Thermodynamic Functions for 1,1,2,2-Tetrabromoethane

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Thermodynamic functions, C_p^0, S^0, $(H^0 - H_0^0)/T$, $-(F^0 - H_0^0)/T$, have been calculated for 1,1,2,2-tetrabromoethane in the ideal gas state from 250° to 750° K. at 1 atm. pressure. The restricted internal rotational contribution has been treated by means of the Lielmezs-Bondi approximate method.

RECENT availability of molecular structural (*5, 6, 10, 11*) and spectrographic data (*1*) has made it possible to estimate the thermodynamic functions, C_p^0, S^0, $(H^0 - H_0^0)/T$, $-(F^0 - H_0^0)/T$, $-(F^0 - H_0^0)/T$, for the 1,1,2,2-tetrabromoethane equilibrium mixture of trans and skew form isomers in the ideal gas state at 1 atm. pressure. Table I presents the thermodynamic functions calculated by the Lielmezs-Bondi approximate method (*3, 6, 8, 9*). The results presented in Table I are fitted to Equation 1:

$$\Lambda = a + bT + cT^2 + dT^3 \qquad (1)$$

where Λ is the thermodynamic function and T is the temperature. The constants a, b, c, d (Equation 1) were evaluated using least-squares curve fitting methods (*12*) and are given in Table II. The use of Equation 1 causes deviations (Table II) in the calculated thermodynamic function values from those shown in Table I. Table III gives the values of the molecular parameters used in the calculation of the thermodynamic functions.

Although there are no available calorimetric data, the over-all reliability of the frequency assignments of both

Table I. 1,1,2,2-Tetrabromoethane Thermodynamic Functions

Temp., °K.	C_p^0, Cal./Mole-°K.	$(H^0 - H_0^0)/T$, Cal./Mole-°K.	$-(F^0 - H_0^0)/T$, Cal./Mole-°K.	S^0, E.U.
250.00	23.65	16.66	74.61	91.27
273.15	24.63	17.30	76.11	93.42
298.15	25.64	17.97	77.66	95.63
300.00	25.71	18.01	77.77	95.78
350.00	27.56	19.26	80.64	99.90
400.00	29.17	20.41	83.29	103.70
450.00	30.57	21.47	85.75	107.22
500.00	31.77	22.44	88.07	110.51
550.00	32.81	23.34	90.25	113.59
600.00	33.71	24.17	92.32	116.49
650.00	34.50	24.94	94.28	119.22
700.00	35.19	25.65	96.16	121.81
750.00	35.81	26.31	97.95	124.26

Table II. Calculated Constants

Function	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^8$	Std. Dev.[a]
C_p^0	8.5059	7.8346	−7.8976	3.0734	±0.013
$(H^0 - H_0^0)/T$	8.0967	4.0991	−2.9240	0.92587	±0.007
$-(F^0 - H_0^0)/T$	55.127	9.3590	−6.8620	2.6455	±0.037
S^0	63.271	13.429	−9.7185	3.5332	±0.024

[a] Standard deviation = $\left[\frac{\sum^{n} (Y - Y_{\text{fit}})^2}{n}\right]$

Table III. Molecular Parameters

Frequencies in wave numbers (ν, cm.$^{-1}$):[a] (*1*)
Trans form:
2985 (ν_1) 1280 (ν_2) 1033 (ν_3) 662 (ν_4) 223 (ν_5) 139 (ν_6)
1115 (ν_7) 586 (ν_8) 200 (ν_9) 56 (ν_{10}) 1133 (ν_{11}) 724 (ν_{12})
184 (ν_{13}) 2998 (ν_{14}) 1143 (ν_{15}) 637 (ν_{16}) 397 (ν_{17}) 282 (ν_{18})

Skew form:
2985 (ν_1) 1242 (ν_2) 1196 (ν_3) 1011 (ν_4) 713 (ν_5) 536 (ν_6) 217 (ν_7)
147 (ν_8) 112 (ν_9) 62 (ν_{10}) 2985 (ν_{11}) 1136 (ν_{12}) 1117 (ν_{13})
701 (ν_{14}) 615 (ν_{15}) 449 (ν_{16}) 190 (ν_{17}) 176 (ν_{18})

Moment of inertia products:[b]
Trans form:

$$I_{ABC} = 59.5275 \times 10^{-112} \text{ g.}^3 \text{ cm.}^6$$

Skew form:

$$I_{ABC} = 44.8338 \times 10^{-112} \text{ g.}^3 \text{ cm.}^6$$

Isomerization energy:[c]

$$\Delta E_{\text{iso}} = 0 \text{ cal./mole} \qquad (10)$$

Molecular shape factor:

$$\sigma = 2 \qquad (1)$$

Molecular weight:

$$M = 345.674$$

Physical constants: (2)

