Physical Properties of Tetra-*n*-alkylgermanes (C_1–C_6)

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Vapor pressure, liquid density, surface tension, viscosity, refractive indices, and dielectric constants are measured at several temperatures for $Ge(CH_3)_4$, $Ge(C_2H_5)_4$, $Ge(C_3H_7)_4$, $Ge(C_4H_9)_4$, $Ge(C_5H_{11})_4$, and $Ge(C_6H_{13})_4$. Both the original numerical data, together with parameters of fitting equations, are given.

The physical property data for GeX_4 compounds, where X represents methyl, ethyl, propyl, butyl, pentyl, and hexyl, as reported in the literature, were incomplete (*1–3, 5, 6, 9–17, 21–23*). Moreover, since statistical evaluation of available data was not included in the source material, confidence in the existing information could not be justified. Therefore, extensive pressure-temperature, liquid density, surface tension, viscosity, refractive index, and dielectric constant observations were made upon the germanium compounds.

Experimental

The germanium compounds designated chemically pure were obtained from Alpha Inorganics. Excluding $Ge(CH_3)_4$ which was distilled under atmospheric conditions, the germanium compounds were fractionally distilled at reduced pressure (10–20 torr) prior to use. Distillation did not appear to alter the properties of the liquids. After repeated distillations, the germanium compounds were placed in turn within the various experimental apparatus for the determination of vapor pressure, liquid density, surface tension, viscosity, refractive index, and dielectric constant.

Vapor pressure. For the determination of vapor pressure by a dynamic method, a modified version of the Ramsay-Young apparatus (*20*) was utilized. This apparatus consisted of an electrically heated boiler, a vapor space with a vertical reentrant glass tube containing a temperature-sensing device, and a condenser. Inserted between a closed-end mercury manometer and the refluxing section is a large volume (a surge tank) to prevent sudden changes in pressure. Pressure measurements were made with a Griffin and George cathetometer with an accuracy of ±0.025 mm. The temperature was measured with a chromel–alumel thermocouple standardized against a Leeds and Northrup calibrated platinum resistance thermometer. Used with the thermocouple was a Leeds-Northrup K-3 Universal potentiometer and a Rubicon galvanometer of sensitivity 0.005 $\mu A/mm$. The error in the measured temperature was not greater than 0.05°C.

Data. Substance: *T,* K, vapor pressure (torr). $Ge(CH_3)_4$: 300.7, 389.12; 300.9, 395.39; 301.9, 410.97; 302.7, 415.71; 303.2, 430.68; 303.8, 435.01; 304.9, 457.25; 306.6, 481.33; 308.6, 509.78; 310.2, 539.79; 311.5, 565.72; 313.0, 600.95; 314.2, 630.54; 315.4, 657.10; 315.9, 670.19; 317.1, 687.32; 316.6, 688.82; 319.5, 754.43; 320.0, 758.02.

$Ge(C_2H_5)_4$: 337.4, 21.41; 340.3, 25.23; 342.4, 28.04; 345.6, 32.56; 349.9, 39.79; 353.2, 46.72; 357.8, 56.86; 361.2, 66.20; 363.9, 73.13; 368.7, 89.50; 375.0, 112.70; 379.2, 130.48, 383.5, 153.17; 387.6, 176.37; 392.0, 202.28; 394.9, 222.97; 398.6, 252.00; 405.3, 308.74; 410.1, 355.44; 414.7, 408.07; 418.2, 453.86; 421.7, 500.26; 425.2, 550.28; 428.9, 609.03; 432.0, 661.75; 433.8, 695.20; 436.7, 748.12.

$Ge(C_3H_7)_4$: 389.6, 19.50; 394.7, 25.67; 398.1, 29.69; 403.8, 37.49; 407.8, 44.42; 412.7, 52.87; 417.6, 63.31; 421.1, 71.42; 424.8, 81.58; 428.8, 93.37; 433.1, 107.79; 436.3, 121.16; 439.3, 134.49; 442.1, 146.48; 444.3, 158.66; 447.1, 171.75; 450.1, 189.79; 453.3, 206.45; 455.6, 226.65; 458.4, 245.92; 462.1, 271.22; 465.1, 297.59; 467.6, 317.31; 470.6, 347.01; 473.6, 375.57; 476.1, 403.33; 478.6, 428.09; 481.4, 456.81; 483.5, 485.56; 486.4, 517.92; 488.6, 553.80; 491.1, 581.84; 493.3, 611.49; 497.7, 676.03.

