

Heat Capacity, Heats of Fusion and Vaporization, and Vapor Pressure of Tetrafluoroethylene¹

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The heat capacity of tetrafluoroethylene of 99.99₀-mole-percent purity was measured in an adiabatic calorimeter from 16° to 210° K. A smoothed table of heat capacity at 5-degree intervals from 0° to 210° K was constructed from the data. The average heat of fusion of three experiments gave 7,714.5 ± 7 abs j mole⁻¹ at the triple-point temperature of 142.00 ± 0.01° K. The three heats of vaporization measurements at the normal boiling temperature of 197.53 ± 0.01° K gave an average value of 16,821 ± 10 abs j mole⁻¹. The results of the vapor-pressure measurements from 142° to 208° K can be represented by the equation

$$\log_{10} p_{\text{mmHg}} = 4.71241 - \frac{972.9810}{T} + 4.816562 \times 10^{-2} T - 2.427347 \times 10^{-4} T^2 + 3.958793 \times 10^{-7} T^3.$$

The entropy of the ideal gas tetrafluoroethylene at 197.53° K and 1 atm was computed from the calorimetric data to be 270.06 ± 0.37 abs j deg⁻¹ mole⁻¹ or 64.55 ± 0.09 cal deg⁻¹ mole⁻¹ (1 cal = 4.1840 abs j). The entropy was computed from molecular and spectroscopic data to be 64.54 cal deg⁻¹ mole⁻¹.

1. Introduction

In continuation of the program for the thermodynamic investigation of high temperature resistant polymers and their respective monomers or prototype molecules, heat-capacity, heats of fusion and vaporization, and vapor-pressure measurements were conducted with tetrafluoroethylene (C₂F₄). This substance has recently become important as the monomer in the production of polytetrafluoroethylene (Teflon) plastic, which has exceedingly high chemical and thermal stability. Heat-capacity studies with this polymer have recently been reported from the National Bureau of Standards.²

2. Apparatus and Method

The heat-capacity and heat-of-fusion measurements with tetrafluoroethylene were made in an adiabatic calorimeter which has been previously described.³ The heat of vaporization was determined in another adiabatic calorimeter constructed by R. B. Scott of the Bureau. This calorimeter was similar in design to those described by Osborne and Ginnings⁴ and by Aston, et al.,⁵ in which a throttle valve was contained within the space enclosed by the adiabatic shield. Briefly, during the vaporization experiments a known electric power was supplied continuously, and the vapor was removed isothermally from the calorimeter by controlling the throttle valve. The material removed from the calorimeter in a measured time interval, was collected by condensation in a small high-pressure cylinder (150 ml) and weighed.

¹ This paper is based on the work sponsored by the Ordnance Corps, U. S. Department of the Army.

² G. T. Furukawa, R. E. McCoskey, and G. J. King, J. Research NBS **49**, 273 (1952) RP2364.

³ R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, J. Research NBS **35**, 39 (1945) RP1661.

⁴ N. S. Osborne and D. C. Ginnings, J. Research NBS **39**, 453 (1947) RP1841.

⁵ J. G. Aston, H. L. Fink, G. J. Janz, and K. E. Russell, J. Am. Chem. Soc. **73**, 1939 (1951).

In the vapor-pressure measurements the same calorimeter used for the vaporization measurements served as a thermostated container. No provision was made to stir the sample. The pressures were read by means of a mercury manometer and a mirror-backed glass scale. The readings were converted to standard mm Hg ($g = 980.665 \text{ cm/sec}^2$, temperature = 0° C) on the basis that the local gravity is 980.076 cm/sec².

The International Temperature Scale⁶ was used, and below 90° K, a provisional scale⁷ was used based on a set of platinum resistance thermometers calibrated against a helium-gas thermometer.

3. Material

The sample was originally received in a high-pressure cylinder (300 g. to 1.5 ft.³) and inhibited against polymerization and other reactions. To remove the inhibitor, the material was passed through a train of gas-washing bottles containing concentrated sulfuric acid, and to remove traces of permanent gases, it was later frozen and pumped three times. About 155 g of the purified material was collected. As this substance is considered to be hazardous, particularly in the uninhibited state, it was kept at temperatures below that of dry-ice at all times, except when being weighed.

The purity of the material was determined in the calorimeter before the thermal measurements from the equilibrium melting temperatures⁸ on the bases that no solid solution was formed and that the liquid solution followed Raoult's law. The equilibrium temperatures and the corresponding reciprocal of the fraction melted, F , are given in table 1.

⁶ H. F. Stimson, J. Research NBS **42**, 209 (1949) RP1962.

⁷ H. J. Hoge and F. G. Brickwedde, J. Research NBS **23**, 351 (1939) RP1188.

