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Thermodynamic Functions for 1,1,2,2,-Tetrachloroethane and 1,1-Difluoro-2,2-Dichloroethane

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Thermodynamic functions C_p°, S°, $(H^\circ-H_0^\circ)/T$, $-(F^\circ-H_0^\circ)/T$, have been calculated for 1,1,2,2,-tetrachloroethane and 1,1-difluoro-2,2-dichloroethane in the ideal gas state from 273.15° to 1000° K. at 1 atm. pressure. The restricted internal rotational contribution has been treated, for both compounds, by employing the Lielmezs-Bondi approximate method.

1,1,2,2-TETRACHLOROETHANE

Recently published spectrographic data (*1*), combined with information from previous spectrographic (*11, 12*) and molecular structural investigations (*4, 11, 13*), has made it possible to estimate the thermodynamic functions, C_p°, S°, $(H^\circ-H_0^\circ)/T$, and $-(F^\circ-H_0^\circ)/T$, for the 1,1,2,2-tetrachloroethane equilibrium mixture of trans and skew form isomers in the ideal gas state at 1 atm. pressure. Table I (deposited with ASIS) presents the thermodynamic functions calculated by the Lielmezs-Bondi approximate method (*2, 5, 8, 9, 10*). The results presented in Table I are fitted to Equation 1

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

where Λ is the thermodynamic function and T is the temperature (°K.). The constants a, b, and c (Equation 1) were calculated using least-squares curve-fitting methods (*14*) and are given in Table II (deposited with ASIS).

Table III gives the values of the molecular parameters used in the calculation of the thermodynamic functions for 1,1,2,2-tetrachloroethane.

Although calorimetric data are not available, comparison of the values presented with previously calculated values (*7*) reveals a maximum difference in heat capacity of 0.6%,

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while for entropy the maximum difference is 1.5%. This suggests that the presented values, based on more recent spectrographic data, may well be within the bounds of experimental accuracy.

1,1,-DIFLUORO-2,2-DICHLOROETHANE

As with the symmetrical tetrachloroethane, recent spectrographic and molecular structural data (*6*) have made it possible to calculate the thermodynamic functions—Table IV; internal rotation contribution is treated by means of Lielmezs-Bondi method (*2, 5, 8, 9, 10*)—for 1,1-difluoro-2,2-dichloroethane. Table V gives the constants of Equation 1, and Table VI, the values of the molecular parameters used in the calculations. The isomerization energy was selected as 600 cal. per mole from the suggested range of 500 to 700 cal. per mole (*6*). The six lowest used frequencies (Table VI) were chosen, as proposed by Kartha, *et al.* (*6*). Calculations were then performed over the given isomerization energy range from 500 to 700 cal. per mole and with the frequencies varying ±10 wave numbers from the estimated values (*6*) in order to determine the deviation in thermodynamic functions over this range. The results of this calculation are shown, with the maximum deviation between function values (expressed as a per cent difference) in Table VII.

Table III[a]. Molecular Parameters for 1,1,2,2-Tetrachloroethane

Frequencies in wave numbers ν (cm.$^{-1}$)[b] (1)

Trans form

2986	1306	1028	765	366	224
1304 (11)	716	319	91	1204	811
298	2986	1188	756	326	288 (11)

Skew form

2986	1279	1242	1018	801	648
3530	240	175	91	2986	1216
1204	795	740	546	287	173(11)

Moment of inertia products[c]

Trans form

$$I_{ABC} = 335,529 \times 10^{-117} \text{ gram}^3 \text{ cm.}^6$$

Skew form

$$I_{ABC} = 269,729 \times 10^{-117} \text{ gram}^3 \text{ cm.}^6$$

Isomerization energy (12)

$$\Delta E_{iso} = 280 \text{ cal./mole}$$

Molecular shape factor (1)

$$\sigma = 2$$

Molecular weight

$$M = 167.850$$

[a] Tables I and II (thermodynamic functions for 1,1,2,2-tetrachloroethane and calculated constants for 1,1,2,2-tetrachloroethane) are deposited with ASIS. [b] Frequencies are for liquid state; however, the over-all change in the value of the thermodynamic functions due to vapor liquid shift is expected to be within ±1% (3). [c] Calculated values, from structural data (4, 11, 13).

Table IV. Thermodynamic Functions for 1,1-Difluoro-2,2-dichloroethane

Temp., ° K.	C_p°, Cal./Mole ° K.	$(H^\circ - H_0^\circ)/T$, Cal./Mole ° K.	$-(F^\circ - H_0^\circ)/T$, Cal./Mole ° K.	S°, E. U.
273.15	23.64	16.09	65.10	81.19
298.15	24.68	16.75	66.54	83.29
350	26.67	18.05	69.33	87.38
400	28.37	19.22	71.82	91.04
450	29.84	20.31	74.14	94.45
500	31.12	21.31	76.34	97.65
550	32.22	22.25	78.41	100.66
600	33.18	23.11	80.38	103.50
650	34.02	23.91	82.27	106.18
700	34.76	24.66	84.07	108.72
750	35.42	25.35	83.79	111.14
800	36.01	26.00	87.45	113.44
850	36.55	26.60	89.04	115.64
900	37.03	27.16	90.58	117.74
950	37.47	27.69	92.06	119.75
1000	37.87	28.19	93.49	121.68

Table V. Calculated Constants for 1,1-Difluoro-2,2-dichloroethane

(Equation 1)

Function	a	$b \times 10^2$	$c \times 10^5$	Maximum Dev.,[a] Cal./Mole ° K.
C_p°	12.502	4.8419	−2.3401	±0.35
$(H^\circ - H_0^\circ)/T$	8.4377	3.1587	−1.1940	±0.10
$-(F^\circ - H_0^\circ)/T$	49.706	6.2373	−1.8781	±0.24
S°	58.143	9.3959	−3.0720	±0.33

[a] Maximum difference between the values in Table VI and values determined through use of Equation 1.