$Ge(C_4H_9)_4$: 435.5, 19.96; 441.8, 26.13; 447.1, 32.70; 451.8, 39.38; 455.9, 45.67; 460.1, 53.95; 464.4, 63.01; 469.1, 74.07; 471.9, 81.53; 475.4, 91.85; 478.6, 101.87; 481.6, 112.75; 484.9, 126.32; 489.8, 143.58; 493.7, 164.27; 497.5, 182.89; 501.2, 202.30; 504.6, 222.43; 507.5, 242.25; 510.4, 261.39; 513.1, 280.84; 516.4, 305.22; 518.8, 328.74; 521.2, 353.74; 524.5, 381.83; 526.6, 403.00; 530.1, 438.92; 532.8, 462.89; 534.9, 492.58; 538.4, 528.19; 541.7, 566.72; 544.4, 610.11; 547.2, 646.53; 549.9, 685.62; 554.7, 749.98; 556.4, 770.03.

$Ge(C_5H_{11})_4$: 471.1, 18.00; 479.6, 25.16, 485.0, 31.25; 491.6, 38.99; 496.5, 46.93; 501.4, 55.72; 506.5, 67.35; 510.4, 76.71; 515.2, 90.06; 520.7, 107.41; 527.4, 129.71; 532.6, 148.65; 536.4, 167.50; 541.4, 190.03; 545.4, 214.59; 549.7, 239.00; 553.4, 263.22; 556.9, 287.47; 561.2, 322.34; 564.2, 344.91; 567.8, 375.47; 570.7, 402.88; 573.9, 435.61; 576.9, 467.66; 580.7, 506.95; 583.2, 539.25; 586.2, 579.22; 588.6, 608.94; 591.2, 644.69; 594.2, 680.56; 599.4, 757.08.

Results. Least squares of the experimental data, fit to the equation:

$$\log_{10} P = A/T + B \log_{10} T + C \tag{1}$$

for each compound are presented in Table I. In Equation 1, *A, B,* and *C* are constants, *P* represents the pressure (torr) at the absolute temperature *T.*

Liquid density. Density determinations were made with 10-ml capped Weld pycnometers calibrated against degassed distilled water. Mass values were measured to the nearest 0.1 mg. Temperature was controlled by a Blue M Electric Co. "Magni-Whirl" constant temperature bath, Model No. MR3262A-1, used with a Precision Scientific Co. low-temperature circulator unit, 154. The temperature was measured by use of mercury in glass thermometers standardized against a Leeds and Northrup calibrated platinum resistance thermometer. The error in the measured temperature was not greater than 0.02°C.

Data. Substance: *T,* K, density $g(ml)^{-1}$. $Ge(CH_3)_4$: 276.8, 0.9934; 278.6, 0.9907; 282.3, 0.9853; 284.6, 0.9820; 288.1, 0.9770; 289.5, 0.9750.

$Ge(C_2H_5)_4$: 279.5, 1.0084; 287.9, 1.0000; 296.6, 0.9914; 303.2, 0.9850; 311.8, 0.9768; 318.3, 0.9706; 328.0, 0.9616; 336.6, 0.9538.

$Ge(C_3H_7)_4$: 281.1, 0.9645; 289.5, 0.9571; 297.3, 0.9505; 305.5, 0.9436; 310.3, 0.9396; 316.9, 0.9341; 325.3, 0.9272; 333.2, 0.9209.

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$Ge(C_4H_9)_4$: 283.4, 0.9401; 290.0, 0.9346; 297.3, 0.9286; 306.6, 0.9211; 312.9, 0.9161; 319.9, 0.9106; 326.3, 0.9056; 332.9, 0.9005.

$Ge(C_5H_{11})_4$: 280.6, 0.9391; 288.3, 0.9329; 295.5, 0.9272; 303.8, 0.9207; 311.6, 0.9146; 320.8, 0.9076; 330.3, 0.9005; 339.6, 0.8936.