⁸ G. T. Furukawa, D. C. Ginnings, R. E. McCoskey, and R. A. Nelson, J. Research NBS **46**, 195 (1951) RP2191.

TABLE 1. Equilibrium melting temperatures of tetrafluoroethylene

Mole fraction impurity = 0.0460 ΔT , $^{\circ}\text{K} = 273.16^{\circ} + ^{\circ}\text{C}$

Reciprocal of fraction melted, $1/F$	T
	$^{\circ}\text{K}$
9.59	141.9762
4.73	141.9936
3.67	141.9959
1.93	142.0012
1.46	142.0013
1.21	142.0016
0.00	^a 142.0048
Triple-point temperature, $142.00 \pm 0.01^{\circ}\text{K}$.	
Purity, 99.99% mole percent.	

^a Extrapolated.

The data were plotted and the purity was computed from the slope of the curve to be 99.99₀ mole percent. The intercept or the triple-point temperature of pure tetrafluoroethylene was found to be $142.00 \pm 0.01^{\circ}\text{K}$. The results of the premelting heat-capacity measurements made during the course of this study indicated that the purity remained essentially the same. (The temperature in degrees Kelvin was obtained from the relation: $^{\circ}\text{K} = 273.16^{\circ} + ^{\circ}\text{C}$. Whenever the temperatures are expressed in the paper to the fourth decimal place, the last two figures are significant only in the measurement of small temperature differences.)

4. Heat Capacity

The heat-capacity measurements were made from 16° to 210°K . In the computation to obtain the net heat capacities, the observed gross-heat capacities were first smoothed, then the smoothed tare heat capacities were subtracted at the corresponding equally spaced integral temperatures. Curvature corrections (see footnote 8) were applied to the gross and tare heat capacities wherever significant. The vapor-pressure data obtained in this work and the liquid densities reported by Ruff and Bretschneider⁹ were used to make vapor saturation corrections.¹⁰

The results of the heat-capacity measurements gave a precision of ± 0.02 percent in the liquid and from ± 0.02 to ± 0.05 percent in the solid range, except for the lowest temperatures. There is, however, a fairly large uncertainty in the vapor-saturation correction to the heat capacity at the higher temperatures because the amount of material in the filling tube is not accurately determinable. Considering these factors, particularly the latter, and other possible sources of error, the uncertainty in the final heat-capacity values given in table 2 is believed to be ± 0.2 percent. In table 2 the values below 15°K were obtained by the extrapolation (see footnote 8) of a Debye function fitted to experimental values between 16° and 30°K .

TABLE 2. Molal heat capacity of tetrafluoroethylene at integral temperatures

Molecular weight = 100.02, $^{\circ}\text{K} = 273.16^{\circ} + ^{\circ}\text{C}$.

T		$C_{\text{satd.}}^{\text{a}}$	T	$C_{\text{satd.}}$
Solid				
$^{\circ}\text{K}$		$\text{abs } j \text{ deg}^{-1} \text{ mole}^{-1}$	$^{\circ}\text{K}$	$\text{abs } j \text{ deg}^{-1} \text{ mole}^{-1}$
0		0.0	120	73.20
5		.33	125	75.95
10		2.64	130	78.90
15		7.94	135	82.07
20		14.79	140	85.46
25		21.29	142.00	^b 86.85
30		26.91	Liquid	
35		31.65	142.00	^b 103.02
40		35.60	145	106.11
45		38.94	150	106.36
50		41.92	155	106.72
55		44.62	160	107.15
60		47.11	165	107.65
65		49.44	170	108.20
70		51.55	175	108.82
75		53.61	180	109.49
80		55.74	185	110.22
85		57.86	190	111.01
90		59.92	195	111.85
95		61.82	197.53	112.31
100		63.88	200	112.77
105		66.02	205	113.75
110		68.26	210	114.79
115		70.65		

^a $C_{\text{satd.}}$ is the heat capacity of the condensed phase under its vapor pressure.

^b Extrapolated.

5. Heat of Fusion

The determination of the heat of fusion involved continuous introduction of electrical energy from a temperature just below the triple point to just above it and the correction for the heat capacity of the sample and container. Also, a small premelting correction was applied. The results of the measurements are given in table 3. The values given in the fifth column are the total heats required to melt the 156.2694 g in the calorimeter. Taking into account the precision obtained, and other possible sources of error, the uncertainty in the heat of fusion is considered to be $\pm 7 \text{ abs } j \text{ mole}^{-1}$.

