the germanium hydrides.

NOMENCLATURE

a	=	empirical constant in Walker's equation
alkyl group	=	methyl, ethyl, *n*-propyl, *i*-propyl or *n*-butyl
b	=	an empirical constant in Walker's equation
b.p.	=	boiling point under 760-mm. pressure
b.p.n.	=	boiling point number of one atom or group using Kinney's equation
c	=	the whole number 1, 2, or 3 in $R_cR'_{4-c}Ge$
central atom	=	Ge in GeH_4, Ge_2H_6, or Ge_3H_8, typically
germanium hydride	=	GeH_4, Ge_2H_6, Ge_3H_8, Ge_4H_{10} or Ge_5H_{12}
log	=	logarithm to base 10
n	=	number of germanium atoms in the molecule using English and Nicholls' equation
R	=	an alkyl group as defined above

Table II. Calculations of Boiling Points

Compound	B.P.N. Calcd.	B.P.N. Found	B.P., °C. Calcd.	B.P., °C. Found	Error	Ref.
GeH_4	7.753	7.753	−88.5	−88.5	0.0	(*24*)
Ge_2H_6	15.336	15.353	28.8	29.0	−0.2	(*10*)
Ge_3H_8	22.919	22.895	110.7	110.5	0.2	(*10*)
Ge_4H_{10}	30.50	30.62	176.1	176.9[a]	−0.8	(*1*)
Ge_5H_{12}	38.09	38.48	231.3	234[a]	−2.7	(*1*)
CH_3GeH_3	10.26	11.53	−42.9	−23.0	−19.9	(*32*)
CH_3GeCl_3	22.81	22.95	109.7	111	−1.3	(*27*)
CH_3GeBr_3	29.53	29.53	168.4	168.4	0.0	(*25*)
CH_3GeI_3	40.36	38.93	246.4	237	9.4	(*14*)
$(CH_3)_2GeH_2$	13.18	13.65	−0.1	7.0	−7.1	(*26*)
$(CH_3)_2GeF_2$	20.47	23.10	86.6	112.5	−25.9	(*25*)
$(CH_3)_2GeCl_2$	24.35	24.34	124.1	124	0.1	(*27*)
$(CH_3)_2GeBr_2$	28.01	27.72	155.9	153.5	2.4	(*25*)
$(CH_3)_3GeH$	16.14	15.13	38.6	26.2	12.4	(*26*)
$(CH_3)_3GeF$	18.84	19.51	69.4	76.6	−7.2	(*25*)
$(CH_3)_3GeCl$	22.59	23.37	107.6	115	−7.4	(*28*)
$(CH_3)_3GeBr$	24.01	23.37	120.9	115	5.9	(*25*)
$C_2H_5GeH_3$	14.39	14.02	16.8	12.0	4.8	(*26*)
$C_2H_5GeF_3$	23.10	23.10	112.4	112.4	0.0	(*13*)
$C_2H_5GeCl_3$	26.94	26.14	146.9	140.0	6.9	(*29*)
$C_2H_5GeBr_3$	33.66	33.65	200.1	200	0.1	(*13*)
$C_2H_5GeI_3$	44.49	45.90	272.5	281	−8.5	(*13*)
$C_2H_5Ge(NCO)_3$	37.23	37.22	225.5	225.4	0.1	(*2*)
$(C_2H_5)_2GeH_2$	19.46	19.27	76.0	74	2.0	(*31*)
$(C_2H_5)_2GeCl_2$	30.63	30.07	177.1	172.7	4.4	(*29*)
$(C_2H_5)_2GeBr_2$	34.29	33.92	204.7	202	2.7	(*12*)
$(C_2H_5)_2GeI_2$	41.11	41.22	251.3	252	−0.7	(*17*)
$(C_2H_5)_2Ge(NCO)_2$	36.59	37.31	221.1	226	−4.9	(*2*)
$(C_2H_5)_3GeH$	24.39	24.34	124.4	124	0.4	(*21*)
$(C_2H_5)_3GeF$	27.09	27.22	148.2	149.3	−0.9	(*21*)
$(C_2H_5)_3GeCl$	30.84	30.48	178.7	175.9	2.8	(*21*)
$(C_2H_5)_3GeBr$	32.26	32.43	189.6	190.9	−1.3	(*21*)
$(C_2H_5)_3GeI$	35.38	35.37	212.5	212.5	0.0	(*21*)
$(C_2H_5)_3GeNCO$	33.40	33.70	198.2	200.4	−2.2	(*2*)
n-$C_3H_7GeH_3$	16.12	15.43	38.4	30	8.4	(*19*)
n-$C_3H_7GeCl_3$	28.67	29.36	161.4	167	−5.6	(*19*)
$(n$-$C_3H_7)_2GeH_2$	24.18	24.62	122.6	126.5	−3.9	(*19*)
$(n$-$C_3H_7)_2GeF_2$	31.47	31.39	183.6	182.8	0.8	(*5*)
$(n$-$C_3H_7)_2GeCl_2$	35.35	34.96	212.3	209.5	2.8	(*5*)
$(n$-$C_3H_7)_2GeBr_2$	39.01	39.46	237.5	240.5	−3.0	(*5*)
$(n$-$C_3H_7)_2GeI_2$	45.83	45.15	280.6	276.5	4.1	(*5*)
$(n$-$C_3H_7)_3GeH$	31.38	31.47	182.9	183.6	−0.7	(*19*)
$(n$-$C_3H_7)_3GeF$	34.08	34.06	203.2	203	0.2	(*3*)
$(n$-$C_3H_7)_3GeCl$	37.83	37.45	229.6	227	2.6	(*3*)
$(n$-$C_3H_7)_3GeBr$	39.25	39.68	239.1	242	−2.9	(*3*)
$(n$-$C_3H_7)_3GeI$	42.37	42.32	259.3	259	0.3	(*3*)
$(n$-$C_3H_7)_3GeNCO$	40.39	40.44	246.6	247	−0.4	(*3*)
i-$C_3H_7GeCl_3$	29.05	29.05	164.5	164.5	0.0	(*30*)
$(i$-$C_3H_7)_2GeH_2$	22.86	22.84	110.2	110	0.2	(*7*)