$Ge(C_6H_{13})_4$: 282.6, 0.9338; 291.9, 0.9265; 299.3, 0.9208; 303.8, 0.9173; 315.0, 0.9089; 323.5, 0.9025; 331.8, 0.8964; 340.0, 0.8905.

Results. Least-squares fits of the experimental data to the equation:

$$d = A + BT + CT^2 \qquad (2)$$

are presented in Table II. The symbols A, B, and C in Equation 2 are constants, and d represents the density at the absolute temperature T.

Surface tension. Surface tension values of $Ge(CH_3)_4$, $Ge(C_2H_5)_4$, $Ge(C_3H_7)_4$, $Ge(C_4H_9)_4$, $Ge(C_5H_{11})_4$, and $Ge(C_6H_{13})_4$ were obtained from Sugden's two-tube bubble-pressure apparatus (*18, 19*). Calibration of the two-tube bubble-pressure tensiometer was accomplished with spectroscopic grade tetrachlormethane. Manometer measurements were made with a Griffin and George cathetometer, with an accuracy of 0.025 mm. Control and measurement of the temperature are the same as described in the Liquid Density section.

Data. Substance: T, K, surface tension (dyne cm^{-1}). $Ge(CH_3)_4$: 279.7, 25.96; 283.7, 25.48; 288.3, 24.92; 293.5, 24.25; 299.1, 23.58.

$Ge(C_2H_5)_4$: 278.2, 25.77; 283.7, 25.17; 290.8, 24.38; 294.9, 24.04; 300.5, 23.17; 308.8, 22.18; 318.7, 21.17; 325.8, 20.04; 330.8, 19.28; 333.7, 18.88.

$Ge(C_3H_7)_4$: 281.1, 25.85; 289.5, 24.81; 297.3, 24.08; 305.5, 23.29; 310.3, 22.63; 316.9, 22.00; 325.3, 21.07; 333.2, 19.99.

$Ge(C_4H_9)_4$: 283.4, 27.36; 290.0, 26.75; 297.3, 25.93; 306.6, 25.05; 312.9, 24.40; 319.9, 23.62; 326.3, 22.95; 332.9, 22.38.

$Ge(C_5H_{11})_4$: 280.1, 28.79; 287.5, 28.02; 295.2, 27.25; 306.5, 26.07; 313.2, 25.30; 320.5, 24.49; 329.2, 23.40; 335.6, 22.58.

$Ge(C_6H_{13})_4$: 278.6, 30.34; 285.3, 29.62; 294.9, 28.39; 318.2, 25.61; 324.8, 24.67; 332.2, 23.90.

Results. The surface tension values presented in the above table were obtained from the equation:

$$\gamma = \frac{\Delta h(D - d)g}{2(1/x_1 - 1/x_2)} \qquad (3)$$

where Δh represents the manometer reading in cm of the liquid in question, g is the gravitational acceleration constant in $cm\text{-}sec^{-2}$, D is the density of the liquid in $g\text{-}cm^{-3}$, and d is the density of the vapor in $g\text{-}cm^{-3}$. With the exception of $Ge(CH_3)_4$, d in Equation 1 was neglected. For temperature ranges where the vapor pressure is relatively low, neglecting d introduces an error much smaller than the uncertainty in Δh. The quantity $1/x_1 - 1/x_2$ was determined by measuring Δh for a liquid of known surface tension, CCl_4. Least-squares fits of the experimental data to the equation:

$$\gamma = A + BT + CT^2 + DT^3 \qquad (4)$$

are presented in Table III.

Viscosity. Viscosities of $Ge(CH_3)_4$, $Ge(C_2H_5)_4$, $Ge(C_3H_7)_4$, $Ge(C_4H_9)_4$, $Ge(C_5H_{11})_4$, and $Ge(C_6H_{13})_4$ were obtained from two Ubbelohde type viscometers. Calibration of the viscometers was accomplished by R. E. Manning and W. A. Lloyd of the Cannon Instrument Co., State College, Pa., by the method of Cannon (*4*). Control and measurement of the temperature are the same as described in the Liquid Density section.