TABLE 3. Molal heat of fusion of tetrafluoroethylene

Molecular weight = 100.02, mass of sample = 156.2694 g, triple-point temperature = 142.00°K , $^{\circ}\text{K} = 273.16^{\circ} + ^{\circ}\text{C}$

Temperature interval	Heat input	Heat capacity	Premelting	ΔH	ΔH
$^{\circ}\text{K}$	$\text{abs } j$	$\text{abs } j$	$\text{abs } j$	$\text{abs } j$	$\text{abs } j \text{ mole}^{-1}$
137.7930 to 143.7828	13,374.1	1,326.9	6.5	12,053.7	7,715.0
136.3972 to 144.1500	13,755.1	1,707.4	4.9	12,052.6	7,714.2
137.4175 to 143.9957	13,504.5	1,457.7	5.9	12,052.7	7,714.3
Mean heat of fusion.....					7,714.5
Standard deviation.....					± 0.2

6. Heat of Vaporization

The heat-of-vaporization experiments were made at the normal boiling point (197.53°K) as determined by the vapor-pressure measurements. The experimentally observed quantity γ , the energy input per mole of sample collected,¹¹ is related to the

⁹ O. Ruff and O. Bretschneider, Z. anorg. allgem. Chem. **210**, 173 (1933).

¹⁰ H. J. Hoge, J. Research NBS **36**, 111 (1946) RP1693.

¹¹ N. S. Osborne, BSJ. Research **4**, 609 (1930) RP168.

molal heat of vaporization, L , by the expression

$$L = \gamma - TV \frac{dp}{dT}$$

where V is the molal volume of the liquid, T , the absolute temperature, and p , the vapor pressure. The experimentally observed quantities, the value of the conversion term (second term to the right of the equality sign), and the heat of vaporization are given in table 4. The molal volume for the conversion term was obtained from the densities of tetrafluoroethylene reported by Ruff and Bretschneider (see footnote 9). Considering the precision and other sources of error, the uncertainty in the heat of vaporization is believed to be ± 10 abs j mole⁻¹. The heat of vaporization, computed from the Clapeyron equation by using the vapor-pressure equation obtained in this work, the liquid densities reported by Ruff and Bretschneider (see

footnote 9), and the Berthelot equation of state, amounted to 16,850 abs j mole⁻¹. This is in fair agreement with the observed value. The constants for the Berthelot equation were reported by Renfrew and Lewis.¹²

7. Vapor Pressure

As there was no provision to stir the sample in the calorimeter, several series of vapor-pressure measurements were made from 142° to 208° K going down the temperature scale as well as up to check the temperature equilibrium. The agreement in the results of the measurements, as shown in table 5, indicates that equilibrium conditions existed. The vapor-pressure equation fitted to the experimental values is given by

$$\log_{10} p_{\text{mmHg}} = 4.71241 - \frac{972.9810}{T} + 4.816562 \\ \times 10^{-2}T - 2.427347 \times 10^{-4}T^2 + 3.958793 \times 10^{-7}T^3$$

In table 5 are given the deviations of the calculated values, based on this equation, from the observed values. Although the deviations from the equation vary somewhat systematically, no attempt was made to obtain a closer-fitting equation.

The normal boiling point was taken to be 197.53 $\pm 0.01^\circ$ K, although the equation gives 197.525° K and the difference in the rounding can be measured by the thermometer and by the manometer. The dp/dT at the normal boiling point is about 41 mm Hg per degree.

TABLE 4. Molal heat of vaporization of tetrafluoroethylene at 197.53° K (1-atm pressure)

Molecular weight = 100.02, °K = 273.16° + °C

γ	$TV \frac{dp}{dT}$	L
abs j mole ⁻¹	abs j mole ⁻¹	abs j mole ⁻¹
16, 884	71	16, 813
16, 901	71	16, 830
16, 890	71	16, 819
Mean		16, 821
Standard deviation		± 4

¹² M. M. Renfrew and E. E. Lewis, Ind. Eng. Chem. **38**, 870 (1946).