Table II. Calculation of Boiling Points (*Continued*)

Compound	B.P.N. Calcd.	B.P.N. Found	B. P., °C. Calcd.	B. P., °C. Found	Error	Ref.
$(i\text{-}C_3H_7)_2GeF_2$	30.15	30.24	173.3	174	−0.7	(6)
$(i\text{-}C_3H_7)_2GeCl_2$	34.03	34.06	202.8	203	−0.2	(6)
$(i\text{-}C_3H_7)_2GeBr_2$	37.69	38.48	228.6	234	−5.4	(6)
$(i\text{-}C_3H_7)_2GeI_2$	44.51	43.76	272.6	268	4.6	(6)
$(i\text{-}C_3H_7)_2Ge(NCO)_2$	39.99	39.21	244.0	239	5.0	(7)
$(i\text{-}C_3H_7)_3GeF$	33.21	33.38	196.8	198	−1.2	(6)
$(i\text{-}C_3H_7)_3GeCl$	36.96	36.73	223.6	222	1.6	(6)
$(i\text{-}C_3H_7)_3GeBr$	38.38	38.48	233.3	234	−0.7	(6)
$(i\text{-}C_3H_7)_3GeI$	41.50	41.53	253.8	254	−0.8	(6)
$n\text{-}C_4H_9GeH_3$	19.94	19.43	81.1	75.6	5.5	(8)
$n\text{-}C_4H_9GeH_2Cl$	26.39	26.14	142.2	140.0	2.2	(8)
$n\text{-}C_4H_9GeH_2Br$	27.81	28.38	154.3	159	−4.7	(8)
$n\text{-}C_4H_9GeH_2I$	30.93	31.13	179.4	181	−1.6	(8)
$n\text{-}C_4H_9GeCl_3$	32.49	31.59	191.4	184	7.4	(8)
$n\text{-}C_4H_9GeBr_3$	39.21	38.93	238.9	237	1.9	(8)
$n\text{-}C_4H_9GeI_3$	50.04	50.92	305.1	310	−4.9	(8)
$(n\text{-}C_4H_9)_2GeH_2$	29.34	30.11	166.8	173	−6.2	(31)
$(n\text{-}C_4H_9)_2GeHCl$	35.80	36.29	215.5	219	−3.5	(8)
$(n\text{-}C_4H_9)_2GeHBr$	37.22	38.48	225.4	234	−8.6	(8)
$(n\text{-}C_4H_9)_2GeHI$	40.34	40.76	246.3	249	−2.7	(8)
$(n\text{-}C_4H_9)_2GeF_2$	36.63	35.80	221.3	215.5	5.8	(9)
$(n\text{-}C_4H_9)_2GeCl_2$	40.51	39.62	247.4	241.6	5.8	(9)
$(n\text{-}C_4H_9)_2GeBr_2$	44.17	43.92	270.5	269	1.5	(9)
$(n\text{-}C_4H_9)_2GeI_2$	50.99	49.85	310.2	304	6.2	(9)
$(n\text{-}C_4H_9)_3GeH$	37.53	38.48	225.8	234	−8.2	(22)
$(n\text{-}C_4H_9)_3GeF$	40.23	40.14	245.6	245	0.6	(4)
$(n\text{-}C_4H_9)_3GeCl$	43.98	44.24	269.4	271	−1.6	(4)
$(n\text{-}C_4H_9)_3GeBr$	45.40	45.56	278.0	279	−1.0	(4)
$(n\text{-}C_4H_9)_3GeI$	48.52	48.62	296.4	297	−0.6	(4)
$(n\text{-}C_4H_9)_3GeNCO$	46.54	46.23	284.8	283	1.8	(4)
$(CH_3)_2(C_2H_5)GeH$	18.89	18.18	69.9	62.2	7.7	(26)
$CH_3(C_2H_5)_3Ge$	25.93	25.57	138.2	135	3.2	(22)
$(CH_3)_2(C_2H_5)_2Ge$	22.81	22.69	109.7	108.5	1.2	(22)
$(CH_3)_3(C_2H_5)Ge$	19.69	19.79	78.5	79.5	−1.0	(22)
$(C_2H_5)_3(n\text{-}C_4H_9)Ge$	33.14	31.17	196.2	181.3	14.9	(16)

Extrapolated normal boiling point.

R′ = an alkyl group from the list above; not same as R
RGe≡ = a germanium compound with one Ge atom to which are bonded one alkyl group and three of same halogens (or isocyanate)
total b.p.n. = boiling point number of a compound using the Kinney equation
X = a fluorine, chlorine, bromine or iodine atom (or an isocyanate group) bonded to germanium

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