Data. Substance: T, K, viscosity (centipoise). $Ge(CH_3)_4$: 276.7, 0.4049; 282.5, 0.3855; 287.3, 0.3690; 293.0, 0.3512; 298.7, 0.3348; 303.8, 0.3233.

$Ge(C_2H_5)_4$: 277.9, 0.8800; 284.3, 0.8202; 288.8, 0.7789; 295.3, 0.7298; 301.2, 0.6835; 307.3, 0.6460; 313.4, 0.6163; 319.5, 0.5866; 325.8, 0.5613; 331.8, 0.5360; 337.1, 0.5170.

$Ge(C_3H_7)_4$: 276.6, 1.842; 280.6, 1.700; 284.4, 1.576; 289.0, 1.444; 294.8, 1.308; 300.5, 1.192; 305.6, 1.085; 310.5, 1.007; 320.5, 0.8782; 324.4, 0.8370; 330.2, 0.7892; 335.9, 0.7297; 340.7, 0.6832.

$Ge(C_4H_9)_4$: 275.6, 5.358; 282.5, 4.317; 288.0, 3.685; 295.0, 3.032; 299.9, 2.690; 303.1, 2.495; 308.0, 2.232; 313.7, 1.991; 318.6, 1.804; 320.3, 1.651; 323.4, 1.648; 328.2, 1.512; 334.3, 1.362; 339.3, 1.255.

$Ge(C_5H_{11})_4$: 276.2, 9.511; 282.8, 7.311; 288.9, 6.005; 294.8, 4.991; 301.0, 4.199; 308.7, 3.438; 314.0, 3.040; 325.8, 2.377; 331.8, 2.132; 338.2, 1.915.

Table I. $\log_{10} P = A/T + B \log_{10} T + C$

Substance	$A \times 10^{-3}$	B	$C \times 10^{-1}$	Av % dev	Press range, torr
$Ge(CH_3)_4$	−1.6254	−1.0200	1.0514	1.23	45–758
$Ge(C_2H_5)_4$	−4.2042	−11.591	4.3097	1.75	21–748
$Ge(C_3H_7)_4$	−4.2762	−8.1423	3.3383	0.95	19–676
$Ge(C_4H_9)_4$	−6.5382	−15.744	5.7861	0.93	20–770
$Ge(C_5H_{11})_4$	−6.6777	−13.470	5.1437	0.63	18–757

Table II. Density as Function of Temperature

$d = A + BT + CT^2$ g(ml)$^{-1}$

Substance	A	$B \times 10^3$	$C \times 10^7$	SD	Temp range, K
$Ge(CH_3)_4$	1.5633	−2.6019	20.560	0.00001	277–290
$Ge(C_2H_5)_4$	1.3556	−1.4816	8.5331	0.00005	280–337
$Ge(C_3H_7)_4$	1.2661	−1.2727	7.0966	0.00005	281–333
$Ge(C_4H_9)_4$	1.2304	−1.2145	6.7145	0.00004	283–333
$Ge(C_5H_{11})_4$	1.2196	−1.1892	6.7537	0.00001	281–340
$Ge(C_6H_{13})_4$	1.2075	−1.1512	6.4039	0.00002	283–340

Table III. Surface Tension as Function of Temperature

$\gamma = A + BT + CT^2 + DT^3$

Substance	$A \times 10^{-2}$	B	$C \times 10^3$	$D \times 10^6$	Temp range, K	SD
$Ge(CH_3)_4$	−11.306	12.214	−42.585	48.981	280–299	0.0022
$Ge(C_2H_5)_4$	2.3475	−1.9621	6.4175	−7.4205	278–334	0.077
$Ge(C_3H_7)_4$	4.5769	−4.0975	13.191	−14.515	281–333	0.050
$Ge(C_4H_9)_4$	−1.3476	1.7638	−6.0639	6.5586	283–333	0.035
$Ge(C_5H_{11})_4$	1.5552	−1.1391	3.6498	−4.2795	280–336	0.045
$Ge(C_6H_{13})_4$	−0.70696	1.2054	−4.3410	4.7242	279–332	0.011