TABLE 5. Vapor pressure of tetrafluoroethylene

°K = 273.16° + °C

T_{obs}	p_{obs}	p_{calc}	$p_{\text{obs}} - p_{\text{calc}}$	T_{obs}	p_{obs}	p_{calc}	$p_{\text{obs}} - p_{\text{calc}}$
Series I				Series IV			
°K	mm Hg	mm Hg	mm Hg	°K	mm Hg	mm Hg	mm Hg
206.66	1, 217.8	1, 217.5	0.3	147.70	16.7	16.6	0.1
207.50	1, 268.6	1, 268.6	0	152.92	28.6	28.5	.1
208.41	1, 325.1	1, 325.8	-.7	155.77	37.8	37.6	.2
				158.89	50.5	50.3	.2
				164.15	79.7	79.8	-.1
				169.69	124.7	124.9	-.2
				175.35	190.5	190.7	-.2
				178.27	233.9	234.2	-.3
				180.96	280.7	281.1	-.4
Series II				Series V			
175.82	197.1	197.2	-0.1	142.00	8.7	8.7	0.0
179.23	249.9	250.2	-.3	147.98	17.1	17.1	.0
182.01	301.0	301.3	-.3	152.33	26.9	26.8	.1
184.37	350.8	351.0	-.2	159.34	52.5	52.4	.1
186.54	402.2	402.2	.0	168.56	114.3	114.3	.0
Series III				172.90	159.2	159.4	-.2
182.96	320.4	320.6	-0.2	178.02	229.8	230.2	-.4
188.27	447.0	447.2	-.2	180.23	267.3	267.7	-.4
190.11	490.2	490.3	-.1	191.74	549.1	549.4	-.3
193.30	601.0	600.9	.1				
196.06	701.8	701.5	.3				
196.06	701.4	701.5	-.1				
198.41	797.5	797.2	.3				
200.61	895.8	895.8	.0				
202.84	1, 005.6	1, 005.4	.2				
205.44	1, 146.1	1, 146.2	-.1				
206.99	1, 236.3	1, 237.4	-1.1				

8. Experimental Entropy

The experimental data were used to compute the entropy of the ideal gas tetrafluoroethylene at 197.53° K and 1 atm. In table 6 are summarized the entropy computations. The Berthelot equation of state and the critical constants reported by Renfrew and Lewis (see footnote 12) were used to compute the gas imperfection. The uncertainty of ± 0.37 abs j deg⁻¹ mole⁻¹ for the entropy of ideal gas C₂F₄ at 197.53° K and 1 atm was obtained by statistically combining the uncertainty in the entropy of liquid C₂F₄ at 197.53° K and in the entropy of vaporization. The uncertainty in the gas imperfection correction was considered negligible.

In terms of the thermochemical calorie (1 cal=4.1840 abs j) the calorimetric entropy of the ideal gas tetrafluoroethylene becomes 64.55 \pm 0.09 cal deg⁻¹ mole⁻¹.

TABLE 6. Summary of the Molal entropy of tetrafluoroethylene

Molecular weight=100.02, °K=273.16°+°C., 1 cal=4.1840 abs j

	abs j deg ⁻¹ mole ⁻¹
S _{16°} (Debye)	3.42
ΔS _{16° to 142.00°} solid, numerical integration	90.73
ΔS _{142.00°} fusion, 7714.5/142.00	54.33
ΔS _{142° to 197.53°} , liquid, numerical integration	35.75
Entropy of the liquid at 197.53° K	184.23 \pm 0.37
ΔS _{197.53°} vaporization 16821/197.53	85.16 \pm 0.05
ΔS _{197.53°} gas imperfection	0.67
Entropy, ideal gas at 197.53° K and 1 atm	270.06 \pm 0.37

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9. Entropy From Molecular and Spectroscopic Data

The entropy due to the external rotation was computed from the molecular constants taken from the electron diffraction results of Karle and Karle¹³ in which the C—F and C=C bond distances and the FCF angle were given as 1.313 \pm 0.010 Å, 1.313 \pm 0.035 Å, and 114 \pm 2°, respectively. The moments of inertia calculated were I_x=152.9 \times 10⁻⁴⁰ g-cm², I_y=254.7 \times 10⁻⁴⁰ g-cm², and I=407.6 \times 10⁻⁴⁰ g-cm². The fundamental constants used in the computation were essentially those given in the National Bureau of Standards Circular 461.¹⁴

The vibrational contribution to the entropy was computed from the recent frequency assignments of D. E. Mann, N. Aquista, and E. K. Plyler at the Bureau.

The entropy computed from the molecular and spectroscopic data is summarized and compared with the calorimetric entropy in table 7. An excellent agreement is shown in the two results.

TABLE 7. Molal entropy of tetrafluoroethylene at 197.53° K from molecular and spectroscopic data

Molecular weight=100.02, °K=273.16°+°C., 1 cal=4.1840 abs j.

	cal deg ⁻¹ mole ⁻¹
S, translation	37.67
S, external rotation	22.58
S, vibration	4.29
S, total, ideal gas at 197.53° K and 1 atm	64.54
S, calorimetric	64.55

¹³ I. L. Karle and J. Karle, J. Chem. Phys. **18**, 963 (1950).

¹⁴ F. D. Rossini, K. S. Pitzer, W. J. Taylor, J. P. Ebert, J. E. Kilpatrick, C. W. Beckett, M. G. Williams, and H. G. Werner, NBS Circular 461 (November 1947).