[a] Listed frequencies are in the liquid state and increase in sequence from ν_1 to ν_{18}. However, the over-all change in the value of the thermodynamic functions owing to vapor liquid shift is expected to be small (*4*). [b] Moment of inertia products were calculated using the vapor (electron diffraction) structural data given by Hassel and Viervoll (*5*). [c] Following Miyagawa (*10*), $\Delta E_{\text{iso}} = 0$ is used in this work. This choice is indirectly affirmed by noting that Powling and Bernstein (*11*) and Krebs and Lamb (*7*) have determined values of the isomerization energy of 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane as being almost the same in the liquid state. Powling and Bernstein have determined that ΔE_{iso} for 1,1,2,2-tetrachloroethane vapor is nearly zero. If the known liquid and vapor state isomerization (ΔE_{iso}) energies are compared, it appears that ΔE_{iso} should also be zero for the 1,1,2,2-tetrabromoethane vapor.

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rotational isomers (*1*), even if they were made for the liquid state, suggests that the presented thermodynamic function values (Table I) may well be within the bounds of experimental accuracy.

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Densities of Molten Zinc Chloride and Its Mixtures with Cesium Chloride

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Liquid state densities of $ZnCl_2$–CsCl mixtures are reported as functions of temperature. The excess molar volume is positive and large near 40 mole % $ZnCl_2$ and negative and small near pure $ZnCl_2$. Measurements on pure $ZnCl_2$ and 97 mole % $ZnCl_2$ were made by both the buoyancy and float methods. Measurements at other compositions were made by the buoyancy method alone.

MOLTEN mixtures of zinc chloride with alkali metal chlorides have unusual structural properties (*1, 2*) that make them of special interest as solvents for chemical reactions (*3–5*). To investigate such reactions by absorption spectrophotometry, it is necessary to have density data so that light absorption may be converted to molar absorptivity units. For this reason, the authors have measured the densities of $ZnCl_2$–CsCl mixtures as functions of temperature.

EXPERIMENTAL

Cesium chloride (99.9%) was recrystallized from water, solvent extracted to remove organic contaminants, and vacuum dried. It was finally purified by passing high-purity HCl followed by high-purity nitrogen through the melt. Zinc chloride was prepared from a very good grade of zinc metal and high-purity HCl and then distilled. These preparations were carried out in all-silica systems that were baked out and isolated from the atmosphere. Weighings and cell loadings were performed in a vacuum-type dry box under a nitrogen atmosphere with a measured water-vapor content of less than 2 p.p.m.

Most of the density measurements were made under dry nitrogen by the buoyancy method with an apparatus described previously (*6*). However, because of the hygroscopicity and volatility of zinc chloride, measurements on this material and the 97 mole % mixture were also made in sealed silica cells by the float method described by Boston (*7*). Results obtained by these two techniques were in agreement to within 0.1% for pure zinc chloride and 0.7% for the 97 mole % mixture.

RESULTS AND DISCUSSION

Results of the density measurements are summarized in Table I where the density, ρ, is given by the usual expression, $\rho = \alpha - \beta t$, and the temperature t is in °C. The present results for pure zinc chloride agree well with those of Wachter and Hildebrand (*8*), somewhat less well with those of Mackenzie and Murphy (*9*), and differ by about 1.5% from those of Duke and Fleming (*10*).

Molar volumes were calculated at several temperatures and the results are plotted in Figure 1. Values for CsCl,

Table I. Density Equations for $ZnCl_2$–CsCl Mixtures

	$\rho = \alpha - \beta t$			
Composition Mole %, $ZnCl_2$	α, grams/cc.	$\beta \times 10^3$, grams/cc. °C.	Std. Dev. $\times 10^3$, Grams/Cc.	Exptl. Temp. Range, °C.
10.0	3.378	1.001	1.1	616–795
25.0	3.190	0.880	1.6	616–792
40.0	3.137	0.957	3.3	598–743
58.0	3.031	0.882	1.9	310–603
66.6	2.991	0.851	1.0	311–602
80.0	2.870	0.718	6.6	400–603
95.0	2.765	0.611	7.8	310–602
96.0	2.724	0.534	0.6	362–488
97.0	2.738	0.571	2.5	362–500
98.0	2.750	0.620	. . .	400–500
99.0	2.684	0.515	0.1	358–496
100.0	2.683	0.511	1.8	357–595