Table VI. Molecular Parameters for 1,1-Difluoro-2,2-dichloroethane

Frequencies in wave numbers ν (cm.$^{-1}$) (6)

Trans form

2999	2999	1373	1149	1269	1058
973	819	737	651	538	399
388	344	281	215[a]	194[a]	90[a]

Skew form

2999	2999	1385	1082	1221	1117
991	819	791	768	595	571
399	344	281	215[a]	194[a]	90[a]

Moment of inertia products (6)

Trans form

$$I_{ABC} = 98,824 \times 10^{-117} \text{ gram}^3 \text{ cm.}^6$$

Skew form

$$I_{ABC} = 83,616 \times 10^{-117} \text{ gram}^3 \text{ cm.}^6$$

Isomerization energy (6)

$$\Delta E_{iso} = 600 \text{ cal./mole}$$

Molecular shape factor (assumed)

$$\sigma = 2$$

Molecular weight

$$M = 134.941$$

[a] Estimated frequencies as in (6).

Table VII. Calculated Deviations over Range Studied for 1,1-Difluoro-2,2-dichloroethane

Isomerization Energy, Cal./Mole	Heat Capacity			Entropy, Δ Wave Numbers			$(H^\circ - H_0^\circ)/T$		
	−10	0	+10	−10	0	+10	−10	0	+10
				Temp. 298.15° K.					
500	24.55	24.51	24.48	83.76	83.34	82.96	16.78	16.74	16.57
600	24.72	24.68	24.65	83.71	83.29	82.91	16.86	16.75	16.64
700	24.89	24.85	24.82	83.64	83.23	82.85	16.91	16.80	16.67
Maximum Dev., %[a]		1.66			1.10			2.06	
				Temp. 1000° K.					
500	37.84	37.84	37.84	122.12	121.68	121.29	28.18	28.14	28.10
600	37.87	37.87	37.86	122.11	121.68	121.28	28.23	28.19	28.15
700	37.89	37.89	37.89	122.11	121.68	121.28	28.27	28.73	28.19
Maximum Dev., %[a]		1.51			0.412			1.47	

[a] Expressed as percentage difference between maximum and minimum values calculated, over range shown, for each function.

Although there are no available experimental data, the over-all relative insensitivity of the calculated functions in terms of the deviation in the chosen frequency and isomerization energy values (Table VII) suggests that the error should not exceed $\pm 2.5\%$ in any of the computed thermodynamic properties.

NOMENCLATURE

a, b, c = constants
C_p° = heat capacity
ΔE_{iso} = isomerization energy
$-(F^\circ-H_0^\circ)/T$ = free energy function
$(H^\circ-H_0^\circ)/T$ = enthalpy function, where H_0° is H° at 0° K.
I_{ABC} = moment of inertia product
M = molecular weight
S° = entropy
T = absolute temperature, $^\circ$ K.
ν = wave number, cm.$^{-1}$
σ = molecular shape factor
Λ = any one of thermodynamic properties, C_p°, $(H^\circ-H_0^\circ)/T$, $-(F^\circ-H_0^\circ)/T$, S°, at temperature T

Superscript

$\circ$ = ideal state (reference state)

Subscript

p = pressure

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Freezing Point Depression in Fluorine Systems

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The eutectic composition in the system fluorine–oxygen difluoride was determined to be 0.59 $\pm$ 0.02 mole fraction fluorine; the eutectic temperature is 43° $\pm$ 0.5° K.

$\mathbf{I}$N SOME test programs using liquid fluorine and liquid hydrogen, it was desirable to lower the freezing point of fluorine without appreciably affecting its chemical reactivity. The use of a eutectic seemed the method of choice, and oxygen difluoride, OF_2, was selected as the other component. Oxygen was also suggested, but was not used because of reports of its quenching effect on the fluorine-hydrogen reaction (2, 7, 8), an effect also found in research on the ignition of $F_2(l)$-$H_2(l)$ (3) and reported in the OF_2-H_2 reaction (11).

Theoretical calculations of the freezing point depression in the F_2-OF_2 system suggested that experimental investigation was warranted.

THEORETICAL

The equilibrium or phase diagram of a two-component solid-liquid system may assume several general forms according to the nature of the components (4); these forms may be classified as eutectic systems, completely miscible solid solutions, or partially miscible solid solutions. If nonpolar compounds are to form solid solutions, they must be of analogous chemical constitution, similar crystal structure, and nearly equal molecular volume. While little is known of the crystal structures of F_2 and OF_2, the first and last conditions above are not satisfied, and solid solutions probably will not form. Furthermore, there is no known tendency toward compound formation between