Table IV. Viscosity as Function of Temperature

$\log_{10} \eta = A + B/T$

Substance	A	B	Temp range, K	SD	
				A	B
$Ge(CH_3)_4$	−3.4620	708.10	277–304	0.00199	7.3825
$Ge(C_2H_5)_4$	−3.1660	842.11	278–337	0.00738	11.046
$Ge(C_3H_7)_4$	−4.6319	1445.9	277–341	0.01191	14.924
$Ge(C_4H_9)_4$	−6.0376	2114.5	276–339	0.02381	32.207
$Ge(C_5H_{11})_4$	−6.4937	2396.9	276–338	0.03857	55.607
$Ge(C_6H_{13})_4$	−6.5884	2509.0	277–338	0.C2687	39.901

Table V. Refractive Index and Dielectric Constant

Substance	Refractive index, 293.2K	Dielectric constant, 297.2K
$Ge(CH_3)_4$	1.3985[a]	1.817
$Ge(C_2H_5)_4$	1.4430	1.971
$Ge(C_3H_7)_4$	1.4510	1.921
$Ge(C_4H_9)_4$	1.4561	2.334
$Ge(C_5H_{11})_4$	1.4592	2.299

[a] Measured at 277.2K.

$Ge(C_6H_{13})_4$: 276.6, 12.46; 284.0, 9.524; 289.8, 7.874; 296.5, 6.345; 302.1, 5.425; 313.0, 4.006; 318.7, 3.567; 326.0, 3.024; 331.8, 2.696; 338.2, 2.379.

Results. Leasts-squares fits of the experimental data to the equation:

$$\log_{10} \eta = A + B/T \quad (5)$$

are presented in Table IV.

Refractive index and dielectric constant. Refractive indices (measured at 5.08726 × 10^{14} sec^{-1}: Na D-line) of $Ge(CH_3)_4$, $Ge(C_2H_5)_4$, $Ge(C_3H_7)_4$, $Ge(C_4H_9)_4$, and $Ge(C_5H_{11})_4$ were obtained from a Bausch and Lomb refractometer (cat. no. 33-45-58) (*7, 8*). The dielectric constants of these compounds (measured at 1592 cps) were obtained from a Wayne Kerr Bridge, Model 201, used with a parallel plate cell. Calibration of the parallel plate cell was accomplished with spectroscopic grade benzene. For both refractive indices and dielectric constant observations, control and measurement of the temperature are the same as described in the Liquid Density section.

Data. Refractive indices and dielectric constants are presented in columns 1 and 2, Table V.

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Received for review December 12, 1972. Resubmitted July 11, 1973. Accepted October 20, i973.

Vapor Pressure of Biphenyl Near Fusion Temperature

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A chromatographic method has been used in a preliminary study (by use of a flow vaporizer) of the vapor pressure of solid and liquid biphenyl at temperatures close to (above and below) the melting point of the solid. The results for the solid are too low. However, the data indicate that the method is feasible, with proper care to equilibration and to temperature measurements.

Data on the pressure of liquid biphenyl are extensive and probably reliable, except for an absence of data near the freezing point. There have been no recent reports of measurements. The numbers given in "Handbook of Chemistry and Physics" (*7*) are taken from the 1947 compilation of Stull (*5*) for which the most recent sources of data on biphenyl were papers published in 1929 and 1930. The vapor pressure of the solid has been measured less often but more recently (*1, 2, 4*). The most precise work was done by Bradley and Cleasby (*1*) over the temperature range, 15.05–40.55°C. Timmermans (*6*) quotes the results in his 1965 volume. Bradley and Cleasby used an effusion method. A slightly higher temperature (46°C) was reached in the work of Bright (*2*). This is still some 24° below the melting point. It is clearly desirable to extend data on the solid up to the melting point.

We have used chromatographic determination of biphenyl concentrations in studies of its pyrolysis (*3*). Although it was not essential in that study to know the vapor pressure, the fact that a flow vaporizer was in the system suggested the possibility of saturating the flow and thus determining vapor pressures. The present data were taken mainly to assess the *feasibility* of using this method to determine the vapor pressure of the solid at temperatures within 20° of the melting point.

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